Nonrelativistic energy levels of D_2

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Collaboration

- Faculty of Physics, University of Warsaw
  - Krzysztof Pachucki
  - Paweł Czachorowski
- Faculty of Chemistry, Adam Mickiewicz University, Poznan
  - Mariusz Puchalski

Energy of an atom or molecule

$\alpha \approx 1/137$ – fine-structure constant

$$E(\alpha) = m\alpha^2\, E^{(2)} + m\alpha^4\, E^{(4)} + m\alpha^5\, E^{(5)} + m\alpha^6\, E^{(6)} + \ldots$$

- The expansion coefficients can be expressed by expectation values of effective Hamiltonians with **the nonrelativistic wave function** – NRQED

$E^{(2)}$	–	nonrelativistic energy	$36\,749.0910(2)$
$E^{(4)}$	–	relativistic correction	$-0.5276(3)$
$E^{(5)}$	–	the leading QED correction	$-0.1983(2)$
$E^{(6)}$	–	higher order QED correction	$-0.0016(8)$
E	–	total energy	$36\,748.3633(9)$

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D_2 energy component		D_0/cm^{-1}
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D_2 energy component			D_0/cm^{-1}	$\delta D_0/D_0$
$E^{(2)}$	–	nonrelativistic energy	$36\,749.0910(2)$	$5 \cdot 10^{-9}$
$E^{(4)}$	–	relativistic correction	$-0.5276(3)$	$6 \cdot 10^{-4}$
$E^{(5)}$	–	the leading QED correction	$-0.1983(2)$	$1 \cdot 10^{-3}$
$E^{(6)}$	–	higher order QED correction	$-0.0016(8)$	$5 \cdot 10^{-1}$
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NAPT vs DNVM

NAPT – nonadiabatic perturbation theory

\+ all the bound states ”at once”

— accuracy limited by cutting the perturbational series

DNVM – direct nonadiabatic variational method

\+ ”unlimited” accuracy

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Pachucki 2009

$$H^{(2)}\,\Psi(\vec{r},\vec{R}) = E^{(2)}\,\Psi(\vec{r},\vec{R})$$

$$H^{(2)} = H_{\rm el} + H_{\rm n}$$

$$\Psi(\vec{r},\vec{R}) = \phi_{\rm el}(\vec{r};\vec{R})\,\chi(\vec{R}) + \delta\phi_{\rm na}(\vec{r},\vec{R})$$

$$H_{\rm el}\,\phi_{\rm el} = \mathcal{E}_{\rm el}(\vec{R})\,\phi_{\rm el}$$

$$\langle \delta\phi_{\rm na} | \phi_{\rm el} \rangle_{\rm el} = 0$$

$$\Big[(H_{\rm el} - \mathcal{E}_{\rm el}) + (\mathcal{E}_{\rm el} + H_{\rm n} - E^{(2)}) \Big] \Big| \phi_{\rm el}(\vec{r};\vec{R})\,\chi(\vec{R}) + \delta\phi_{\rm na}(\vec{r},\vec{R}) \Big\rangle = 0$$

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NAPT(2)

Pachucki 2009

Perturbative expansion for the effective nuclear Hamiltonian

$$(\mathcal{E}_{\rm el} + \mathcal{E}_{\rm a} + H_{\rm n} - E^{(2)})|\chi\rangle = -(H_{\rm n}^{(2)} + H_{\rm n}^{(3)} + H_{\rm n}^{(4)} + \ldots)|\chi\rangle$$

$$H_{\rm n}^{(2)} \sim \left(\frac{m_{\rm e}}{\mu_{\rm n}}\right)^2$$

$$H_{\rm n}^{(3)} \sim \left(\frac{m_{\rm e}}{\mu_{\rm n}}\right)^2 + \mathcal{O}\left[\left(\frac{m_{\rm e}}{\mu_{\rm n}}\right)^3\right]$$

$$H_{\rm n}^{(4)} = \mathcal{O}\left[\left(\frac{m_{\rm e}}{\mu_{\rm n}}\right)^3\right]$$

$$\delta E^{(2)} = E^{(2)} - E^{(2)}_{\rm NAPT(2)} \sim \left(\frac{m_{\rm e}}{\mu_{\rm n}}\right)^3$$

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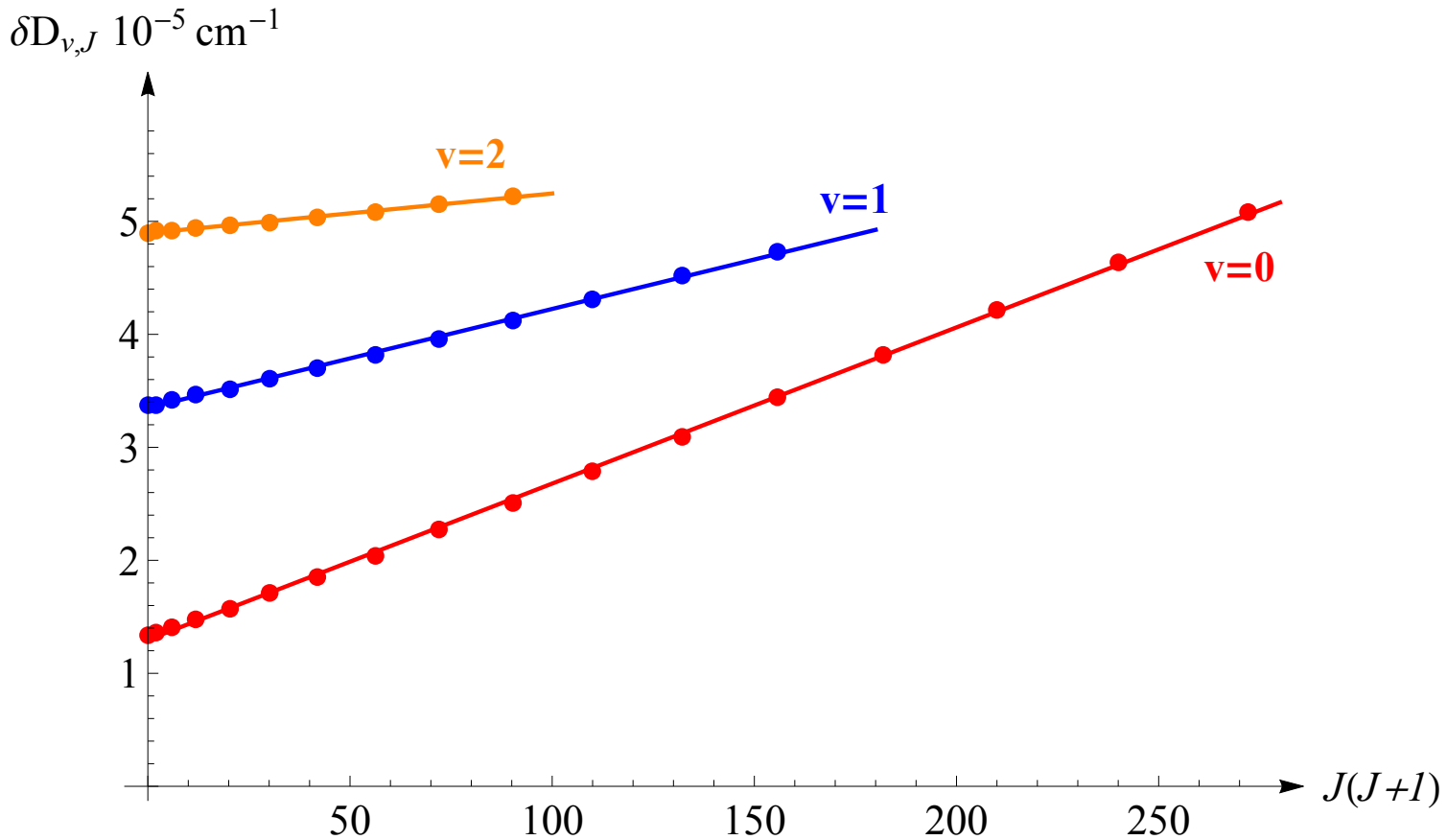
$\delta E^{(2)} = E^{(2)} - E^{(2)}_{\mathrm{NAPT}(2)}$ for D_2



James-Coolidge-type functions

The James-Coolidge-type basis function

$$\psi_{\{n\}}(\vec{r}_1,\vec{r}_2) = (1 \pm \hat{P}_{12})\,(1 \pm \hat{i})$$
$$(r_{1A} - r_{1B})^{n_2}(r_{2A} - r_{2B})^{n_3}(r_{1A} + r_{1B})^{n_4}(r_{2A} + r_{2B})^{n_5}$$
$$e^{-\beta\,(r_{1A}+r_{1B}+r_{2A}+r_{2B})}\, r_{12}^{n_1}\, R^{-n_1-n_2-n_3-n_4-n_5-3}$$

Closed-form integrals f derived by K. Pachucki[a]

$$f(\{n\};R,\beta) = R^{-n_1-n_2-n_3-n_4-n_5-1}$$
$$\int \frac{d^3r_1}{4\pi} \int \frac{d^3r_2}{4\pi} \frac{e^{-\beta\, r_{1A}}}{r_{1A}} \frac{e^{-\beta\, r_{1B}}}{r_{1B}} \frac{e^{-\beta\, r_{2A}}}{r_{2A}} \frac{e^{-\beta\, r_{2B}}}{r_{2B}} \frac{1}{r_{12}^{1-n_1}}$$
$$(r_{1A} - r_{1B})^{n_2}(r_{2A} - r_{2B})^{n_3}(r_{1A} + r_{1B})^{n_4}(r_{2A} + r_{2B})^{n_5}$$

[a] K. Pachucki, Phys. Rev. A **80**, 032520 (2009).

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Advertisment

H2SPECTRE

- Fortran code with the NAPT implemented made public!
- Publication with theoretical background and usage
  – in preparation 8(
- AMUR - Adam Mickiewicz University Repository
  – URL will be anounced in the publication
  – for now contact Pawel.Czachorowski@fuw.edu.pl

```
komasa@e0311:~/Iso_naqed19/h2spectr_4.5$ ./H2spectre.exe -V 2  --napt
D2 Level
(Int. points=  200 , Int. range= 10.0)
 -------------------------------------------
 D2     Level
0 0

 v' =  0   J' =  0

  Contribution     Value[cm-1]    Error[cm-1]
     E2(NAPT)      36749.09098    8.6E-05
     E4               -0.52821    1.2E-06
       E4(B0)         -0.52918
       E4(rec)         0.00120
       E4(2nd)        -0.00023
     E5               -0.19831    1.5E-04
     E6               -0.00209    6.2E-06
       E6(B0)         -0.00210
       E6(2nd)         0.00001
     E7                0.00010    2.6E-05
     Efs              -0.00020    1.2E-07
     Total         36748.36227    1.7E-04
 -------------------------------------------
```

```
komasa@e0311:~/Iso_naqed19/h2spectr_4.5$ ./H2spectre.exe -V 2  --napt  --wavl
D2 Transition
(Int. points=  200 , Int. range= 10.0)
 -------------------------------------------
 D2     Transition
0 1  0 0

 v' =  0   J' =  1    -->   v" =  0   J" =  0

  Contribution     Value[cm-1]    Error[cm-1]
     E2(NAPT)       59.7798252    9.3E-07
     E4              0.0013106    2.5E-09
       E4(B0)        0.0013098
       E4(rec)       0.0000015
       E4(2nd)      -0.0000007
     E5              -0.0005170    3.9E-07
     E6              -0.0000045    1.3E-08
       E6(B0)        -0.0000045
       E6(2nd)        0.0000000
     E7               0.0000002    6.2E-08
     Efs             -0.0000005    2.8E-10
     Total           59.7806141    1.0E-06
 -------------------------------------------
Wavelength[um]      167.2783084    2.8E-06
 -------------------------------------------
```

Advertisment

H2SPECTRE

The Full Infrared Spectrum of Molecular Hydrogen

E. Roueff[1], H. Abgrall[1], P. Czachorowski[2], K. Pachucki[2], M. Puchalski[3], and J. Komasa[3]

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[3] Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland
e-mail: komasa@man.poznan.pl

ABSTRACT

Context. The high spectral resolution R ~ 45,000 provided by IGRINS (Immersion Grating INfrared Spectrometer) at MacDonald Observatory and R ~ 100,000 achieved by CRIRES (CRyogenic high-resolution InfraRed Echelle Spectrograph) at VLT challenges the present knowledge of infrared spectra.
Aims. We aim to predict the full infrared spectrum of molecular hydrogen at a comparable accuracy.
Methods. We take advantage of the recent theoretical ab-initio studies on molecular hydrogen to compute both the electric quadrupole and magnetic dipole transitions taking place within the ground electronic molecular state of Hydrogen
Results. We compute the full infrared spectrum of molecular hydrogen at an unprecedented accuracy and derive for the first time the emission probabilities including both electric quadrupole ($\Delta J = 0, \pm 2$) and magnetic dipole transitions ($\Delta J = 0$) as well as the total radiative lifetime of each rovibrational state. Inclusion of magnetic dipole transitions increases the emission probabilities by factors of a few for highly excited rotational levels.

Key words. Physical data and processes – Molecular data – Infrared: general

number of transitions: 4711

vu	ju	vl	jl	Etr (1/cm)	delta (1/cm)	lambda (micron)	delta (micron)	Aqu (1/s)	Ama (1/s)	A (1/s)	At (1/s)	Tu (1/cm)	delta (1/cm)
0	2	0	0	354.373130	3.7E-06	28.218843793	2.9E-07	2.943E-11	0.000E+00	2.943E-11	2.943E-11	354.3739	2.3E-04
0	3	0	1	587.032025	6.1E-06	17.034845756	1.8E-07	4.761E-10	0.000E+00	4.761E-10	4.761E-10	705.5196	2.3E-04
0	4	0	2	814.424302	8.4E-06	12.278611990	1.3E-07	2.755E-09	0.000E+00	2.755E-09	2.755E-09	1168.7982	2.2E-04
0	5	0	3	1034.670685	1.1E-05	9.664910918	1.0E-07	9.836E-09	0.000E+00	9.836E-09	9.836E-09	1740.1983	2.2E-04
0	6	0	4	1246.099547	1.3E-05	8.025041036	8.4E-08	2.643E-08	0.000E+00	2.643E-08	2.643E-08	2414.8977	2.1E-04
0	7	0	5	1447.280936	1.4E-05	6.909508548	6.7E-08	5.879E-08	0.000E+00	5.879E-08	5.879E-08	3187.4712	2.0E-04
0	8	0	6	1637.046000	1.6E-05	6.108563839	6.0E-08	1.142E-07	0.000E+00	1.142E-07	1.142E-07	4051.9437	2.0E-04
0	9	0	7	1814.492375	1.7E-05	5.511183258	5.2E-08	2.001E-07	0.000E+00	2.001E-07	2.001E-07	5001.9636	1.9E-04
0	10	0	8	1978.977263	1.9E-05	5.053115155	4.9E-08	3.236E-07	0.000E+00	3.236E-07	3.236E-07	6030.9211	8.9E-04
0	11	0	9	2130.108614	2.0E-05	4.694613923	4.4E-08	4.980E-07	0.000E+00	4.980E-07	4.980E-07	7132.0644	9.7E-04
0	12	0	10	2267.681181	2.1E-05	4.409790972	4.1E-08	7.029E-07	0.000E+00	7.029E-07	7.029E-07	8298.6824	1.0E-03
0	13	0	11	2391.728142	2.1E-05	4.181077198	3.7E-08	9.633E-07	0.000E+00	9.633E-07	9.633E-07	9523.7926	1.1E-03
0	14	0	12	2502.410681	2.2E-05	3.996146626	3.5E-08	1.269E-06	0.000E+00	1.269E-06	1.269E-06	10801.0131	1.2E-03
0	15	0	13	2600.027482	2.2E-05	3.846113192	3.3E-08	1.617E-06	0.000E+00	1.617E-06	1.617E-06	12123.8201	1.3E-03
0	16	0	14	2684.977572	2.2E-05	3.724425896	3.1E-08	1.999E-06	0.000E+00	1.999E-06	1.999E-06	13485.9987	1.5E-03
0	17	0	15	2757.733488	2.2E-05	3.626166224	2.9E-08	2.407E-06	0.000E+00	2.407E-06	2.407E-06	14881.5536	1.6E-03
0	18	0	16	2818.817246	2.2E-05	3.547587286	2.8E-08	2.831E-06	0.000E+00	2.831E-06	2.831E-06	16304.8808	1.7E-03
0	19	0	17	2868.779482	2.2E-05	3.485802956	2.7E-08	3.259E-06	0.000E+00	3.259E-06	3.259E-06	17750.3331	1.8E-03
0	20	0	18	2908.181426	2.2E-05	3.438575018	2.6E-08	3.680E-06	0.000E+00	3.680E-06	3.680E-06	19212.9895	2.0E-03
0	21	0	19	2937.579741	2.1E-05	3.404162910	2.4E-08	4.081E-06	0.000E+00	4.081E-06	4.081E-06	20687.9129	2.1E-03
0	22	0	20	2957.513679	2.1E-05	3.381218511	2.4E-08	4.451E-06	0.000E+00	4.451E-06	4.451E-06	22170.5032	2.3E-03
0	23	0	21	2968.494159	2.0E-05	3.368711361	2.3E-08	4.779E-06	0.000E+00	4.779E-06	4.779E-06	23656.4071	2.4E-03
0	24	0	22	2970.994204	2.0E-05	3.365876643	2.3E-08	5.056E-06	0.000E+00	5.056E-06	5.056E-06	25141.4974	2.6E-03
0	24	1	22	30.285422	6.6E-06	331.066389338	7.2E-05	6.334E-17	0.000E+00	6.334E-17	5.056E-06	25141.4974	2.6E-03
0	25	0	23	2965.440121	1.9E-05	3.372180719	2.2E-08	5.274E-06	0.000E+00	5.274E-06	5.274E-06	26621.8472	2.8E-03
0	25	1	23	118.343261	6.8E-06	84.49995304	4.9E-06	6.223E-14	0.000E+00	6.223E-14	5.274E-06	26621.8472	2.8E-03
0	26	0	24	2952.202695	1.8E-05	3.387301290	2.1E-08	5.424E-06	0.000E+00	5.424E-06	5.424E-06	28093.7001	3.0E-03
0	26	1	24	201.398456	7.0E-06	49.652813624	1.7E-06	9.404E-13	0.000E+00	9.404E-13	5.424E-06	28093.7001	3.0E-03
0	27	0	25	2931.587453	1.8E-05	3.411121162	2.1E-08	5.503E-06	0.000E+00	5.503E-06	5.503E-06	29553.4347	3.2E-03
0	27	1	25	279.847254	7.1E-06	35.733779256	9.1E-07	5.148E-12	0.000E+00	5.148E-12	5.503E-06	29553.4347	3.2E-03
0	28	0	26	2903.822736	1.7E-05	3.443736381	2.0E-08	5.586E-06	0.000E+00	5.586E-06	5.586E-06	30997.5228	3.4E-03
0	28	1	26	354.175248	7.2E-06	28.234610003	5.7E-07	1.764E-11	0.000E+00	1.764E-11	5.586E-06	30997.5228	3.4E-03
0	29	0	27	2869.043657	1.6E-05	3.485481991	1.9E-08	5.430E-06	0.000E+00	5.430E-06	5.430E-06	32422.4783	3.6E-03
0	29	1	27	424.885217	7.3E-06	23.535768249	4.0E-07	4.620E-11	0.000E+00	4.620E-11	5.430E-06	32422.4783	3.6E-03
0	30	0	28	2827.268848	1.5E-05	3.536982345	1.9E-08	5.275E-06	0.000E+00	5.275E-06	5.275E-06	33824.7916	3.8E-03
0	30	1	28	492.510070	7.3E-06	20.304153374	3.0E-07	1.018E-10	0.000E+00	1.018E-10	5.275E-06	33824.7916	3.8E-03
0	31	0	29	2778.364537	1.5E-05	3.599239720	1.9E-08	5.040E-06	0.000E+00	5.040E-06	5.040E-06	35280.8428	4.0E-03
0	31	1	29	557.434092	7.4E-06	17.932904440	2.4E-07	1.996E-10	0.000E+00	1.996E-10	5.040E-06	35280.8428	4.0E-03
1	0	0	2	3806.792992	2.2E-05	2.626883053	1.5E-08	8.532E-07	0.000E+00	8.532E-07	8.532E-07	4161.1670	1.4E-03
1	1	0	3	3568.221737	2.0E-05	2.802516417	1.6E-08	4.222E-07	0.000E+00	4.222E-07	8.516E-07	4273.7415	1.4E-03
1	1	0	1	4155.253762	2.6E-05	2.406591888	1.5E-08	4.287E-07	7.137E-10	4.294E-07	8.516E-07	4273.7415	1.4E-03
1	2	0	4	3329.040990	1.7E-05	3.003868089	1.5E-08	2.895E-07	0.000E+00	2.895E-07	8.472E-07	4497.8393	1.4E-03
1	2	0	2	4143.465293	2.6E-05	2.413438823	1.5E-08	3.029E-07	2.141E-09	3.051E-07	8.472E-07	4497.8393	1.4E-03
1	2	0	0	4497.838423	2.9E-05	2.223291810	1.4E-08	2.526E-07	0.000E+00	2.526E-07	8.472E-07	4497.8393	1.4E-03
1	2	1	0	336.672301	3.5E-06	29.702473207	3.1E-07	2.786E-11	0.000E+00	2.786E-11	8.472E-07	4497.8393	1.4E-03
1	3	0	5	3091.201926	1.5E-05	3.234987632	1.6E-08	2.082E-07	0.000E+00	2.082E-07	8.380E-07	4831.3924	1.4E-03
1	3	0	3	4125.872611	2.5E-05	2.423729703	1.5E-08	2.781E-07	4.285E-09	2.824E-07	8.380E-07	4831.3924	1.4E-03
1	3	0	1	4712.904636	3.1E-05	2.121833725	1.4E-08	3.470E-07	0.000E+00	3.470E-07	8.380E-07	4831.3924	1.4E-03
1	3	1	1	557.650874	5.7E-06	17.932366766	1.8E-07	4.497E-10	0.000E+00	4.497E-10	8.380E-07	4831.3924	1.4E-03
1	4	0	6	2856.482463	1.3E-05	3.500809169	1.6E-08	1.497E-07	0.000E+00	1.497E-07	8.226E-07	5271.3804	1.5E-03
1	4	0	4	4102.582010	2.5E-05	2.437489360	1.5E-08	2.650E-07	7.146E-09	2.721E-07	8.226E-07	5271.3804	1.5E-03

DNVM – direct nonadiabatic variational method

Four-body nonadiabatic Schrödinger equation solved variationally

The trial wave function

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = \sum_{k=1}^{K} c_k \, \hat{S} \, \psi_{\{k\}}(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B)$$

Four-particle basis of exponential functions (*naJC*)

$$\psi_{\{k\}} = \exp\left[-\alpha \, r_{AB} - \beta \left(r_{1A} + r_{1B} + r_{2A} + r_{2B}\right)\right] \times r_{AB}^{k_0} \, r_{12}^{k_1} \left(r_{1A} - r_{1B}\right)^{k_2} \left(r_{2A} - r_{2B}\right)^{k_3} \left(r_{1A} + r_{1B}\right)^{k_4} \left(r_{2A} + r_{2B}\right)^{k_5}$$

Schrödinger equation in a matrix form

$$\left(\mathbb{H} - E_K \, \mathbb{N}\right) c = 0$$

$$E_K \xrightarrow{K \to \infty} E^{(2)}$$

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$$\psi_{\{k\}} = \exp\left[-\alpha\, r_{AB} - \beta\,(r_{1A}+r_{1B}+r_{2A}+r_{2B})\right] \times r_{AB}^{k_0}\, r_{12}^{k_1}\,(r_{1A}-r_{1B})^{k_2}(r_{2A}-r_{2B})^{k_3}(r_{1A}+r_{1B})^{k_4}(r_{2A}+r_{2B})^{k_5}$$

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Schrödinger equation in a matrix form

$$\left(\mathbb{H} - E_K \, \mathbb{N}\right) c = 0$$

$$E_K \xrightarrow{K \to \infty} E^{(2)}$$

Nonadiabatic wave function for an arbitrary J

$$\Psi^{J,M} = \Psi_{\Sigma}^{J,M} + \Psi_{\Pi}^{J,M} + \Psi_{\Delta}^{J,M} + \dots$$

where

$$\Psi_{\Sigma}^{J,M} = Y_J^M \, \Phi_{\Sigma}^J \,, \qquad \text{for } J \geq 0$$
$$\Psi_{\Pi}^{J,M} = \rho^i \left(\nabla_R^i Y_J^M \right) \Phi_{\Pi}^J \,, \qquad \text{for } J \geq 1$$
$$\Psi_{\Delta}^{J,M} = (\rho^i \rho'^j)^{(2)} \left(\nabla_R^i \nabla_R^j Y_J^M \right) \, \Phi_{\Delta}^J \,, \qquad \text{for } J \geq 2$$

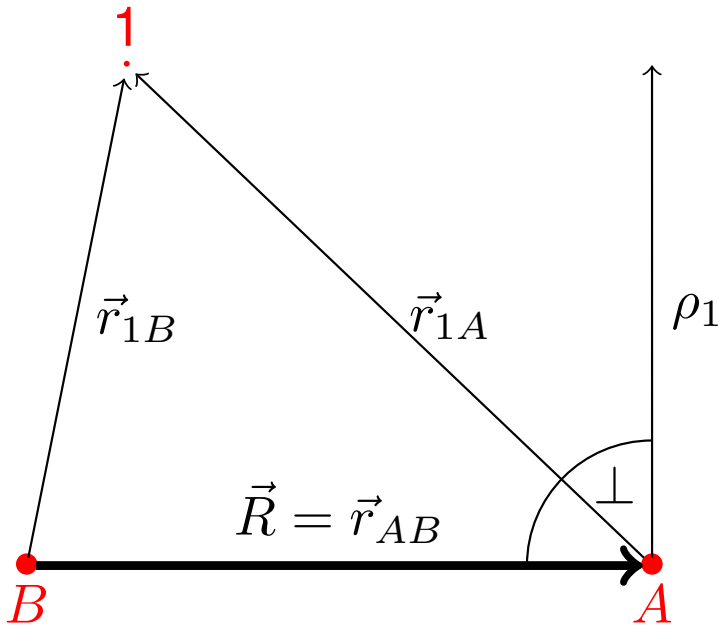
using Einstein notation and the following symbols

$$(\rho^i \rho'^j)^{(2)} \equiv \frac{1}{2} \Big(\rho^i \rho'^j + \rho^j \rho'^i - \left(\delta^{ij} - n^i n^j \right) \, \vec{\rho} \cdot \vec{\rho}' \Big)$$

$$\vec{\rho}, \vec{\rho}' \equiv \vec{\rho}_1 \text{ or } \vec{\rho}_2 \qquad n^i \equiv R^i / R$$

$$\rho_a^i = \left(\delta^{ij} - n^i n^j \right) \, r_{aA}^j$$

Nonadiabatic wave function, cont.



$$\Phi^J_\Lambda = \sum_{\{k\}} c_{\{k\}} \left(1 + \mathcal{P}_{12}\right) \Phi^J_{\Lambda\{k\}}$$

primitive basis function

$$\Phi_{\{k\}} = e^{-\alpha R - \beta(\zeta_1+\zeta_2)} R^{k_0} r_{12}^{k_1} \eta_1^{k_2} \eta_2^{k_3} \zeta_1^{k_4} \zeta_2^{k_5}$$

$$\zeta_a = r_{aA} + r_{aB}, \qquad \eta_a = r_{aA} - r_{aB}, \qquad \vec{R} = \vec{r}_{AB}$$

Four-body integrals

$$G = \int \frac{d^3R}{4\,\pi} \int \frac{d^3r_{1A}}{4\,\pi} \int \frac{d^3r_{2A}}{4\,\pi}\, e^{-u_1\,R - w_1\,r_{12} - y\,\eta_1 - x\,\eta_2 - u\,\zeta_1 - w\,\zeta_2} \times R^{n_0}\, r_{12}^{n_1}\, \eta_1^{n_2}\, \eta_2^{n_3}\, \zeta_1^{n_4}\, \zeta_2^{n_5}\, /\mathcal{D}$$

where

$$\mathcal{D} = R\, r_{12}\, r_{1A}\, r_{1B}\, r_{2A}\, r_{2B} = \frac{1}{16}\, R\, r_{12}\, (\zeta_1 + \eta_1)\, (\zeta_1 - \eta_1)\, (\zeta_2 + \eta_2)\, (\zeta_2 - \eta_2)$$

Master integral

$$g = \int \frac{d^3R}{4\,\pi} \int \frac{d^3r_{1A}}{4\,\pi} \int \frac{d^3r_{2A}}{4\,\pi}\, \frac{e^{-u_1\,R - w_1\,r_{12} - y\,\eta_1 - x\,\eta_2 - u\,\zeta_1 - w\,\zeta_2}}{\mathcal{D}}$$

D. M. Fromm and R. N. Hill, Phys. Rev. A 36, 1013 (1987)
E. Remiddi, Phys. Rev. A, 44, 5492 (1991)
F. E. Harris, Phys. Rev. A 55, 1820 (1997)

Master integral

Pachucki method

Pachucki differential equations[1]

$$\sigma \frac{\partial g^{(n)}}{\partial a} + \frac{1}{2} \frac{\partial \sigma}{\partial a} g^{(n)} + P_a = 0$$

a – a nonlinear parameter u_1, w_1, y, x, u, w
σ – 6th degree polynomial in these parameters
P_a – a combination of logarithmic functions

For *naJC* basis functions

$$g(w_1 = y = x = 0, w = u)$$

$$= \frac{1}{16\,u^4} \left[\frac{-u^3 \ln(2u)}{t(t+2u)} + \frac{u^3 \ln(4u)}{(t-2u)(t+2u)} - \frac{2u^4 \ln(t+2u)}{t(t-2u)(t+2u)} \right]$$

[1] K. Pachucki, Phys. Rev. A **80**, 032520 (2009)
K. Pachucki, Phys. Rev. A **86**, 052514 (2012)

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Technical issues

- $\sim 10^5 \times 10^5$ dense matrices buildup and diagonalization
- quad-double precision (212 bit)
- up to 700 GB of RAM
- parallelization of diagonalization routine

Convergence in DNVM

Convergence of $E^{(2)}_{0,0}$ (a.u.) and $D_{0,0}$ (cm^{-1}) for the ground level of D_2

Ω	K	$E^{(2)}_{0,0}$	$D_{0,0}$
9	33 733	$-1.167\,168\,809\,240\,572$	$36\,749.090\,980\,266$
10	49 959	$-1.167\,168\,809\,276\,440$	$36\,749.090\,988\,138$
11	71 736	$-1.167\,168\,809\,282\,247$	$36\,749.090\,989\,411$
12	100 772	$-1.167\,168\,809\,283\,632$	$36\,749.090\,989\,716$
13	138 348	$-1.167\,168\,809\,283\,929$	$36\,749.090\,989\,780$
14	186 660	$-1.167\,168\,809\,284\,013$	$36\,749.090\,989\,800$
∞	∞	$-1.167\,168\,809\,284\,05(4)$	$36\,749.090\,989\,81(1)$

[a] S. Bubin, M. Stanke and L. Adamowicz, J. Chem. Phys., **135**, 074110 (2011).

[b] M. Puchalski, A. Spyszkiewicz, J. Komasa and K. Pachucki, Phys. Rev. Lett., **121**, 073001 (2018).

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	Ref.[a]	$-1.167\,168\,809\,21(5)$	$36\,749.090\,97(1)$
	Ref.[b]	$-1.167\,168\,809\,27(4)$	$36\,749.090\,98(1)$

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Rovibrational states of D_2

Rovibrational levels of D_2 (in cm^{-1})

v\J	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
0	36748.3634	36688.5828	36569.2963	36391.0490	36154.6478	35861.1488	35511.8412	35108.2289	34652.0088	34145.0488	33589.3635	32987.0905	32340.4669	31651.8060	30923.4758	30157.8783	29357.4315	28524.5520	27661.6407	26771.0694	25855.1707	24916.2279	23956.4683	22978.0571	21983.0935	20973.6071	19951.5567	18918.8293	17877.2405	16828.5352	15774.3900	14716.4151	13656.1575	12595.1047	11534.6886	10476.2901	9421.2440	8370.8452	7326.3541	6289.0044	5260.0106	4240.5776	3231.9113	2235.231
1	33754.7463	33697.0758	33582.0029	33410.0597	33182.0337	32898.9554	32562.0824	32172.8812	31733.0063	31244.2778	30708.6583	30128.2296	29505.1695	28841.7298	28140.2145	27402.9610	26632.3216	25830.6476	25000.2755	24143.5140	23262.6347	22359.8626	21437.3699	20497.2704	19541.6158	18572.3932	17591.5237	16600.8620	15602.1976	14597.2554	13587.6991	12575.1334	11561.1078	10547.1215	9534.6279	8525.0406	7519.7400	6520.0811	5527.4021	4543.0351	3568.3189	2604.6139	1653.3230	715.916
2	30880.2430	30824.6456	30713.7129	30547.9643	30328.1686	30055.3317	29730.6810	29355.6472	28931.8440	28461.0461	27945.1666	27386.2346	26786.3718	26147.7718	25472.6790	24763.3702	24022.1367	23251.2697	22453.0464	21629.7184	20783.5020	19916.5706	19031.0480	18129.0038	17212.4502	16283.3399	15343.5655	14394.9594	13439.2953	12478.2906	11513.6089	10546.8645	9579.6270	8613.4269	7649.7624	6690.1076	5735.9218	4788.6608	3849.7912	2920.8076	2003.2555	1098.7610		
3	28122.7615	28069.2076	27962.3556	27802.7132	27591.0311	27328.2917	27015.6934	26654.6328	26246.6848	25793.5810	25297.1880	24759.4845	24182.5401	23568.4939	22919.5347	22237.8832	21525.7751	20785.4464	20019.1210	19228.9994	18417.2497	17586.0095	16737.3351	15873.2873	14995.8389	14106.9182	13208.4000	12302.1065	11389.8096	10473.2340	9554.0614	8633.9359	7714.4708	6797.2565	5883.8701	4975.8879	4074.9000	3182.5291	2300.4554	1430.4494	574.4182			
4	25480.6486	25429.1157	25326.3000	25172.6976	24969.0422	24716.2938	24415.6231	24068.3944	23676.1459	23240.5687	22763.4852	22246.8277	21692.6167	21102.9411	20479.9386	19825.7789	19142.6472	18432.7304	17698.2055	16941.2288	16163.9280	15368.3950	14556.6818	13730.7962	12892.7006	12044.3114	11187.4992	10324.0917	9455.8769	8584.6075	7712.0074	6839.7795	5969.6154	5103.2079	4242.2662	3388.5358	2543.8247	1710.0382	889.2289				
5	22952.7114	22903.1852	22804.3772	22656.7728	22461.0894	22218.2657	21929.4464	21595.9654	21219.3265	20801.1827	20343.3156	19847.6143	19316.0545	18750.6790	18153.5798	17526.8807	16872.7226	16193.2502	15490.6008	14766.8946	14024.2276	13264.6654	12490.2391	11702.9433	10904.7348	10097.5334	9283.2241	8463.6608	7640.6720	6816.0677	5991.6492	5169.2212	4350.6073	3537.6706	2732.3404	1936.6489	1152.7828	383.1585					
6	20538.2479	20490.7226	20395.9113	20254.2889	20066.5579	19833.6368	19556.6462	19236.8915	18875.8444	18475.1232	18036.4718	17561.7401	17052.8634	16511.8438	15940.7327	15341.6146	14716.5931	14067.7784	13397.2768	12707.1824	11999.5701	11276.4914	10539.9706	9792.0047	9034.5628	8269.5895	7499.0087	6724.7301	5948.6581	5172.7034	4398.7986	3628.9187	2865.1080	2109.5182	1364.4607	632.4843								
7	18237.0868	18191.5664	18100.7600	17965.1331	17785.3739	17562.3826	17297.2573	16991.2773	16645.8854	16262.6681	15843.3359	15389.7037	14903.6716	14387.2068	13842.3268	13271.0842	12675.5536	12057.8202	11419.9700	10764.0828	10092.2265	9406.4537	8708.8007	8001.2872	7285.9202	6564.6983	5839.6198	5112.6937	4385.9547	3661.4828	2941.4313	2228.0638	1523.8081	831.3351	153.6817									
8	16049.6405	16006.1398	15919.3685	15789.7833	15618.0596	15405.0808	15151.9249	14859.8479	14530.2666	14164.7400	13764.9495	13332.6805	12869.8040	12378.2591	11860.0373	11317.1686	10751.7089	10165.7299	9561.3111	8940.5334	8305.4757	7658.2131	7000.8179	6335.3630	5663.9281	4988.6099	4311.5357	3634.8825	2960.9045	2291.9703	1630.6160	979.6255	342.1539											
9	13976.9722	13935.5186	13852.8377	13729.3782	13565.8044	13362.9849	13121.9801	12844.0261	12530.5179	12182.9911	11803.1038	11392.6185	10953.3842	10487.3206	9996.4033	9482.6509	8948.1137	8394.8655	7824.9967	7240.6106	6643.8215	6036.7566	5421.5600	4800.4013	4175.4879	3549.0832	2923.5329	2301.3016	1685.0260	1077.5947	482.2723													
10	12020.8819	11981.5173	11903.0111	11785.8056	11630.5553	11438.1169	11209.5363	10946.0334	10648.9863	10319.9134	9960.4560	9572.3616	9157.4667	8717.6828	8254.9820	7771.3865	7268.9587	6749.7950	6216.0214	5669.7926	5113.2944	4548.7496	3978.4290	3404.6679	2829.8912	2256.6490	1687.6092	1125.9370	574.8194	38.2756														
11	10184.0153	10146.7989	10072.5866	9961.8154	9815.1328	9633.3864	9417.6115	9169.0172	8888.9705	8578.9799	8240.6789	7875.8101	7486.2101	7073.7960	6640.5542	6188.5304	5719.8236	5236.5818	4741.0024	4235.3355	3721.8929	3203.0627	2681.3328	2159.3251	1639.8473	1125.9722	621.1627	129.4853																
12	8470.0026	8435.0143	8365.2566	8261.1634	8123.3777	7952.7421	7750.2867	7517.2160	7254.8939	6964.8287	6648.6575	6308.1321	5945.1055	5561.5208	5159.4021	4740.8480	4308.0294	3863.1902	3408.6539	2946.8363	2480.2668	2011.6212	1543.7728	1079.8706	623.4674	178.7378																		
13	6883.6348	6850.9801	6785.8889	6688.7948	6560.3401	6401.3676	6212.9089	5996.1728	5752.5308	5483.5039	5190.7489	4876.0459	4541.2881	4188.4733	3819.6987	3437.1601	3043.1557	2640.0964	2230.5252	1817.1485	1402.8863	990.9510	584.9779	189.2547																				
14	5431.0906	5400.9066	5340.7582	5251.0815	5132.5237	4985.9347	4812.3575	4613.0166	4389.3065	4142.7793	3875.1345	3588.2093	3283.9721	2964.5198	2632.0792	2289.0159	1937.8510	1581.2918	1222.2810	864.0776	510.3933	165.6395																						
15	4120.2289	4092.6936	4037.8462	3956.1303	3848.2050	3714.9379	3557.3966	3376.8392	3174.7048	2952.6049	2712.3169	2455.7797	2185.0946	1902.5323	1610.5491	1311.8159	1009.2686	706.1933	406.3736	114.3694																						
16	2960.9710	2936.3160	2887.2361	2814.1894	2717.8581	2599.1427	2459.1559	2299.2164	2120.8431	1925.7521	1715.8578	1493.2790	1260.3555	1019.6781	774.1419	527.0394	282.2304	44.4834																						
17	1965.8035	1944.3335	1901.6362	1838.1950	1754.7324	1652.2069	1531.8105	1394.9679	1243.3394	1078.8290	903.6027	720.1223	531.2062	340.1405	150.8950																						
18	1150.4486	1132.5743	1097.0897	1044.5231	975.6684	891.5869	793.6143	683.3726	562.7936	434.1618	300.1927	164.1806	30.3695																						
19	534.7343	521.0330	493.9347	454.0526	402.3180	339.9993	268.7360	190.6028	108.2387	25.1501																									
20	143.4642	134.8278	117.9548	93.6691	63.2806	28.7401																													
21	1.6642	0.0491																																	

Physical constants uncertainty

Constant	Rel. uncertainty	$\delta D_0/\mathrm{cm}^{-1}$
Deuteron-electron mass ratio	$3.5 \cdot 10^{-11}$	$2.7 \cdot 10^{-8}$
Rydberg constant	$1.9 \cdot 10^{-12}$	$1.4 \cdot 10^{-7}$

CODATA 2014

$$m_\mathrm{d}/m_\mathrm{e} = 3\,670.482\,967\,85(13)$$

CODATA 2018

$$m_\mathrm{d}/m_\mathrm{e} = 3\,670.482\,967\,88(13)$$

Derivative over nuclear mass

PCCP 21, 10272 (2019)

(v, J)	$E^{(2)}_{v,J}$/a.u.	$D_{v,J}/\mathrm{cm}^{-1}$	$\frac{\partial E^{(2)}_{v,J}}{\partial \mu_\mathrm{d}} \cdot 10^6$
$(0, 0)$	$-1.167\,168\,809\,284\,05(4)$	$36\,749.090\,989\,81(1)$	
$(0, 1)$	$-1.166\,896\,432\,359\,76(4)$	$36\,689.311\,164\,76(1)$	
$(0, 2)$	$-1.166\,352\,930\,288\,83(4)$	$36\,570.026\,248\,10(1)$	
$(0, 3)$	$-1.165\,540\,786\,627\,44(4)$	$36\,391.781\,317\,40(1)$	
$(0, 4)$	$-1.164\,463\,677\,472\,61(4)$	$36\,155.383\,182\,70(1)$	
$(0, 5)$	$-1.163\,126\,414\,451\,1(2)$	$35\,861.887\,874\,01(4)$	
$(0, 6)$	$-1.161\,534\,872\,009\,1(2)$	$35\,512.584\,683\,27(4)$	

Derivative over nuclear mass

PCCP 21, 10272 (2019)

(v, J)	$E^{(2)}_{v,J}$/a.u.	$D_{v,J}/\mathrm{cm}^{-1}$	$\frac{\partial E^{(2)}_{v,J}}{\partial \mu_\mathrm{d}} \cdot 10^6$
$(0, 0)$	$-1.167\,168\,809\,284\,05(4)$	$36\,749.090\,989\,81(1)$	-1.02
$(0, 1)$	$-1.166\,896\,432\,359\,76(4)$	$36\,689.311\,164\,76(1)$	-1.10
$(0, 2)$	$-1.166\,352\,930\,288\,83(4)$	$36\,570.026\,248\,10(1)$	-1.24
$(0, 3)$	$-1.165\,540\,786\,627\,44(4)$	$36\,391.781\,317\,40(1)$	-1.46
$(0, 4)$	$-1.164\,463\,677\,472\,61(4)$	$36\,155.383\,182\,70(1)$	-1.75
$(0, 5)$	$-1.163\,126\,414\,451\,1(2)$	$35\,861.887\,874\,01(4)$	-2.10
$(0, 6)$	$-1.161\,534\,872\,009\,1(2)$	$35\,512.584\,683\,27(4)$	-2.52

Comparison with experimental data for D_2

Dissociation energy of the ground level

Contrib.	$D_{0,0}$
$E^{(2)}$	$36\,749.090\,989\,81(1)$
$E^{(4)}$	$-0.528\,206\,05(9)$
$E^{(5)}$	$-0.198\,256(3)$
$E^{(6)}$	$-0.002\,087(6)$
$E^{(7)}$	$0.000\,103(26)$
$E_{\rm FS}$	$-0.000\,202$
E	$36\,748.362\,342(26)$
Exper.[a]	$36\,748.362\,86(68)$
Diff.	$0.000\,57(68)$

[a] J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, F. Merkt, J. Chem. Phys., **130**, 174306 (2009).

Comparison with experimental data for D_2

Selected transition energies, $(v'', J'') \leftarrow (v', J')$

Contrib.	$(0,2) \leftarrow (1,2)$
$E^{(2)}$	$2\,987.291\,387\,53(1)$
$E^{(4)}$	$0.017\,498$
$E^{(5)}$	$-0.015\,33(8)$
$E^{(6)}$	$-0.000\,137$
$E^{(7)}$	$0.000\,007(2)$
$E_{\rm FS}$	$-0.000\,015$
E	$2\,987.293\,41(9)$
Exper.	$2\,987.293\,52(15)$[a]
Diff.	$0.000\,11(17)$

[a] M. Niu, E. Salumbides, G. Dickenson, K. Eikema, W. Ubachs, J. Mol. Spectrosc., **300**, 44 (2014).

[b] P. Wcisło, et al., Journal of Quantitative Spectroscopy and Radiative Transfer, **213**, 41 (2018).

[c] D. Mondelain, S. Kassi, T. Sala, D. Romanini, D. Gatti, A. Campargue, J. Mol. Spectrosc., **326**, 5 (2016).

[d] P. Maddaloni, P. Malara, E. De Tommasi, M. De Rosa, I. Ricciardi, G. Gagliardi, F. Tamassia, G. Di Lonardo, P. De Natale, J. Chem. Phys., **133**, 154317 (2010).

Comparison with experimental data for D_2

Selected transition energies, $(v'', J'') \leftarrow (v', J')$

Contrib.	$(0,2) \leftarrow (1,2)$	$(0,2) \leftarrow (2,4)$
$E^{(2)}$	$2\,987.291\,387\,53(1)$	$6\,241.120\,920\,12(1)$
$E^{(4)}$	$0.017\,498$	$0.040\,174$
$E^{(5)}$	$-0.015\,33(8)$	$-0.033\,167(18)$
$E^{(6)}$	$-0.000\,137$	$-0.000\,297(1)$
$E^{(7)}$	$0.000\,007(2)$	$0.000\,016(4)$
$E_{\rm FS}$	$-0.000\,015$	$-0.000\,031$
E	$2\,987.293\,41(9)$	$6\,241.127\,615(19)$
Exper.	$2\,987.293\,52(15)^a$	$6\,241.127\,647(11)^a$
		$6\,241.127\,655(13)^b$
		$6\,241.127\,637(17)^c$
Diff.	$0.000\,11(17)$	$0.000\,040(23)$

[a] M. Niu, E. Salumbides, G. Dickenson, K. Eikema, W. Ubachs, J. Mol. Spectrosc., **300**, 44 (2014).

[b] P. Wcisło, et al., Journal of Quantitative Spectroscopy and Radiative Transfer, **213**, 41 (2018).

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Comparison with experimental data for D_2

Selected transition energies, $(v'', J'') \leftarrow (v', J')$

Contrib.	$(0,2) \leftarrow (1,2)$	$(0,2) \leftarrow (2,4)$	$(0,1) \leftarrow (1,3)$
$E^{(2)}$	$2\,987.291\,387\,53(1)$	$6\,241.120\,920\,12(1)$	$3\,278.517\,313\,65(1)$
$E^{(4)}$	$0.017\,498$	$0.040\,174$	$0.023\,746(1)$
$E^{(5)}$	$-0.015\,33(8)$	$-0.033\,167(18)$	$-0.017\,82(1)$
$E^{(6)}$	$-0.000\,137$	$-0.000\,297(1)$	$-0.000\,160(1)$
$E^{(7)}$	$0.000\,007(2)$	$0.000\,016(4)$	$0.000\,009(5)$
E_{FS}	$-0.000\,015$	$-0.000\,031$	$-0.000\,017$
E	$2\,987.293\,41(9)$	$6\,241.127\,615(19)$	$3\,278.523\,06(1)$
Exper.	$2\,987.293\,52(15)^a$	$6\,241.127\,647(11)^a$ $6\,241.127\,655(13)^b$ $6\,241.127\,637(17)^c$	$3\,278.522\,0(2)^d$
Diff.	$0.000\,11(17)$	$0.000\,040(23)$	$0.001\,1(2)$

[a] M. Niu, E. Salumbides, G. Dickenson, K. Eikema, W. Ubachs, J. Mol. Spectrosc., **300**, 44 (2014).

[b] P. Wcisło, et al., Journal of Quantitative Spectroscopy and Radiative Transfer, **213**, 41 (2018).

[c] D. Mondelain, S. Kassi, T. Sala, D. Romanini, D. Gatti, A. Campargue, J. Mol. Spectrosc., **326**, 5 (2016).

[d] P. Maddaloni, P. Malara, E. De Tommasi, M. De Rosa, I. Ricciardi, G. Gagliardi, F. Tamassia, G. Di Lonardo, P. De Natale, J. Chem. Phys., **133**, 154317 (2010).

Conclusion

$$E(\alpha) = m\alpha^2\, E^{(2)} + m\alpha^4\, E^{(4)} + m\alpha^5\, E^{(5)} + m\alpha^6\, E^{(6)} + m\alpha^7\, E^{(7)} + \ldots$$

- **Variational solutions to four-body Schrödinger equation enable $10^{-8}\,\mathrm{cm}^{-1}$ (10^{-13}) accuracy on nonrelativistic D_0 and transition energy**
- Outlook:

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- **Variational solutions to four-body Schrödinger equation enable $10^{-8}\,\mathrm{cm}^{-1}$ (10^{-13}) accuracy on nonrelativistic D_0 and transition energy**
- Outlook:
  - The DNVM wave function will be applied to evaluate relativistic corrections
  - $m\alpha^5\, E^{(5)}$ QED term and the missing $m\alpha^7\, E^{(7)}$ correction limit the accuracy of the current theoretical predictions

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