Application of the Canonical Van Vleck Second-Order Operator Perturbation Theory to the Analysis of Anharmonic Vibrational Spectra of Medium-Size Molecules: Uracil as a Benchmark Example

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SUPPORTING INFORMATION

Definition of Molecular Geometry (Angstroms and Degrees):

Center Number I	Atomic Number	Reference Centers J	K	L	Bond Length I:J	Bond Angle I:J:K	Dihedral Angle I:J:K:L
1	7(N)						
2	6(C)	1			1.38518623		
3	7(N)	2	1		1.37966783	112.713321	
4	6(C)	3	2	1	1.40335570	128.637223	0.000000
5	6(C)	4	3	2	1.45335326	113.290125	0.000000
6	6(C)	5	4	3	1.34800497	119.755049	0.000000
7	1(H)	1	2	3	1.00619326	115.143611	180.000000
8	8(O)	2	3	4	1.21479313	124.208884	180.000000
9	1(H)	3	4	5	1.01081674	116.041307	180.000000
10	8(O)	4	3	2	1.21832721	120.541354	180.000000
11	1(H)	5	4	3	1.07614464	118.721555	180.000000
12	1(H)	6	5	4	1.07980647	122.505874	180.000000

Cartesian Coordinates After Orientation of Axes:

Atom	Atomic Number	Isotope Species	Coordinates (Angstroms) X	Y	Z	Atomic Mass
1	7(N)	N(14)	-1.17421064	1.01553709	0.00000000	14.00307400
2	6(C)	C(12)	-1.21941361	-0.36891139	0.00000000	12.00000000
3	7(N)	N(14)	0.03519661	-0.94287700	0.00000000	14.00307400
4	6(C)	C(12)	1.28803960	-0.31058621	0.00000000	12.00000000
5	6(C)	C(12)	1.19958649	1.14007286	0.00000000	12.00000000
6	6(C)	C(12)	-0.00923806	1.73661339	0.00000000	12.00000000
7	1(H)	H(1)	-2.07062627	1.47255338	0.00000000	1.00782522
8	8(O)	O(16)	-2.25841942	-0.99834707	0.00000000	15.99491502
9	1(H)	H(1)	0.04821744	-1.95360988	0.00000000	1.00782522
10	8(O)	O(16)	2.31351324	-0.96840459	0.00000000	15.99491502
11	1(H)	H(1)	2.11010449	1.71369666	0.00000000	1.00782522
12	1(H)	H(1)	-0.12660743	2.81002219	0.00000000	1.00782522

Internal Coordinate Definition:

Number	Description	Definition	Type
1	N1-H str	N(1) - H(7)	Bond Stretch
2	C2=O str	C(2) - O(8)	Bond Stretch
3	N3-H str	N(3) - H(9)	Bond Stretch
4	C4=O str	C(4) - O(10)	Bond Stretch
5	C5-H str	C(5) - H(11)	Bond Stretch
6	C6-H str	C(6) - H(12)	Bond Stretch
7	N1-C2 str	N(1) - C(2)	Bond Stretch
8	C2-N3 str	C(2) - N(3)	Bond Stretch
9	N3-C4 str	N(3) - C(4)	Bond Stretch
10	C4-C5 str	C(4) - C(5)	Bond Stretch
11	C5-C6 str	C(5) - C(6)	Bond Stretch
12	C6-N1 str	C(6) - N(1)	Bond Stretch
13	C2-N1-H7bend	C(2) - N(1) - H(7)	Angle Bend
14	C6-N1-H7bend	C(6) - N(1) - H(7)	Angle Bend
15	N1-C2-O8bend	N(1) - C(2) - O(8)	Angle Bend
16	N3-C2-O8bend	N(3) - C(2) - O(8)	Angle Bend
17	C4-N3-H9bend	C(4) - N(3) - H(9)	Angle Bend
18	C5-C4-O10ben	C(5) - C(4) - O(10)	Angle Bend
19	C4-C5-H11ben	C(4) - C(5) - H(11)	Angle Bend
20	C6-C5-H11ben	C(6) - C(5) - H(11)	Angle Bend
21	C5-C6-H12ben	C(5) - C(6) - H(12)	Angle Bend
22	N1-C2-N3-C4	N(1) - C(2) - N(3) - C(4)	Torsion
23	N1-C6-C5-C4	N(1) - C(6) - C(5) - C(4)	Torsion
24	N3-C2-N1-C6	N(3) - C(2) - N(1) - C(6)	Torsion
25	N3-C4-C5-H11	N(3) - C(4) - C(5) - H(11)	Torsion
26	C4-N3-C2-O8	C(4) - N(3) - C(2) - O(8)	Torsion
27	H7-N1-C6-H12	H(7) - N(1) - C(6) - H(12)	Torsion
28	H9-N3-C4-O10	H(9) - N(3) - C(4) - O(10)	Torsion
29	O10-C4-C5-H1	O(10) - C(4) - C(5) - H(11)	Torsion
30	H11-C5-C6-H1	H(11) - C(5) - C(6) - H(12)	Torsion

Cartesian Force Constants, [atto J / Angstrom^2] :--

	1	2	3	4	5	6
1	13.684618					
2	-0.787263	10.957077				
3	0.000000	0.000000	0.835669			
4	-2.322737	-0.052554	0.000000	14.404826		
5	0.529235	-3.953498	0.000000	2.789511	11.198153	
6	0.000000	0.000000	-0.929407	0.000000	0.000000	3.240741
7	0.198410	0.717053	0.000000	-3.710535	0.516835	0.000000
8	0.674005	-0.545938	0.000000	1.319620	-2.962713	0.000000
9	0.000000	0.000000	0.135694	0.000000	0.000000	-0.857097
10	-0.112548	-0.396344	0.000000	-0.779423	0.526533	0.000000
11	-0.426088	-0.637916	0.000000	-0.427593	1.127968	0.000000
12	0.000000	0.000000	-0.084856	0.000000	0.000000	-0.245749
13	-0.924437	-0.087843	0.000000	-0.107157	0.310828	0.000000
14	-0.077128	0.588331	0.000000	0.197126	-0.335039	0.000000
15	0.000000	0.000000	0.164109	0.000000	0.000000	0.001170
16	-4.551868	-1.080211	0.000000	0.446076	-0.946848	0.000000
17	-1.626573	-3.006395	0.000000	-0.405958	-0.528855	0.000000
18	0.000000	0.000000	-0.595175	0.000000	0.000000	-0.051261
19	-5.870503	2.544722	0.000000	0.107277	0.007299	0.000000
20	2.513748	-2.429972	0.000000	0.615494	-0.135252	0.000000
21	0.000000	0.000000	-0.089331	0.000000	0.000000	-0.027717
22	0.042667	-0.526064	0.000000	-8.308219	-4.045216	0.000000
23	-1.057944	-0.902828	0.000000	-4.063361	-4.066372	0.000000
24	0.000000	0.000000	0.318813	0.000000	0.000000	-1.277843
25	-0.110579	0.046693	0.000000	0.141379	0.577760	0.000000
26	0.041385	0.032290	0.000000	-0.004369	-0.179159	0.000000
27	0.000000	0.000000	0.069278	0.000000	0.000000	-0.028388
28	-0.045063	0.121040	0.000000	0.207556	-0.306471	0.000000
29	0.119801	0.144854	0.000000	0.043913	-0.174454	0.000000
30	0.000000	0.000000	0.000623	0.000000	0.000000	0.116585
31	-0.033849	0.069405	0.000000	-0.002039	0.007697	0.000000
32	0.071091	-0.004528	0.000000	0.033245	-0.044012	0.000000
33	0.000000	0.000000	0.135220	0.000000	0.000000	0.000504
34	0.045889	-0.568633	0.000000	-0.077003	0.032838	0.000000
35	0.025732	-0.241475	0.000000	-0.045074	0.053234	0.000000
36	0.000000	0.000000	0.039362	0.000000	0.000000	0.058463

	7	8	9	10	11	12
7	10.636911					
8	-0.330712	13.010300				
9	0.000000	0.000000	0.906680			
10	-2.788004	-1.171714	0.000000	12.418031		
11	-0.486109	-3.023310	0.000000	-3.238147	11.390219	
12	0.000000	0.000000	-0.769302	0.000000	0.000000	3.078296
13	0.164961	-0.630728	0.000000	-1.677342	-0.290258	0.000000
14	-0.402628	-0.301608	0.000000	-0.127934	-3.845177	0.000000
15	0.000000	0.000000	0.133982	0.000000	0.000000	-1.158433
16	-0.501303	0.119703	0.000000	0.313473	0.860518	0.000000
17	-0.175049	0.000196	0.000000	0.743363	-0.031301	0.000000
18	0.000000	0.000000	0.006243	0.000000	0.000000	0.019483
19	0.015303	-0.025244	0.000000	-0.006868	0.015669	0.000000
20	-0.023239	-0.121920	0.000000	-0.022804	-0.047576	0.000000
21	0.000000	0.000000	0.051103	0.000000	0.000000	-0.009710
22	-1.400570	-0.416092	0.000000	0.233679	0.273016	0.000000
23	0.170119	0.463255	0.000000	-0.080090	-0.159667	0.000000
24	0.000000	0.000000	0.324786	0.000000	0.000000	0.119186
25	-1.085702	0.032543	0.000000	0.162646	-0.547195	0.000000
26	0.105513	-6.950121	0.000000	0.007300	-0.199201	0.000000
27	0.000000	0.000000	-0.253790	0.000000	0.000000	0.013509
28	-1.557952	0.404689	0.000000	-7.751570	4.206750	0.000000
29	-0.104678	0.530788	0.000000	4.177527	-4.471134	0.000000
30	0.000000	0.000000	0.293513	0.000000	0.000000	-1.159612
31	0.009661	0.023353	0.000000	0.079616	0.073156	0.000000
32	0.004742	-0.107667	0.000000	-0.445071	-0.115946	0.000000
33	0.000000	0.000000	0.039597	0.000000	0.000000	0.003923
34	0.018821	0.000578	0.000000	-0.091691	-0.013719	0.000000
35	0.008152	0.008737	0.000000	0.027381	0.013041	0.000000
36	0.000000	0.000000	-0.011409	0.000000	0.000000	0.193266

	13	14	15	16	17	18
13	13.331669					
14	-0.152801	9.990241				
15	0.000000	0.000000	1.522077			
16	-6.340040	2.056321	0.000000	12.239688		
17	2.401051	-3.200642	0.000000	-1.415591	11.979900	
18	0.000000	0.000000	-0.802570	0.000000	0.000000	2.080735
19	-0.005330	-0.089641	0.000000	-0.287684	0.225537	0.000000
20	-0.073053	-0.030567	0.000000	-0.308795	0.244559	0.000000
21	0.000000	0.000000	0.048629	0.000000	0.000000	-0.118921
22	0.017183	-0.106601	0.000000	-0.097057	-0.026371	0.000000
23	-0.060531	0.037092	0.000000	0.200458	-0.030576	0.000000
24	0.000000	0.000000	-0.017349	0.000000	0.000000	0.078921
25	-0.097197	-0.033611	0.000000	-0.024017	-0.007530	0.000000
26	-0.041113	0.004719	0.000000	-0.015622	0.010427	0.000000
27	0.000000	0.000000	0.064033	0.000000	0.000000	-0.010776
28	-0.129339	0.480646	0.000000	0.032831	-0.055689	0.000000
29	0.867673	-0.544594	0.000000	-0.224650	-0.171254	0.000000
30	0.000000	0.000000	0.337932	0.000000	0.000000	0.053581
31	-4.288868	-2.185712	0.000000	-0.241490	-0.278276	0.000000
32	-2.211965	-2.258230	0.000000	0.235232	0.173601	0.000000
33	0.000000	0.000000	-0.407881	0.000000	0.000000	-0.035655
34	0.055897	0.441964	0.000000	-0.988610	0.621085	0.000000
35	-0.031258	-0.104525	0.000000	0.519484	-5.439658	0.000000
36	0.000000	0.000000	0.114301	0.000000	0.000000	-0.624605

	19	20	21	22	23	24
19	6.057552					
20	-2.658320	2.423022				
21	0.000000	0.000000	0.180512			
22	-0.040297	-0.057021	0.000000	9.680700		
23	-0.016626	0.067342	0.000000	4.983601	4.550742	
24	0.000000	0.000000	-0.055252	0.000000	0.000000	0.603078
25	0.006776	0.026475	0.000000	0.016261	-0.075855	0.000000
26	-0.003744	-0.002659	0.000000	-0.050880	0.013184	0.000000
27	0.000000	0.000000	0.017524	0.000000	0.000000	-0.056843
28	0.014026	0.000132	0.000000	-0.138517	0.039546	0.000000
29	-0.011243	0.017441	0.000000	-0.019000	0.034080	0.000000
30	0.000000	0.000000	-0.004291	0.000000	0.000000	-0.026531
31	-0.008051	-0.013313	0.000000	0.005056	-0.001059	0.000000
32	0.010474	0.009915	0.000000	-0.006215	0.014071	0.000000
33	0.000000	0.000000	0.032011	0.000000	0.000000	-0.007576
34	0.017799	0.000697	0.000000	-0.010887	-0.038258	0.000000
35	0.001116	0.005668	0.000000	-0.003158	-0.020322	0.000000
36	0.000000	0.000000	-0.024559	0.000000	0.000000	-0.003389

	25	26	27	28	29	30
25	0.952603					
26	-0.088063	7.254872				
27	0.000000	0.000000	0.255603			
28	0.030882	0.045975	0.000000	9.335414		
29	0.091770	0.020123	0.000000	-4.968135	4.575358	
30	0.000000	0.000000	-0.065533	0.000000	0.000000	0.521972
31	0.005690	0.004098	0.000000	0.004518	-0.010206	0.000000
32	-0.023201	-0.005017	0.000000	0.029326	0.048475	0.000000
33	0.000000	0.000000	0.003561	0.000000	0.000000	-0.027077
34	0.001259	-0.000481	0.000000	-0.002787	0.037228	0.000000
35	0.000214	0.000544	0.000000	0.002192	-0.009682	0.000000
36	0.000000	0.000000	-0.008179	0.000000	0.000000	-0.041162

	31	32	33	34	35	36
31	4.457281					
32	2.309580	2.276320				
33	0.000000	0.000000	0.351808			
34	0.012473	-0.007239	0.000000	1.018841		
35	0.001278	0.013019	0.000000	-0.506059	5.721420	
36	0.000000	0.000000	-0.088435	0.000000	0.000000	0.396345

Force Constants in Internal Coordinates (AttoJ / A^2, AttoJ / A, AttoJ):

	1	2	3	4	5	6
1	7.459118					
2	-0.032077	12.720560				
3	-0.002050	-0.036357	7.256095			
4	-0.020153	0.083233	-0.028134	12.463421		
5	-0.001621	-0.004247	-0.000890	0.007087	5.920841	
6	0.003260	0.009985	-0.000592	0.009470	0.007245	5.775221
7	0.046699	0.972250	0.116260	-0.568745	0.040842	-0.017139
8	0.005664	0.933181	0.139252	-0.348374	0.015108	-0.029795
9	0.009664	-0.080351	0.041243	1.379327	0.001861	-0.050588
10	0.016425	0.099347	-0.164197	1.363675	-0.020695	-0.018426
11	-0.067972	0.027208	-0.118598	0.253028	-0.015529	0.093365
12	0.015252	0.032231	0.045178	-0.226791	-0.027906	0.129527
13	0.177174	0.023596	-0.194957	0.748066	-0.015351	-0.132086
14	0.085827	-0.008531	-0.199397	0.748238	-0.009429	-0.136691
15	-0.083229	0.781909	-0.307149	0.787443	-0.043979	-0.024050
16	-0.042355	0.740268	-0.354017	0.869837	-0.037725	-0.039487
17	-0.006081	-0.026146	-0.006932	0.023446	0.007623	-0.000085
18	-0.010214	-0.063011	0.049400	-0.111942	-0.030440	0.012386
19	0.030925	-0.058509	0.165636	-0.771752	0.185603	-0.112723
20	0.035967	-0.058877	0.159032	-0.765054	0.171030	-0.125272
21	0.016496	-0.032827	-0.000470	0.023265	-0.008128	-0.015134

	7	8	9	10	11	12
7	8.132105					
8	1.654597	7.289304				
9	-0.982931	0.249810	5.935722			
10	-1.413086	-1.099934	1.061659	6.706709		
11	-1.293667	-0.656471	0.179055	1.369703	9.576595	
12	1.284773	-0.042427	-0.274570	-0.924709	0.243201	7.615435
13	-2.870287	-1.016601	1.410533	2.274211	1.519439	-1.682612
14	-3.089687	-1.056018	1.473683	2.292986	1.551825	-1.452582
15	-3.216676	-2.501392	1.179353	2.677522	2.058790	-1.049899
16	-3.947363	-2.077468	1.052014	2.969317	2.098378	-0.986087
17	-0.168191	-0.422586	0.028895	0.173925	0.213345	0.120534
18	0.919978	0.591374	-1.005400	-0.728704	-0.502531	0.681376
19	1.851407	1.453514	-0.367000	-1.773923	-1.620019	0.744231
20	1.706874	1.455117	-0.344937	-1.852779	-1.325026	0.712051
21	-0.138303	0.153934	0.279795	0.143076	0.070847	-0.619705

	13	14	15	16	17	18
13	6.081094					
14	5.715537	6.384128				
15	4.387582	4.720113	7.934104			
16	4.862554	5.096494	7.168273	8.632083		
17	0.242862	0.269925	0.680945	0.770354	0.972073	
18	-1.317602	-1.302544	-1.375697	-1.508655	0.116313	2.148333
19	-1.849055	-1.787727	-2.836648	-3.002518	0.000688	1.059020
20	-1.622398	-1.539663	-2.645546	-2.830747	-0.024052	1.126145
21	0.697070	0.707129	0.250391	0.287948	0.001385	0.038014

	19	20	21	22	23	24
19	4.313659					
20	3.792591	4.212770				
21	0.271138	0.257688	1.125219			
22	0.000000	0.000000	0.000000	1.069651		
23	0.000000	0.000000	0.000000	-0.165802	0.335826	
24	0.000000	0.000000	0.000000	0.656056	-0.165061	0.760508
25	0.000000	0.000000	0.000000	-0.590720	0.166626	-0.625049
26	0.000000	0.000000	0.000000	-0.596475	0.044345	-0.167562
27	0.000000	0.000000	0.000000	-0.128518	0.014931	-0.179382
28	0.000000	0.000000	0.000000	0.041361	-0.032509	0.090428
29	0.000000	0.000000	0.000000	0.141790	-0.043554	0.136244
30	0.000000	0.000000	0.000000	-0.282886	0.139238	-0.308367

	25	26	27	28	29	30
25	1.104919					
26	0.131113	0.608670				
27	0.143867	0.047758	0.133627			
28	-0.148334	-0.051863	-0.013694	0.210827		
29	-0.522544	-0.074828	-0.009204	0.139076	0.580418	
30	0.334870	0.047729	0.105630	-0.006032	0.034606	0.409403