Hydrogen molecule and fundamental interactions

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Where precision matters

The goal is to achieve the highest possible accuracy to test fundamental interactions

- discrepancies between theory and exp can be interpreted in terms of extra forces between nuclei
- spin-spin coupling in HD is particularly sensitive to new physics
- we aim at present for 10^{-6} cm^{-1} accuracy for H_2 levels
- example: the most accurate determination of D and T magnetic moments

H_2 experimental data - challenge for theory

$$D_0(H_2) = 36118.06962(37)\ \mathrm{cm}^{-1}\quad [1]$$
$$\Delta v(1 \to 0) = 4161.16632(18)\ \mathrm{cm}^{-1}\quad [2]$$

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

[2] G.D. Dickenson et al, 2013 (Wim Ubachs' group)

- current theoretical accuracy is of about 10^{-4} cm^{-1}
- the accuracy 10^{-6} cm^{-1} is feasible (nonrelativistic energies, relativistic recoil and higher order QED needs to be improved)

Numerical approach

Our approach is based on explicitly correlated exponential basis set

$$\phi = e^{-w_1\, r_{12} - u_3\, r_{1A} - u_2\, r_{1B} - w_2\, r_{2A} - w_3\, r_{2B}}\, R^{n_0}\, r_{12}^{n_1}\, r_{1A}^{n_2}\, r_{1B}^{n_3}\, r_{2A}^{n_4}\, r_{2B}^{n_5}$$

- differential equation approach for calculating integrals with an arbitrary precision
- BO approximation with nonadiabatic perturbation theory
- or the direct nonadiabatic wave function

Energy of an atom or molecule

$\alpha \approx 1/137$ – fine-structure constant, $\beta = m_e/\mu_n \sim 10^{-3}$

$$
\begin{array}{ccccccccc}
E(\alpha) & = & E_{\mathrm{NR}} & + & \alpha^2 E_{\mathrm{REL}} & + & \alpha^3 E_{\mathrm{QED}} & + & \alpha^4 E_{\mathrm{HQED}} + \ldots \\
 & & + & & + & & + & & \vdots \\
 & & \beta E_{\mathrm{AD}} & & \alpha^2 \beta E^{\mathrm{rec}}_{\mathrm{REL}} & & \alpha^3 \beta E^{\mathrm{rec}}_{\mathrm{QED}} & & \\
 & & + & & \vdots & & \vdots & & \\
 & & \beta^2 E_{\mathrm{NA}} & & & & & & \\
 & & \vdots & & & & & &
\end{array}
$$

- The expansion coefficients can be expressed by expectation values of effective Hamiltonians with **the nonrelativistic wave function**
- Valid for small systems with light nuclei

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$$
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 & + & & + & & + & & \vdots \\
 & \beta\, E_{\rm AD} & & \alpha^2\, \beta\, E^{\rm rec}_{\rm REL} & & \alpha^3\, \beta\, E^{\rm rec}_{\rm QED} & & \\
 & + & & \vdots & & \vdots & & \\
 & \beta^2\, E_{\rm NA} & & & & & & \\
 & \vdots & & & & & &
\end{array}
$$

$E_{\rm BO}$ – the Born-Oppenheimer energy

$\beta\, E_{\rm AD}$ – adiabatic correction

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

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

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

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

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Relativistic correction

$$E(\alpha) = (E_0 + E_{\mathrm{AD}} + E_{\mathrm{NA}}) + \alpha^2\, E_{\mathrm{REL}} + \alpha^3\, E_{\mathrm{QED}} + \alpha^4\, E_{\mathrm{HQED}}$$

Expectation value of the Breit-Pauli Hamiltonian

$$\begin{aligned}
\mathcal{E}_{\mathrm{REL}} &= \sum_a \left[-\frac{1}{8} \left\langle \Psi \left| p_a^4 \right| \Psi \right\rangle + \sum_I \frac{Z_I \pi}{2} \left\langle \Psi \left| \delta(\vec{r}_{aI}) \right| \Psi \right\rangle \right] \\
&+ \sum_{a>b} \left[\pi \left\langle \Psi \left| \delta(\vec{r}_{ab}) \right| \Psi \right\rangle + \frac{1}{2} \left\langle \Psi \left| \vec{p}_a \frac{1}{r_{ab}} \vec{p}_b + \vec{p}_a \cdot \vec{r}_{ab} \frac{1}{r_{ab}^3} \vec{r}_{ab} \cdot \vec{p}_b \right| \Psi \right\rangle \right] \\
&+ \frac{2\,\pi}{3} \sum_I Z_I \frac{r_{\mathrm{ch}}^2(I)}{\chi_e^2} \left\langle \Psi \left| \sum_a \delta(\vec{r}_{aI}) \right| \Psi \right\rangle
\end{aligned}$$

The leading QED correction, $\alpha^3 E_{\mathrm{QED}}$

$$E(\alpha) = (E_0 + \beta E_{\mathrm{AD}} + \beta^2 E_{\mathrm{NA}}) + \alpha^2 E_{\mathrm{REL}} + \alpha^3 E_{\mathrm{QED}} + \alpha^4 E_{\mathrm{HQED}}$$

$$\begin{aligned}\mathcal{E}_{\mathrm{QED}} = & \sum_{i>j}\left\{\left[\frac{164}{15}+\frac{14}{3}\ln\alpha\right]\langle\Psi|\delta(\boldsymbol{r}_{ij})|\Psi\rangle \right. \\ & \left. -\frac{14}{3}\left\langle\Psi\left|\frac{1}{4\pi}P\left(\frac{1}{r_{ij}^3}\right)\right|\Psi\right\rangle\right\} \\ + & \sum_i\left[\frac{19}{30}+\ln(\alpha^{-2})-\ln k_0\right]\sum_I\frac{4Z_I}{3}\langle\Psi|\delta(\boldsymbol{r}_{iI})|\Psi\rangle\end{aligned}$$

– results from exchange of one or two virtual photons, vacuum polarization, electron self-energy, etc.

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

$$\vec{\nabla} = \sum_a \vec{\nabla}_a$$

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

Higher order QED corrections

$$E(\alpha) = (E_0 + E_{\rm AD} + E_{\rm NA}) + \alpha^2\, E_{\rm REL} + \alpha^3\, E_{\rm QED} + \alpha^4\, E_{\rm HQED}$$

- difficult to calculate, known for the hydrogen and helium atoms [1]

  $\mathcal{E}_{\rm HQED} = \langle H_{BP}\, \frac{1}{(E_0 - H_0)'}\, H_{BP}\rangle$ including vibrational excitations !!!

- approximate formula which accounts for the leading one-loop self-energy and the vacuum polarization

$$\mathcal{E}_{\rm HQED} \approx \sum_I 4\,\pi\, Z_I^2 \left(\frac{139}{128} + \frac{5}{192} - \frac{\ln 2}{2}\right) \sum_a \langle\phi_{\rm el}|\delta(\vec{r}_{aI})|\phi_{\rm el}\rangle$$

[1] K. P., *Phys. Rev. A* **74**, 062510 (2006);

master integral

$$f(r) = r \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \frac{e^{-w_1\, r_{12}}}{r_{12}} \frac{e^{-u_3\, r_{1A}}}{r_{1A}} \frac{e^{-u_2\, r_{1B}}}{r_{1B}} \frac{e^{-w_2\, r_{2A}}}{r_{2A}} \frac{e^{-w_3\, r_{2B}}}{r_{2B}}$$

other integrals with additional powers of interparticle distances can be obtained by differentiation with respect to corresponding parameter.

It satisfies the differential equation

$$\left[\sigma_4 \frac{d^2}{d\,r^2}\, r\, \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_0\, r\right] f(r) = F(r),$$

with σ being a polynomial in nonlinear parameters and F a combination of exponential and exponential integral functions.

This differential equation allows for the derivation of all integrals with additional positive powers of interparticle distances.

master integral

$$\left[\sigma_4 \frac{d^2}{d\,r^2}\, r\, \frac{d^2}{d\,r^2} + \sigma_2 \frac{d}{d\,r}\, r\, \frac{d}{d\,r} + \sigma_0\, r\right] f(r) = F(r),$$

$$\begin{aligned}
w_2 &= w + x, \quad w_3 = w - x, \quad u_2 = u - y, \quad u_3 = u + y, \\
\sigma &= \sigma_0 + t^2\,\sigma_2 + t^4\,\sigma_4, \\
\sigma_4 &= w_1^2, \\
\sigma_2 &= w_1^4 - 2\,w_1^2\,(u^2 + w^2 + x^2 + y^2) + 16\,u\,w\,x\,y \\
\sigma_0 &= w_1^2\,(u + w - x - y)\,(u - w + x - y)\,(u - w - x + y)\,(u + w + x + y) \\
&\quad + 16\,(w\,x - u\,y)\,(u\,x - w\,y)\,(u\,w - x\,y)
\end{aligned}$$

Taylor series

$$
\begin{aligned}
f(r) &= r\,X_0 + r^2\left(X_r - \frac{3}{2}\right) \\
&\quad + r^3\left[-\frac{w_1^2\,X_0}{12} - \frac{w_1}{4} + \frac{(u^2+w^2+x^2+y^2)\,X_0 - w\,X_1 - u\,X_2 - 2\,(u+w)}{6}\right. \\
&\qquad \left. + \frac{x\,y}{3\,w_1} - \frac{2\,x\,y\,(2\,u\,w\,X_0 + u\,X_1 + w\,X_2)}{3\,w_1^2}\right] \\
&\quad + r^4\left[\frac{7}{54}\,w_1^2 + \frac{w_1\,(u+w)}{12} + \frac{3\,u\,w - 3\,x\,y - 11\,u^2 - 11\,w^2 - 9\,x^2 - 9\,y^2}{36}\right. \\
&\qquad \left. + X_r\left(-\frac{w_1^2}{18} + \frac{u^2+w^2+x^2+y^2}{6}\right)\right] + O(r^5).
\end{aligned}
$$

where

$$
X_0 = \frac{1}{2\,w_1}\left[\frac{\pi^2}{6} + \frac{1}{2}\ln^2\left(\frac{2\,u+w_1}{2\,w+w_1}\right) + \mathrm{L}_2\left(1 - \frac{2\,(u+w)}{2\,u+w_1}\right) + \mathrm{L}_2\left(1 - \frac{2\,(u+w)}{2\,w+w_1}\right)\right],
$$

$$
X_1 = \ln\left(\frac{2\,u+w_1}{2\,(u+w)}\right), \quad X_2 = \ln\left(\frac{2\,w+w_1}{2\,(u+w)}\right),
$$

$$
X_r = \frac{1}{2}\,\ln[r^2\,(2\,u+w_1)(2\,w+w_1)] + \gamma_{\mathrm{E}}. \qquad (1)
$$

h2solve.f: code for two-center integrals & H_2

- General purpose code for evaluation of two-center two-electron integrals with arbitrary parameters y, x, u, w, but $w_1 = 0$

$$f(r, n_0, n_1, n_2, n_3, n_4) = r \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, r_{12}^{n_0}\, (r_{1A} - r_{1B})^{n_1}\, (r_{2A} - r_{2B})^{n_2} \times (r_{1A} + r_{1B})^{n_3}\, (r_{2A} + r_{2B})^{n_4}\, \frac{e^{-u\,(r_{1A}+r_{1B})-w\,(r_{2A}+r_{2B})-y\,(r_{1A}-r_{1B})-x\,(r_{2A}-r_{2B})}}{r_{12}\, r_{1A}\, r_{1B}\, r_{2A}\, r_{2B}} \tag{2}$$

- arbitrary states of H_2, arbitrary precision, arbitrary high powers of interparticle distances
- the evaluation method is based on the Taylor expansion in the internuclear distance r, this series is absolutely convergent, as fast as for the exponential function

H_2: new results for nonadiabatic energies

$\Omega = \sum_i n_i$	E_0
6	-1.1640249221963
7	-1.1640250158018
8	-1.1640250287392
9	-1.1640250305334
10	-1.1640250308163
11	-1.1640250308659
12	-1.1640250308755
∞	-1.1640250308796(33)
Bubin, Adamowicz	-1.16402503084(6)

accuracy of the extrapolated result $\delta E = 7 \cdot 10^{-7}$ cm^{-1}

Dissociation energy of the ground state of H_2

JCTC **5, 3039 (2009)**

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

Dissociation energy – comparison with experiment

	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)

[2] E. E. Eyler, N. Melikechi, *Phys. Rev. A* **48**, R18 (1993);
[3] Y. Zang *et al.*, *Phys. Rev. Lett.* **92**, 203003 (2004);
[4] Liu, Salumbides, Hollenstein, Koelemeij, Eikema, Ubachs, Merkt, *JCP* **130**, 174306 (2009)
[5] Liu, Sprecher, Jungen, Ubachs, Merkt, *JCP* **132**, 154301 (2010);
[6] Piszczatowski, Lach, Przybytek, Komasa, Pachucki, Jeziorski, *JCTC* **5**, 3039 (2009)

Dissociation energy of HD – a comparison

PCCP 12, 9188 (2010)

	D_0/cm^{-1}	δ/cm^{-1}
	36 405.7828(10)	
Theory		
Stanke *et al.* (2009) $+\alpha^3+\alpha^4$	36 405.7814	−0.0014
Wolniewicz (1995)	36 405.787	0.004
Kołos, Rychlewski (1993)	36 405.763	−0.020
Experiment		
Liu *et al.* (2010)	36 405.783 66(36)	0.000 9
Zhang *et al.* (2004)	36 405.828(16)	0.045
Balakrishnan *et al.* (1993)	36 405.83(10)	0.05
Eyler, Melikechi (1993)	36 405.88(10)	0.10
Herzberg (1970)	36 406.2(4)	0.4

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Eyler, Melikechi (1993)	36 405.88(10)	0.10
Herzberg (1970)	36 406.2(4)	0.4

Magnetic moments from the NMR shielding

- HD in magnetic field
- using the newly measured μ_p, Walz & collaborators, (2004)
- $\frac{\mu_A\,(1-\sigma_A)}{\mu_B\,(1-\sigma_B)} = \frac{f_A}{f_B}\,\frac{I_A}{I_B}$, Garbacz (2012)
- $\delta\sigma(HD) = 0.020\,179\,6(3)$, $\sim 10^{-3}$ neglected effects
- $\mu_d = 0.857\,438\,234\,6(53)\,\mu_N$
- the most accurate deuteron magnetic moment
- possible determination for other nuclei, ^{3}He