Benchmarking of Computational Methods

HYDROGEN MOLECULE DISSOCIATION

$H_2 \rightarrow 2\,H$

Description of reaction: When hydrogen molecule is excited both vibrationally and rotationally, there are only certain quantized motions that are allowed. For vibrational motion, there are only 15 allowable states before the molecule dissociates, which are v=0,...,14. We calculate the vibrational levels for the grand rotational state (Para, J=0) in Plot 1 and the first excited rotational state (Ortho, J=1).

Plot 1: Energy spacing for each vibration of the ground rotational state which converges to the dissociation limit.
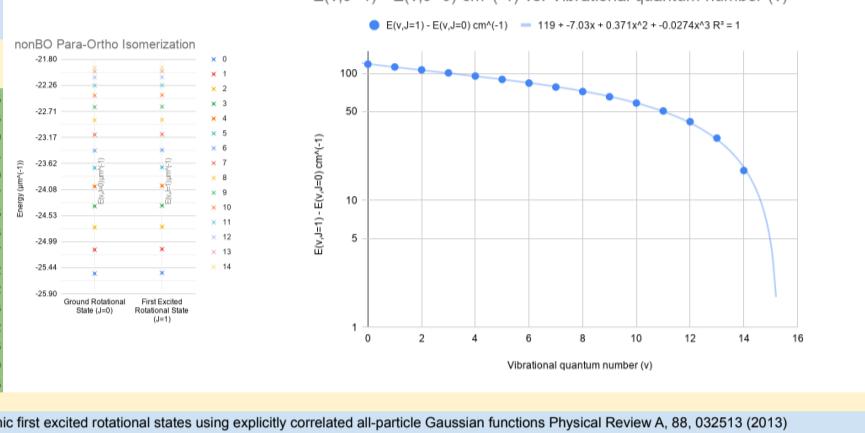

E(v,J=1), E(v,J=0), and energy of two hydrogen atoms

— Energy of two hydrogen atoms   J=0 R^2 = 0   — E(v,J=0)   -1.16 + 0.02x + -5.84E-04x^2 R^2 = 1

Quantum Logical Electrons and Nuclei (QLEAN) method with non-BOA

Plot 2:   **Plot 3:**

Trendline Prediction (nonBO) of Energy Difference for E(v=15,J=1) - E(v=15,J=0) = 4.0425

Hydrogen (H_2) Molecule	Para	Ortho	Para	Ortho	Energy Spacing in Wavenumber
Rotational Excitation (J)	Ground Rotational State (J=0)	First Excited Rotational State (J=1)	Ground Rotational State (J=0)	First Excited Rotational State (J=1)	nonBO Diff
Vibrational quantum number (v)	E(v,J=0) hartree	E(v,J=1) hartree	E(v,J=0) µm^(-1)	E(v,J=1) µm^(-1)	E(v,J=1) - E(v,J=0) cm^(-1)
0	-1.16402503084	-1.16348513950	-25.547396	-25.535547	118.4925
1	-1.14506537210	-1.14455241846	-25.131280	-25.120022	112.5803
2	-1.12717793574	-1.12669138810	-24.738696	-24.728018	106.7849
3	-1.11034047897	-1.10987981810	-24.369157	-24.359046	101.1034
4	-1.09453917282	-1.09410426590	-24.022358	-24.012813	95.4510
5	-1.07976944651	-1.07936034343	-23.698200	-23.689221	89.7877
6	-1.06603723556	-1.06565426881	-23.396431	-23.388408	84.0515
7	-1.05336076146	-1.05300461195	-23.118596	-23.110780	78.1658
8	-1.04177303677	-1.04144482266	-22.864275	-22.857072	72.0347
9	-1.03132538201	-1.03102679537	-22.634976	-22.628423	65.5322
10	-1.02209239452	-1.02182590707	-22.432335	-22.426486	58.4872
11	-1.01417906063	-1.01394823840	-22.258658	-22.253592	50.6596
12	-1.00773111494	-1.00754119225	-22.117141	-22.112973	41.6832
13	-1.00295040007	-1.00280939710	-22.012217	-22.009122	30.9466
14	-1.00011594689	-1.00003771446	-21.950008	-21.948291	17.1700

The energy spacing of E(v=15,J=1) - E(v=15,J=0) is predicted to be: **4.0425**

nonBO Para-Ortho Isomerization

E(v,J=1) - E(v,J=0) cm^(-1) vs. Vibrational quantum number (v)

● E(v,J=1) - E(v,J=0) cm^(-1)   — 119 + -7.03x + 0.371x^2 + -0.0274x^3 R^2 = 1
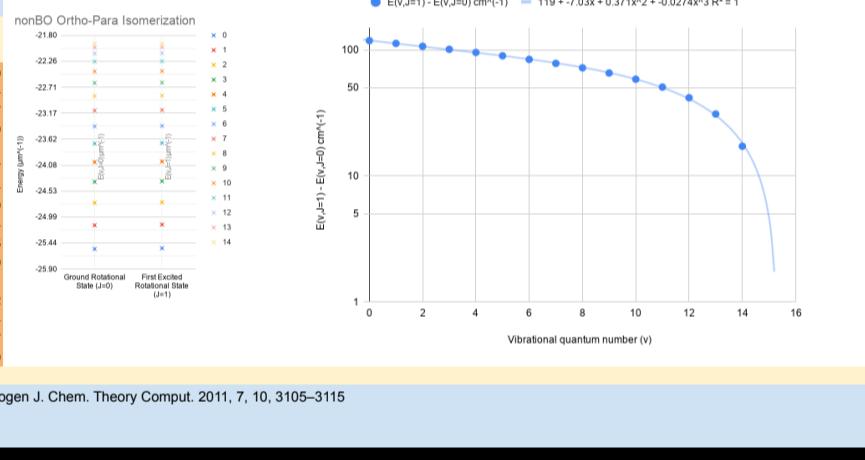
Komasa 2011 (BO computation)

Plot 4:   **Plot 5:**

Trendline Prediction (BO) of Energy Difference for E(v=15,J=1) - E(v=15,J=0) = 4.0369

Hydrogen (H_2) Molecule	Para	Ortho	Para	Ortho	Energy Spacing in Wavenumber
Rotational Excitation (J)	Ground Rotational State (J=0)	First Excited Rotational State (J=1)	Ground Rotational State (J=0)	First Excited Rotational State (J=1)	BO Diff
Vibrational quantum number (v)	E(v,J=0) cm^(-1)	E(v,J=1) cm^(-1)	E(v,J=0) µm^(-1)	E(v,J=1) µm^(-1)	E(v,J=0) - E(v,J=1) cm^(-1)
0	36118.0696	35999.5827	-3.61180696	-3.59995827	118.4869
1	31956.9034	31844.329	-3.19569034	-3.1844329	112.5744
2	28031.067	27924.2753	-2.8031067	-2.79242753	106.7917
3	24335.6787	24234.5818	-2.43356787	-2.42345818	101.0969
4	20867.7039	20772.2598	-2.08677039	-2.07722598	95.4441
5	17626.14	17536.3593	-1.762614	-1.75363593	89.7807
6	14612.2901	14528.2461	-1.46122901	-1.45282461	84.044
7	11830.1543	11751.9964	-1.18301543	-1.17519964	78.1579
8	9286.979	9214.9526	-0.9286979	-0.92149526	72.0264
9	6994.0292	6928.5057	-0.69940292	-0.69285057	65.5235
10	4967.6786	4909.1996	-0.49676786	-0.49091996	58.479
11	3230.9712	3180.3202	-0.32309712	-0.31803202	50.651
12	1815.8955	1774.2213	-0.18158955	-0.17742213	41.6742
13	766.7551	735.8177	-0.07667551	-0.07358177	30.9374
14	144.7964	127.6357	-0.01447964	-0.01276357	17.1607
15	These states are not experimentally measured				4.0369

nonBO Ortho-Para Isomerization

E(v,J=1) - E(v,J=0) cm^(-1) vs. Vibrational quantum number (v)

● E(v,J=1) - E(v,J=0) cm^(-1)   — 119 + -7.03x + 0.371x^2 + -0.0274x^3 R^2 = 1

Dabrowski 1984 (Experiment)

Plot 6:   **Plot 7:**

Trendline Prediction (Experiment) of Energy Difference for E(v=15,J=1) - E(v=15,J=0) = 4.31

Hydrogen (H_2) Molecule	Para	Ortho	Energy Spacing in Wavenumber
Rotational Excitation (J)	Ground Rotational State (J=0)	First Excited Rotational State (J=1)	Exp. Diff
Vibrational quantum number (v)	E(v,J=0) cm^(-1)	E(v,J=1) cm^(-1)	E(v,J=1) - E(v,J=0) cm^(-1)
0	0	118.5	118.5
1	4161.14	4273.75	112.61
2	8086.93	8193.81	106.88
3	11782.36	11883.51	101.15
4	15250.31	15345.81	95.5
5	18491.92	18581.71	89.79
6	21505.78	21589.82	84.04
7	24287.91	24366.14	78.23
8	26831.16	26903.18	72.02
9	29124.09	29189.64	65.55
10	31150.47	31208.93	58.46
11	32887.13	32937.8	50.67
12	34302.2	34343.93	41.73
13	35351.36	35382.31	30.95
14	35973.38	35990.52	17.14
15	These states are not experimentally measured		4.31

Experimental Ortho-Para Isomerization

E(v,J=1) - E(v,J=0) cm^(-1) vs. Vibrational quantum number (v)

● E(v,J=1) - E(v,J=0) cm^(-1)   — 119 + -7.03x + 0.371x^2 + -0.0274x^3 R^2 = 1

Comparison of non-BO versus BO Computations to Experiment

Plot 8 and 9:

Vibrational quantum number (v)	nonBO Diff.	BO Diff.	Exp. Diff.	((Exp. Diff.) - (nonBO Diff.))*100	((Exp. Diff.) - (BO Diff.))*100	|(nonBO Diff.) - (BO Diff.)|	%
0	118.4925	118.4869	118.5	0.755	1.310	0.5553	0.47%
1	112.5803	112.5744	112.61	2.969	3.560	0.5911	0.53%
2	106.7849	106.7917	106.88	9.514	8.830	0.6836	0.64%
3	101.1034	101.0969	101.15	4.663	5.310	0.6475	0.64%
4	95.4510	95.4441	95.5	4.896	5.590	0.6936	0.73%
5	89.7877	89.7807	89.79	0.225	0.930	0.7048	0.78%
6	84.0515	84.044	84.04	-1.149	-0.400	0.7486	0.89%
7	78.1658	78.1579	78.23	6.422	7.210	0.7882	1.01%
8	72.0347	72.0264	72.02	-1.467	-0.640	0.8271	1.15%
9	65.5322	65.5235	65.55	1.781	2.650	0.8693	1.33%
10	58.4872	58.479	58.46	-2.723	-1.900	0.8235	1.41%
11	50.6596	50.651	50.67	1.038	1.900	0.8624	1.70%
12	41.6832	41.6742	41.73	4.679	5.580	0.9012	2.16%
13	30.9466	30.9374	30.95	0.343	1.260	0.9175	2.96%
14	17.1700	17.1607	17.14	-3.003	-2.070	0.9334	5.44%
15	4.0425	4.0369	4.31	27.000	27.560	0.5600	13.85%

(Exp. Diff.) - (nonBO Diff.) and (Exp. Diff.) - (BO Diff.)

— (Exp. Diff.) - (nonBO Diff.))*100   — ((Exp. Diff.) - (BO Diff.))*100

% Difference (BO/nonBO) vs. Vibrational quantum number (v)

Comparison of QLEAN versus NOMO Computations

Vibrational quantum number (v)	QLEAN E(v,J=0) hartree	NOMO E(v,J=0) hartree	| QLEAN-NOMO | = Diff (hartree)	
0	-1.16402503084	-1.130346	0.03367903084	QLEAN is variationally lower in energy than the Nuclear Orbital plus Molecular Orbital (NOMO) method, hence QLEAN is more accurate. The NOMO method gets less accurate when the vibrational number increases.
1	-1.14506537210	-1.111238	0.03382737210	

Executive Summary of QLEAN method: Using the Rayleigh-Ritz variational method with explicitly correlated Gaussian basis functions in non-Born-Oppenheimer (non-BO) QLEAN method, fifteen (0-14) energy levels for the ground rotational and first excited rotational excited states of molecular hydrogen have been calculated and compared to previous calculations and experiment. We used 10,000 basis functions for our predictions. We compare our results to the Best known Born-Oppenheimer (BO) method and to the experiment. QLEAN method is highly accurate in predicting all states including highly excited states. There is a 5% breakdown of the BO prediction in the highest bound state. QLEAN is consistently lower in the predictions, with the exception of the v=2 state. We attribute this anomaly to the experimental value being not precise enough for comparison. The lowest energy of molecular hydrogen is -1.164 hartrees (QLEAN).

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