Accurate theory of the hydrogen molecule

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Motivation

- benchmark calculation of relativistic and QED effects in molecular systems
- improved comparison with experimental values for H_2 levels (currently at 10^{-8} precision level)
- m_e/m_p from the vibrational spectrum, other constants . . .
- to discover new effects, like that in muonic versus electronic-hydrogen Lamb shift (PSI 2010), any hints ?

Collaborators

- J. Komasa (Poznań, Poland)
- B. Jeziorski and his group (Warsaw, Poland)

Determination of the dissociation energy of H_2 – a historical perspective

- 1927 2.88 eV Heitler and London (lower bound)
- 1929 4.46(4) eV Richardson and Davidson present value 4.478 eV
- 1935 4.454(13) eV James and Coolidge
- 1960 36113.6(3) Herzberg and Monfils
- 1968 36117.4 Kolos and Wolniewicz (lower bound)
- 1970 36118.6(5) Stwalley
- 1993 36118.049 Kolos and Rychlewski
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- 2009 36118.06962(37) Liu *et al.* (Ubachs and Merkt groups)

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Challenges

- beyond Born-Oppenheimer: combined finite nuclear mass and (relativistic) QED corrections to rovibrational energies, shielding constant,. . .
- higher order QED effects $\sim \alpha^4$ *Ry*
- extension of the computational technique to an arbitrary light molecule

Atomic or molecular energy

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

$$
\begin{array}{lccccccc}
E(\alpha,\beta) = & E_0 & + & \alpha^2 E_{\mathrm{REL}} & + & \alpha^3 E_{\mathrm{QED}} & + & \alpha^4 E_{\mathrm{HQED}} + \ldots \\
 & + & & + & & + & & \vdots \\
 & \beta E_{\mathrm{AD}} & & \alpha^2 \beta E^{\mathrm{rec}}_{\mathrm{REL}} & & \alpha^3 \beta E^{\mathrm{rec}}_{\mathrm{QED}} & & \\
 & + & & \vdots & & \vdots & & \\
 & \beta^2 E_{\mathrm{NA}} & & & & & & \\
 & \vdots & & & & & &
\end{array}
$$

E_0 – Born-Oppenheimer energy

E_{AD} – adiabatic correction

E_{NA} – nonadiabatic correction

$\alpha^2 E_{\mathrm{REL}}$ – relatywistic correction

$\alpha^3 E_{\mathrm{QED}}$ – leading radiative (QED) correction

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

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Nonrelativistic Schrödinger equation

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

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

$$H_{\rm el} = -\sum_a \frac{\nabla_a^2}{2\,m_{\rm e}} + V$$

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

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

Diatomic molecules, coordinate system origin at the bond midpoint

Adiabatic approximation

perturbative expansion

$$\phi = \phi_{\mathrm{a}} + \delta\phi_{\mathrm{na}}$$

$$E = E_{\mathrm{a}} + \delta E_{\mathrm{na}}$$

adiabatic assumption

$$\phi_{\mathrm{a}}(\vec{r}, \vec{R}) = \phi_{\mathrm{el}}(\vec{r})\, \chi(\vec{R})$$

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

nuclear equation

$$\left[H_{\mathrm{n}} + \mathcal{E}_{\mathrm{el}}(R) + \mathcal{E}_{\mathrm{a}}(R) - E_{\mathrm{a}}\right] |\chi\rangle = 0$$

$$\mathcal{E}_{\mathrm{a}}(R) = \left\langle \phi_{\mathrm{el}} | H_{\mathrm{n}} | \phi_{\mathrm{el}} \right\rangle_{\mathrm{el}}$$

Nonadiabatic corrections from NAPT

Comparison with direct variational calculations

Molecule	Method	E_{00}
H_2	Variational[1]	36 118.79756(2)
	NAPT[2]	36 118.7978(2)
	Difference	0.0002
D_2	Variational	36 749.0910
	NAPT[3]	36 749.0910(2)
	Difference	0.0000
HD	Variational[4]	36 406.5105(4)
	NAPT[5]	36 406.5108(2)
	Difference	0.0003

[1] M. Stanke, D. Kędziera, S. Bubin, M. Molski, L. Adamowicz, *JCP* **128**, 114313 (2008);
[2] K. Pachucki, J. Komasa, *JCP* **130**, 164113 (2009);
[3] Piszczatowski, Lach, Przybytek, Komasa, Pachucki, Jeziorski, *JCTC* **5**, 3039 (2009)
[4] M. Stanke, S. Bubin, M. Molski, L. Adamowicz, *Phys. Rev. A* **79**, 032507 (2009);
[5] K. Pachucki, J. Komasa, *PCCP* **12**, 9188 (2010)

Relativistic correction

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

Expectation value of the Breit-Pauli Hamiltonian

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

Leading radiative correction

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

$$\begin{aligned}
\mathcal{E}_{\mathrm{QED}} = & \sum_{a>b} \left\{ \left[\frac{164}{15} + \frac{14}{3} \ln \alpha \right] \langle \phi_{\mathrm{el}} | \delta(\vec{r}_{ab}) | \phi_{\mathrm{el}} \rangle \right. \\
& \left. - \frac{14}{3} \left\langle \phi_{\mathrm{el}} \left| \frac{1}{4\pi} P\left(\frac{1}{r_{ab}^3} \right) \right| \phi_{\mathrm{el}} \right\rangle \right\} \\
+ & \sum_a \left[\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0 \right] \sum_l \frac{4Z_l}{3} \langle \phi_{\mathrm{el}} | \delta(\vec{r}_{al}) | \phi_{\mathrm{el}} \rangle
\end{aligned}$$

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

Higher order QED corrections

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

- very difficult to calculate, known only for hydrogen and helium [6]
- approximate formula

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

[6] K. Pachucki, *Phys. Rev. A* **74**, 062510 (2006);

Variational approach in the exponential basis

Wave function expanded in terms of exponential functions

$$\phi = \sum c\, e^{-\alpha\, r_{1A} - \beta\, r_{1B} - \gamma\, r_{2A} - \delta\, r_{2B}}\, r_{1A}^{i}\, r_{1B}^{j}\, r_{2A}^{k}\, r_{2B}^{l}\, r_{12}^{n}$$

with

$$i + j + k + n + l \leq \Omega$$

Matrix elements with this basis functions have been investigated for many years, and are considered to be very difficult in the accurate evaluation.

Integrals

master integral

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

others by recurrence relations

$$f_n(i,j,k,l;r) = \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \frac{e^{-u_3\, r_{1A}}}{r_{1A}^{1-i}} \frac{e^{-u_2\, r_{1B}}}{r_{1B}^{1-j}} \frac{e^{-w_2\, r_{2A}}}{r_{2A}^{1-k}} \frac{e^{-w_3\, r_{2B}}}{r_{2B}^{1-l}} \frac{r}{r_{12}^{1-n}}$$

$\rightarrow$ analytic solution for arbitrary powers

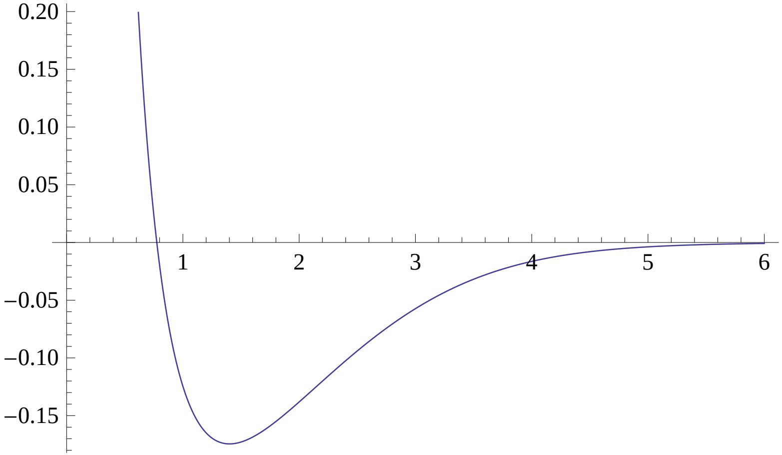
Special case: symmetric

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

$$f(0,0,0,0,0;r) = \frac{1}{4\,u\,w} \Big[e^{r\,(u+w)}\, \mathrm{Ei}(-2\,r\,(u+w)) + e^{-r(u+w)} \left(\gamma + \ln \frac{2\,r\,u\,w}{u+w}\right) - e^{r(u-w)}\, \mathrm{Ei}(-2\,r\,u) - e^{r(w-u)}\, \mathrm{Ei}(-2\,r\,w) \Big]$$

$$f(2,0,0,0,0;r) = \frac{(u^2+w^2)}{6\,u^2\,w^2}\, f(0,0,0,0,0;r) + \frac{e^{-r\,(u+w)}\, r^2}{12\,u\,w} + \frac{r}{24\,u^2\,w^2} \Big[(u+w)\, e^{-r\,(u+w)} - (u-w)\, e^{r\,(u-w)}\, \mathrm{Ei}(-2\,r\,u) - (w-u)\, e^{r\,(w-u)}\, \mathrm{Ei}(-2\,r\,w) - (u+w)\, e^{r\,(u+w)}\, \mathrm{Ei}(-2\,r\,(u+w)) + (u+w)\, e^{-r\,(u+w)} \left(\gamma + \ln \frac{2\,r\,u\,w}{u+w}\right) \Big]$$

Born-Oppenheimer potential



$E(1.4011) = -1.174\,475\,931\,400\,216\,7(3)$

Dissociation energy of all rovibrational states of H_2, HD i D_2

Rovibrational levels of H_2 (in cm^{-1})

$v\backslash J$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	36118.0696	35999.5827	35763.6964	35412.5507	34949.2721	34377.8800	33703.1726	32930.5991	32066.1266	31116.1067	30087.1493	28986.0061	27819.4682	26594.2780	25317.0575	23994.2505
1	31956.9034	31844.3290	31620.2311	31286.6781	30846.6902	30304.1479	29663.6809	28930.5440	28110.4874	27209.6288	26234.3321	25191.0967	24086.4605	22926.9171	21718.8492	20468.4759
2	28031.0670	27924.2753	27711.7087	27395.3676	26978.1720	26463.8724	25856.9411	25162.4519	24385.9548	23533.3534	22610.7880	21624.5312	20580.8960	19486.1590	18346.4985	17167.9474
3	24335.6787	24234.5818	24033.3726	23733.9878	23339.2543	22852.8015	22278.9563	21622.6265	20889.1803	20084.3279	19214.0114	18284.3049	17301.3289	16271.1794	15199.8715	14093.2980
4	20867.7039	20772.2598	20582.3263	20299.7818	19927.3669	19468.6008	18927.6785	18309.3586	17618.8479	16861.6882	16043.6518	15170.6479	14248.6434	13283.5982	12281.4160	11247.9099
5	17626.1400	17536.3593	17357.7260	17092.0653	16742.0411	16311.0741	15803.2433	15223.1787	14575.9499	13866.9601	13101.8471	12286.3973	11426.4734	10527.9578	9596.7126	8638.5554
6	14612.2901	14528.2461	14361.0627	14112.5194	13785.2138	13382.4836	12908.3120	12367.2247	11764.1860	11104.4981	10393.7108	9637.5433	8841.8215	8012.4332	7155.3007	6276.3735
7	11830.1543	11751.9964	11596.5661	11365.6062	11061.6626	10688.0095	10248.5600	9747.7694	9190.5379	8582.1192	7928.0390	7234.0292	6505.9792	5749.9080	4971.9605	4178.4321
8	9286.9790	9214.9526	9071.7726	8859.1575	8579.6206	8236.3999	7833.3746	7374.9763	6866.1012	6312.0299	5718.3612	5090.9637	4435.9509	3759.6871	3068.8309	2370.4348
9	6994.0292	6928.5057	6798.3271	6605.2057	6351.6504	6040.9022	5676.8602	5264.0027	4807.3140	4312.2229	3784.5601	3230.5444	2656.8077	2070.4770	1479.3467	892.2132
10	4967.6786	4909.1996	4793.1191	4621.1702	4395.9005	4120.6166	3799.3225	3436.6592	3037.8559	2608.7032	2155.5628	1685.4344	1206.1180	726.5520	257.5346	
11	3230.9712	3180.3202	3079.9265	2931.5894	2737.9677	2502.5403	2229.5680	1924.0695	1591.8264	1239.4455	874.5218	506.0045	145.0445			
12	1815.8955	1774.2213	1691.8517	1570.7364	1413.7847	1224.8610	1008.8062	771.5140	520.1248	263.4848	13.3741					
13	766.7551	735.8177	675.0810	586.8399	474.5979	343.1936	199.1012	51.2532								
14	144.7964	127.6357	94.9453	50.2393	0.0265											

$v\backslash J$	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
0	22632.0799	21236.5171	19813.2627	18367.7376	16905.0813	15430.1579	13947.5677	12461.6638	10976.5735	9496.2237	8024.3709	6564.6364	5120.5483	3695.5928	2293.2796	917.2285
1	19181.8142	17864.6524	16522.5351	15160.7573	13784.3676	12398.1776	11006.7791	9614.5672	8225.7696	6844.4839	5474.7238	4120.4784	2785.7900	1474.8629	192.2238	
2	15956.3587	14717.3851	13456.4677	12178.8362	10889.5174	9593.3530	8295.0256	6999.0945	5710.0438	4432.3453	3170.5449	1929.3851	713.9904			
3	12957.2014	11797.1591	10618.5796	9426.7112	8226.6608	7023.4255	5821.9382	4627.1316	3444.0280	2277.8701	1134.3209					
4	10188.7828	9109.6212	8015.9040	6913.0252	5806.3338	4701.1940	3603.0755	2517.6864	1451.1807	410.5020						
5	7659.2518	6664.5260	5660.0900	4651.6971	3645.2264	2646.8145	1663.0640	701.3929								
6	5381.6434	4477.1860	3569.2356	2664.3109	1769.4191	892.4054	42.5995									
7	3375.8309	2570.9911	1771.2705	984.8942	221.6033											
8	1672.1303	982.4662	311.5626													
9	319.5464															

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

$v\backslash J$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	36405.7828	36316.5549	36138.7136	35873.4735	35522.6205	35088.4710	34573.8214	33981.8890	33316.2492	32580.7701	31779.5467	30916.8389	29997.0121	29024.4839	28003.6768
1	32773.6224	32688.2505	32518.1034	32264.3604	31928.7546	31513.5337	31021.4092	30455.4998	29819.2695	29116.4637	28351.0463	27527.1389	26648.9645	25720.7960	24746.9115
2	29318.9058	29237.3125	29074.7056	28832.2304	28511.5704	28114.9074	27644.8730	27104.4929	26497.1260	25826.4033	25096.1664	24310.4092	23473.2236	22588.7509	21661.1387
3	26038.1525	25960.2800	25805.0987	25573.7219	25267.7856	24889.4100	24441.1515	23925.9482	23347.0616	22708.0166	22012.5422	21264.5155	20467.9102	19626.7494	18745.0660
4	22928.8940	22854.7061	22706.8788	22486.4954	22195.1476	21834.8977	21408.2320	20918.0081	20367.3975	19759.8282	19098.9275	18388.4681	17632.3192	16834.4021	15998.6523
5	19989.7501	19919.2343	19778.7372	19569.3140	19292.5156	18950.3510	18545.2424	18079.9739	17557.6361	16981.5705	16355.3151	15682.5527	14967.0643	14212.6878	13423.2833
6	17220.5367	17153.7075	17020.5708	16822.1567	16559.9785	16235.9975	15852.5788	15412.4415	14918.6057	14374.3390	13783.1048	13148.5131	12474.2769	11764.1743	11022.0166
7	14622.4158	14559.3194	14433.6367	14246.3756	13999.0170	13693.4808	13332.0831	12917.4886	12452.6597	11940.8057	11385.3335	10789.8022	10157.8828	9493.3238	8799.9242
8	12198.0988	12138.8187	12020.7590	11844.9092	11612.7237	11326.0890	10987.2827	10598.9285	10163.9475	9685.5103	9166.9919	8611.9292	8023.9860	7406.9236	6764.5794
9	9952.1180	9896.7836	9786.6084	9622.5684	9406.0989	9139.0636	8823.7159	8462.6556	8058.7844	7615.2618	7135.4634	6622.9449	6081.4127	5514.7025	4926.7680
10	7891.1923	7839.9908	7738.0776	7586.4219	7386.4504	7140.0186	6849.3743	6517.1183	6146.1638	5739.6971	5301.1434	4834.1375	4342.5051	3830.2546	3301.5839
11	6024.7189	5977.9115	5884.7877	5746.3189	5563.9384	5339.5138	5075.3150	4773.9796	4438.4781	4072.0831	3678.3444	3261.0743	2824.3466	2372.5158	1910.2635
12	4365.4408	4323.3876	4239.7798	4115.6059	3952.3271	3751.8548	3516.5234	3249.0634	2952.5769	2630.5204	2286.6991	1925.2806	1550.8364	1168.4295	783.7811
13	2930.3661	2893.5633	2820.4750	2712.1287	2570.0495	2396.2435	2193.1810	1963.7825	1711.4152	1439.9049	1153.5779	857.3517	556.9166	259.1098	
14	1742.0495	1711.1919	1650.0313	1559.6737	1441.7714	1298.5202	1132.6624	947.5072	746.9799	535.7292	319.3516	104.8977			
15	830.4030	806.5001	759.3242	690.1412	600.8685	494.1095	373.2271	242.4988	107.4717						
16	235.0929	219.7427	189.8566	147.1120	94.1833	35.1032									
17	3.6424	0.4156													

$v\backslash J$	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
0	26938.9769	25834.6998	24695.0621	23524.1599	22325.9517	21104.2469	19862.6992	18604.8024	17333.8914	16053.1441	14765.5876	13474.1053	12181.4463	10890.2366	9602.9923	8322.1343	7050.0050	5788.8882	4541.0321	3308.6771	2094.0906	899.6125
1	23731.5555	22678.9061	21593.0497	20477.9600	19337.4841	18175.3317	16995.0699	15800.1215	14593.7664	13379.1463	12159.2718	10937.0326	9715.2096	8496.4896	7283.4834	6078.7473	4884.8089	3704.1997	2539.4972	1393.3807	268.7111	
2	20694.5047	19692.9066	18660.3180	17600.6100	16517.5391	15414.7380	14295.7132	13163.8442	12022.3880	10874.4865	9723.1763	8571.4037	7422.0414	6277.9114	5141.8124	4016.5555	2905.0113	1810.1737	735.2519			
3	17826.8681	16876.1115	15896.6777	14892.3583	13866.8443	12823.7206	11766.4648	10698.4508	9622.9561	8543.1737	7462.2285	6383.1991	5309.1459	4243.1485	3188.3557	2148.0549	1125.7723	125.4269				
4	15128.9885	14229.2866	13303.3617	12354.9540	11387.7220	10405.2397	9411.0003	8408.4239	7400.8713	6391.6642	5384.1125	4381.5522	3387.3960	2405.2063	1438.8004	492.4142						
5	12602.7041	11754.7747	10883.2755	9991.9332	9084.4176	8164.3445	7235.2860	6300.7862	5364.3875	4429.6661	3500.2837	2580.0600	1673.0818	783.8704								
6	10251.6236	9456.8054	8641.3516	7809.0275	6963.5779	6108.7389	5248.2595	4385.9352	3525.6567	2671.4828	1827.7489	999.2369	191.4601									
7	8081.5132	7341.9385	6585.0622	5814.7666	5034.9701	4249.6559	3462.9182	2679.0314	1902.5582	1138.5187	392.6763											
8	6100.8550	5419.7136	4725.1884	4021.4061	3312.6267	2603.3098	1898.2188	1202.5889	522.4130													
9	4321.6815	3703.6489	3077.0439	2446.4679	1816.8504	1193.6140	582.9620															
10	2760.9065	2212.9053	1662.6275	1115.6479	578.3592	58.5350																
11	1442.6887	975.4703	515.1674	69.8220																		
12	403.5930	36.2340																				

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

$v\backslash J$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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	164.1866	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													

$v\backslash J$	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
0	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
1	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
2	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
3	22237.8832	21525.7751	20785.4464	20019.1210	19228.9994	18417.2497	17586.0005	16737.3351	15873.2873	14995.8389	14106.9182	13208.4000	12302.1065	11389.8096	10473.2340
4	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
5	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
6	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
7	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
8	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
9	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
10	7771.3865	7268.9587	6749.7950	6216.0214	5669.7926	5113.2944	4548.7496	3978.4290	3404.6679	2829.8912	2256.6490	1687.6692	1125.9370	574.8194	38.2756
11	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	4740.8480	4308.0294	3863.1902	3408.6539	2946.8363	2480.2668	2011.6212	1543.7728	1079.8706	623.4674	178.7378				
13	3437.1601	3043.1557	2640.0964	2230.5252	1817.1485	1402.8863	990.9510	584.9779	189.2547						
14	2289.0159	1937.8510	1581.2918	1222.2810	864.0776	510.3933	165.6395								
15	1311.8159	1009.2686	706.1933	406.3736	114.3694										
16	527.0394	282.2304	44.4834												

$v\backslash J$	30	31	32	33	34	35	36	37	38	39	40	41	42	43
0	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	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	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	9554.0614	8633.9359	7714.4708	6797.2565	5883.8701	4975.8879	4074.9000	3182.5291	2300.4554	1430.4494	574.4182			
4	7712.0074	6839.7795	5969.6154	5103.2079	4242.2662	3388.5358	2543.8247	1710.0382	889.2289					
5	5991.6492	5169.2212	4350.6073	3537.6706	2732.3404	1936.6489	1152.7828	383.1585						
6	4398.7986	3628.9187	2865.1080	2109.5182	1364.4607	632.4843								
7	2941.4313	2228.0638	1523.8081	831.3351	153.6817									
8	1630.6160	979.6255	342.1539											
9	482.2723													

Dissociation energy of H_2 and D_2 in cm^{-1}

		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. 2004	Eyler	36118.062(10)	36748.343(10)
Expt. 2010	Merkt&Ubachs	36118.0696(4)	

Dissociation energy of H_2 and D_2 in cm^{-1}

		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. 2004	Eyler	36118.062(10)	36748.343(10)
Expt. 2010	Merkt&Ubachs	36118.0696(4)	36748.3629(6)

Excitation energies of H_2 and D_2

		$J = 0 \rightarrow 1$	$v = 0 \rightarrow 1$
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)

Comparison of theoretical and experimental results for D_0 in cm^{-1} of HD

Component	D_0	δ
This work	36 405.7828(10)	
Theory		
Stanke (2009)	36 405.7814[a]	−0.0014
Wolniewicz (1995)	36 405.787	0.004
Kołos and Rychlewski (1993)	36 405.763	−0.020
Kołos, Szalewicz, Monkhorst (1986)	36 405.784	0.001
Wolniewicz (1983)	36 405.73	0.05
Bishop and Cheung (1978)	36 405.49	−0.29
Experiment		
Merkt & Ubachs (2010)	36 405.78366(36)	0.0009
Zhang (2004)	36 405.828(16)	0.045
Balakrishnan (1993)	36 405.83(10)	0.05
Eyler and Melikechi (1993)	36 405.88(10)	0.10
Herzberg (1970)	36 406.2(4)	0.4

[a] Their $D_0 = 36\,405.9794\ \mathrm{cm}^{-1}$ has been augmented by a sum of our α^3 and α^4 QED corrections equal to $-0.1980\ \mathrm{cm}^{-1}$.

ΔE between rotational levels of the ground vibrational state ($v = 0$) of HD, in cm^{-1}

Component	$\Delta E(0 \to 1)$	$\Delta E(0 \to 2)$
BO	89.270 629	267.196 840
Adiabatic correction	−0.036 086	−0.107 842
Nonadiabatic correction	−0.007 782(6)	−0.023 287(19)
α^0 subtotal	89.226 761(6)	267.065 711(19)
α^2 correction	0.001 948(2)	0.005 813(5)
$\alpha^0+\alpha^2$ subtotal	89.228 709(6)	267.071 524(20)
α^3 correction	−0.000 771(1)	−0.002 303(2)
α^4 correction	−0.000 007(4)	−0.000 018(9)
Total	89.227 933(8)	267.069 205(22)
Evenson (1988)/Stoicheff (1957)	89.227 950(5)	267.086(10)

ΔE between rotational levels of the ground vibrational state ($v = 0$) of HD, in cm^{-1}

Component	$\Delta E(0 \to 1)$	$\Delta E(0 \to 2)$
BO	89.270 629	267.196 840
Adiabatic correction	−0.036 086	−0.107 842
Nonadiabatic correction	−0.007 782(6)	−0.023 287(19)
α^0 subtotal	89.226 761(6)	267.065 711(19)
α^2 correction	0.001 948(2)	0.005 813(5)
α^0+α^2 subtotal	89.228 709(6)	267.071 524(20)
α^3 correction	−0.000 771(1)	−0.002 303(2)
α^4 correction	−0.000 007(4)	−0.000 018(9)
Total	89.227 933(8)	267.069 205(22)
Evenson (1988)/Stoicheff (1957)	89.227 950(5)	267.086(10)
Drouin (2010)	89.227 9326(3)	

Summary

- analytic formulae for two-center Slater integrals
- highest accuracy ever achieved for BO potential of H_2
- very good convergence with exponential basis set
- higher order QED corrections can be evaluated as accurately as for H_2^+
- more problematic are the finite nuclear mass corrections
- possible generalizations to the 3- and more electrons molecule