

## Example I: MP2 calculations for Benzene

In this example we will calculate the ground state energy of the benzene molecule employing the MP2 (second order Moller-Plesat perturbation theory, and using the MP2 module in NWChem with a RHF reference  $|\Phi\rangle$ .

Input file:

```
echo

geometry units angstroms print xyz autosym
  symmetry d6h
  C      0.99261      0.99261      0.00000
  H      1.75792      1.75792      0.00000
end
```

*Geometry specification*

The SYMMETRY directive is optional. The default is no symmetry (i.e., C1 point group). Automatic detection of point group symmetry is available through the use of autosym in the GEOMETRY directive main line (discussed in Section 6.1). Note: if the SYMMETRY directive is present the autosym keyword is ignored.

If only symmetry-unique atoms are specified, the others will be generated through the action of the point group operators, but the user is free to specify all atoms. The user must know the symmetry of the molecule being modeled, and be able to specify the coordinates of the atoms in a suitable orientation relative to the rotation axes and planes of symmetry. Appendix C lists a number of examples of the GEOMETRY directive input for specific molecules having symmetry patterns recognized by NWChem. The exact point group symmetry will be forced upon the molecule, and atoms within  $10^{-3}$  a.u. of a symmetry element (e.g., a mirror plane or rotation axis) will be forced onto that element. Thus, it is not necessary to specify to a high precision those coordinates that are determined solely by symmetry.

```
basis
H library 3-21G
C library 3-21G
end
```

*Basis set specification*

```
scf
singlet
rhf
end
```

*SCF module provides reference,  $|\Phi\rangle$ , for the MP2 calculations*

```
mp2
end
```

*MP2 module input*

```
task mp2 energy
```

Output:

**STEP1:** SCF module which produces molecular orbitals further used to generate molecular one- and two-electron integrals (these integrals are requested by the MP2 module)

iter	energy	gnorm	gmax	time
1	-229.3668943492	7.17D-01	2.50D-01	1.3
2	-229.4161883623	7.84D-02	2.32D-02	1.4
3	-229.4167722587	3.49D-03	1.08D-03	1.6
4	-229.4167733860	1.71D-06	5.91D-07	1.7
5	-229.4167733860	3.46D-08	8.90D-09	1.8

Final RHF results

-----  
Total SCF energy = -229.416773386013  
One-electron energy = -709.316419398519  
Two-electron energy = 277.459106104096  
Nuclear repulsion energy = 202.440539908410

**STEP2:** MP2 calculations, program solves the MP2 perturbation equations, and the results are outputted as

NWChem MP2 Semi-direct Energy/Gradient Module

-----  
total energy calculations of benzene, MP2/3-21G

Basis functions = 66  
Molecular orbitals = 66  
Frozen core = 0  
Frozen virtuals = 0  
Active alpha occupied = 21  
Active beta occupied = 21  
Active alpha virtual = 45  
Active beta virtual = 45  
Use MO symmetry = F  
Use skeleton AO sym = T

*Number of occupied and  
virtual orbitals used in the  
perturbation expansion*

AO/Fock/Back tols = 1.0D-09 1.0D-09 1.0D-09

GA uses MA = T GA memory limited = F

Available:

local mem= 5.24D+07  
global mem= 0.00D+00  
local disk= 9.71D+09

1 passes of 21: 222618

0

2098740.

Semi-direct pass number 1 of 1 for RHF alpha+beta at 2.3s  
Node 0 wrote 16.4 Mb in 10.4 s Agg I/O rate: 1.6 Mb/s  
Done moints\_semi at 18.0s  
Done maket at 21.9s  
Done multipass loop at 21.9s

```
-----  
SCF energy -229.416773386013  
Correlation energy -0.530846852219  
Singlet pairs -0.330552437639  
Triplet pairs -0.200294414580  
Total MP2 energy -229.947620238232  
-----
```

*SCF and correlation energies*

## Example II: Structural optimization of benzene within the MP2 approximation

In this example we will optimize the structure of benzene using results generated from prior energy calculation. Since most of the parameters are already stored in the database the input is very simple.

Input file:

```
echo
```

```
title "optimization of benzene MP2/3-21G"
```

```
restart c6h6-mp2
```

The "restart" directive indicates that we will reusing the results from our previous calculation. Notice the name of the database file

```
scratch_dir ./scratch
```

```
permanent_dir ./perm
```

Previously generated files in permanent directory will be reused

```
driver
```

The driver block defines optimization parameters.

```
maxiter 20
```

Maximum number of iterations is 20

```
xyz benzene-mp2
```

The structural snapshots of the system will be generated at each step in xyz format with file prefix s2 ( e.g. s2-001.xyz, ...)

```
end
```

```
task mp2 optimize
```

Task directive to commence structural optimization using mp2 method

As the optimization process consists of series of total energy evaluations the contents of the output file are very much similar to that in Example I. At each step the total energy and force information will be outputted as follows

Step	Energy	Delta E	Gmax	Grms	Xrms	Xmax	Walltime
@ 1	-229.94774638	-1.3D-04	0.00020 ok	0.00009 ok	0.00654	0.01443	62.5

↑  
Step number

↑ ↑ ↑  
Total Energy and its Change with respect to last step

↑ ↑  
Maximum value of the force and its RMS average

The best way to keep track of the optimization calculation is to run the following command on the output file:

```
grep @ outputfile
```

```
> fgrep @ benzene-mp2-opt.out
@ Step      Energy      Delta E      Gmax      Grms      Xrms      Xmax      Walltime
@ -----
@ 0      -229.94762024  0.0D+00  0.00321  0.00140  0.00000  0.00000  27.1
@ 1      -229.94774638 -1.3D-04  0.00020  0.00009  0.00654  0.01443  62.5
@ 2      -229.94774690 -5.2D-07  0.00000  0.00000  0.00040  0.00087  116.0
@ 2      -229.94774690 -5.2D-07  0.00000  0.00000  0.00040  0.00087  116.0
>
```

**Table 1: Structural comparisons between different theories for benzene**

Theory	Energy	C-C Distance (Å)	C-H Distance (Å)
HF/3-21G	-229.41944545	1.38457	1.07210
MP2/3-21G	-229.94774690	1.40663	1.08687
B3LYP/3-21G	-230.97575878	1.39731	1.08413

## Example III: Frequency calculation of benzene within the MP2 approximation

In this example we will calculate the vibrational frequency of benzene for the optimized geometry calculated in Example II.

Input file:

```
echo
```

```
title "frequency generation of benzene MP2/3-21G"
```

```
restart c6h6-mp2
```

The "restart" directive indicates that we will reusing the results from our previous geometry optimization calculation.

```
scratch_dir ./scratch
```

```
permanent_dir ./perm
```

Previously generated files in permanent directory will be reused

```
freq
```

```
animate
```

```
end
```

The frequency block is optional. The animation keyword directs the program to generate XYZ files to animate vibrational modes.

```
task mp2 freq
```

Task directive to commence frequency calculation using mp2 method

Output file:

....

Raw Frequencies including rotational and translation degrees of freedom

-----  
NORMAL MODE EIGENVECTORS IN CARTESIAN COORDINATES  
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(Frequencies expressed in cm-1)

	1	2	3	4	5	6
Frequency	-27.09	-27.09	-9.55	-9.55	9.71	27.02
1	0.08005	0.08002	0.00000	0.00000	0.00000	-0.07409
2	0.08005	-0.08002	0.00000	0.00000	0.00000	0.07409
3	0.00000	0.00000	0.12641	0.07743	0.11320	0.00000
4	0.08004	0.08005	0.00000	0.00000	0.00000	-0.02712
5	0.08001	-0.08003	0.00000	0.00000	0.00000	-0.10121
6	0.00000	0.00000	-0.13027	0.07076	0.11320	0.00000
7	0.08001	0.08003	0.00000	0.00000	0.00000	0.10121
8	0.08004	-0.08005	0.00000	0.00000	0.00000	0.02712

9	0.00000	0.00000	0.00385	-0.14819	0.11320	0.00000
10	0.08005	0.08002	0.00000	0.00000	0.00000	0.07409
11	0.08005	-0.08002	0.00000	0.00000	0.00000	-0.07409
12	0.00000	0.00000	-0.12641	-0.07743	0.11320	0.00000
13	0.08004	0.08005	0.00000	0.00000	0.00000	0.02712
14	0.08001	-0.08003	0.00000	0.00000	0.00000	0.10121
15	0.00000	0.00000	0.13027	-0.07076	0.11320	0.00000
16	0.08001	0.08003	0.00000	0.00000	0.00000	-0.10121
17	0.08004	-0.08005	0.00000	0.00000	0.00000	-0.02712
18	0.00000	0.00000	-0.00385	0.14819	0.11320	0.00000
19	0.08018	0.08008	0.00000	0.00000	0.00000	-0.13160
20	0.08018	-0.08008	0.00000	0.00000	0.00000	0.13160
21	0.00000	0.00000	0.22413	0.13729	0.11315	0.00000
22	0.08015	0.08020	0.00000	0.00000	0.00000	-0.04817
23	0.08006	-0.08011	0.00000	0.00000	0.00000	-0.17978
24	0.00000	0.00000	-0.23096	0.12546	0.11315	0.00000
25	0.08006	0.08011	0.00000	0.00000	0.00000	0.17978
26	0.08015	-0.08020	0.00000	0.00000	0.00000	0.04817
27	0.00000	0.00000	0.00683	-0.26274	0.11315	0.00000
28	0.08018	0.08008	0.00000	0.00000	0.00000	0.13160
29	0.08018	-0.08008	0.00000	0.00000	0.00000	-0.13160
30	0.00000	0.00000	-0.22413	-0.13729	0.11315	0.00000
31	0.08015	0.08020	0.00000	0.00000	0.00000	0.04817
32	0.08006	-0.08011	0.00000	0.00000	0.00000	0.17978
33	0.00000	0.00000	0.23096	-0.12546	0.11315	0.00000
34	0.08006	0.08011	0.00000	0.00000	0.00000	-0.17978
35	0.08015	-0.08020	0.00000	0.00000	0.00000	-0.04817
36	0.00000	0.00000	-0.00683	0.26274	0.11315	0.00000

	7	8	9	10	11	12
Frequency	411.97	411.97	645.42	645.42	678.01	685.28
1	0.00000	0.00000	-0.04373	-0.10391	0.00000	0.00000
2	0.00000	0.00000	0.04765	-0.10217	0.00000	0.00000
3	-0.05412	-0.13092	0.00000	0.00000	0.11461	-0.03279
4	0.00000	0.00000	0.13132	-0.05341	0.00000	0.00000
5	0.00000	0.00000	-0.00284	0.07288	0.00000	0.00000
6	-0.08632	0.11233	0.00000	0.00000	0.11461	-0.03279
7	0.00000	0.00000	0.00007	0.07293	0.00000	0.00000
8	0.00000	0.00000	-0.12919	-0.05837	0.00000	0.00000
9	0.14044	0.01859	0.00000	0.00000	0.11461	-0.03279
10	0.00000	0.00000	0.04373	0.10391	0.00000	0.00000
11	0.00000	0.00000	-0.04765	0.10217	0.00000	0.00000
12	-0.05412	-0.13092	0.00000	0.00000	-0.11461	-0.03279
13	0.00000	0.00000	-0.13132	0.05341	0.00000	0.00000
14	0.00000	0.00000	0.00284	-0.07288	0.00000	0.00000
15	-0.08632	0.11233	0.00000	0.00000	-0.11461	-0.03279
16	0.00000	0.00000	-0.00007	-0.07293	0.00000	0.00000
17	0.00000	0.00000	0.12919	0.05837	0.00000	0.00000
18	0.14044	0.01859	0.00000	0.00000	-0.11461	-0.03279
19	0.00000	0.00000	0.06083	-0.10178	0.00000	0.00000
20	0.00000	0.00000	-0.05691	-0.10402	0.00000	0.00000
21	-0.11573	-0.27998	0.00000	0.00000	0.09478	0.39060
22	0.00000	0.00000	0.11265	-0.08683	0.00000	0.00000
23	0.00000	0.00000	-0.07186	-0.05220	0.00000	0.00000
24	-0.18460	0.24022	0.00000	0.00000	0.09478	0.39060

25	0.00000	0.00000	0.07379	-0.04942	0.00000	0.00000
26	0.00000	0.00000	-0.10926	-0.09105	0.00000	0.00000
27	0.30034	0.03976	0.00000	0.00000	0.09478	0.39060
28	0.00000	0.00000	-0.06083	0.10178	0.00000	0.00000
29	0.00000	0.00000	0.05691	0.10402	0.00000	0.00000
30	-0.11573	-0.27998	0.00000	0.00000	-0.09478	0.39060
31	0.00000	0.00000	-0.11265	0.08683	0.00000	0.00000
32	0.00000	0.00000	0.07186	0.05220	0.00000	0.00000
33	-0.18460	0.24022	0.00000	0.00000	-0.09478	0.39060
34	0.00000	0.00000	-0.07379	0.04942	0.00000	0.00000
35	0.00000	0.00000	0.10926	0.09105	0.00000	0.00000
36	0.30034	0.03976	0.00000	0.00000	-0.09478	0.39060

Thermodynamics  
stuff

Temperature = 298.15K

Zero-Point correction to Energy = 63.088 kcal/mol ( 0.100537 au)  
 Thermal correction to Energy = 65.855 kcal/mol ( 0.104947 au)  
 Thermal correction to Enthalpy = 66.447 kcal/mol ( 0.105891 au)

Total Entropy = 64.162 cal/mol-K  
 - Translational = 38.962 cal/mol-K (mol. weight = 78.0469)  
 - Rotational = 20.753 cal/mol-K (symmetry # = 12)  
 - Vibrational = 4.448 cal/mol-K

Cv (constant volume heat capacity) = 17.280 cal/mol-K  
 - Translational = 2.979 cal/mol-K  
 - Rotational = 2.979 cal/mol-K  
 - Vibrational = 11.321 cal/mol-K

Note if symmetry not  
found in input then  
this might have to be  
adjusted

-----  
 NORMAL MODE EIGENVECTORS IN CARTESIAN COORDINATES  
 -----

Projected Frequencies

(Projected Frequencies expressed in cm-1)

	1	2	3	4	5	6
P.Frequency	0.00	0.00	0.00	0.00	0.00	0.00
1	0.01066	0.00000	0.00000	0.00000	0.00870	0.13460
2	0.01205	0.00000	0.00000	0.00000	0.12520	-0.04987
3	0.00000	-0.03241	0.13594	0.12354	0.00000	0.00000
4	0.04500	0.00000	0.00000	0.00000	0.02150	0.10518
5	-0.11608	0.00000	0.00000	0.00000	0.07744	0.05995
6	0.00000	0.13052	-0.06244	0.11771	0.00000	0.00000
7	0.13879	0.00000	0.00000	0.00000	0.05646	0.02478
8	-0.02228	0.00000	0.00000	0.00000	0.11240	-0.02044
9	0.00000	0.13187	0.11043	-0.07215	0.00000	0.00000
10	0.11897	0.00000	0.00000	0.00000	0.04907	0.04177
11	-0.09625	0.00000	0.00000	0.00000	0.08483	0.04296
12	0.00000	0.18573	-0.01332	-0.01081	0.00000	0.00000
13	0.08464	0.00000	0.00000	0.00000	0.03627	0.07120



14	0.03187	0.00000	0.00000	0.00000	0.13259	-0.06685
15	0.00000	0.02280	0.18506	-0.00498	0.00000	0.00000
16	-0.00916	0.00000	0.00000	0.00000	0.00131	0.15159
17	-0.06192	0.00000	0.00000	0.00000	0.09763	0.01354
18	0.00000	0.02145	0.01219	0.18488	0.00000	0.00000
19	-0.03118	0.00000	0.00000	0.00000	-0.00690	0.17047
20	0.05390	0.00000	0.00000	0.00000	0.14080	-0.08573
21	0.00000	-0.11668	0.19360	0.17544	0.00000	0.00000
22	0.02968	0.00000	0.00000	0.00000	0.01579	0.11830
23	-0.17324	0.00000	0.00000	0.00000	0.05614	0.10894
24	0.00000	0.17214	-0.15805	0.16511	0.00000	0.00000
25	0.19595	0.00000	0.00000	0.00000	0.07776	-0.02421
26	-0.00696	0.00000	0.00000	0.00000	0.11811	-0.03357
27	0.00000	0.17453	0.14838	-0.17146	0.00000	0.00000
28	0.16082	0.00000	0.00000	0.00000	0.06467	0.00591
29	-0.13810	0.00000	0.00000	0.00000	0.06923	0.07883
30	0.00000	0.27001	-0.07098	-0.06271	0.00000	0.00000
31	0.09996	0.00000	0.00000	0.00000	0.04198	0.05807
32	0.08903	0.00000	0.00000	0.00000	0.15389	-0.11584
33	0.00000	-0.01881	0.28067	-0.05238	0.00000	0.00000
34	-0.06632	0.00000	0.00000	0.00000	-0.02000	0.20058
35	-0.07724	0.00000	0.00000	0.00000	0.09192	0.02666
36	0.00000	-0.02120	-0.02576	0.28419	0.00000	0.00000

	7	8	9	10	11	12
P.Frequency	411.97	411.97	645.42	645.42	678.01	685.34
1	0.00000	0.00000	-0.04344	-0.10403	0.00000	0.00000
2	0.00000	0.00000	0.04793	-0.10203	0.00000	0.00000
3	-0.05397	-0.13098	0.00000	0.00000	0.11461	-0.03280
4	0.00000	0.00000	0.13147	-0.05305	0.00000	0.00000
5	0.00000	0.00000	-0.00305	0.07287	0.00000	0.00000
6	-0.08645	0.11223	0.00000	0.00000	0.11461	-0.03280
7	0.00000	0.00000	-0.00013	0.07293	0.00000	0.00000
8	0.00000	0.00000	-0.12903	-0.05873	0.00000	0.00000
9	0.14042	0.01875	0.00000	0.00000	0.11461	-0.03280
10	0.00000	0.00000	0.04344	0.10403	0.00000	0.00000
11	0.00000	0.00000	-0.04793	0.10203	0.00000	0.00000
12	-0.05397	-0.13098	0.00000	0.00000	-0.11461	-0.03280
13	0.00000	0.00000	-0.13147	0.05305	0.00000	0.00000
14	0.00000	0.00000	0.00305	-0.07287	0.00000	0.00000
15	-0.08645	0.11223	0.00000	0.00000	-0.11461	-0.03280
16	0.00000	0.00000	0.00013	-0.07293	0.00000	0.00000
17	0.00000	0.00000	0.12903	0.05873	0.00000	0.00000
18	0.14042	0.01875	0.00000	0.00000	-0.11461	-0.03280
19	0.00000	0.00000	0.06111	-0.10161	0.00000	0.00000
20	0.00000	0.00000	-0.05662	-0.10418	0.00000	0.00000
21	-0.11542	-0.28011	0.00000	0.00000	0.09478	0.39059
22	0.00000	0.00000	0.11289	-0.08651	0.00000	0.00000
23	0.00000	0.00000	-0.07171	-0.05240	0.00000	0.00000
24	-0.18487	0.24001	0.00000	0.00000	0.09478	0.39059
25	0.00000	0.00000	0.07393	-0.04922	0.00000	0.00000
26	0.00000	0.00000	-0.10901	-0.09136	0.00000	0.00000
27	0.30029	0.04010	0.00000	0.00000	0.09478	0.39059
28	0.00000	0.00000	-0.06111	0.10161	0.00000	0.00000
29	0.00000	0.00000	0.05662	0.10418	0.00000	0.00000

30	-0.11542	-0.28011	0.00000	0.00000	-0.09478	0.39059
31	0.00000	0.00000	-0.11289	0.08651	0.00000	0.00000
32	0.00000	0.00000	0.07171	0.05240	0.00000	0.00000
33	-0.18487	0.24001	0.00000	0.00000	-0.09478	0.39059
34	0.00000	0.00000	-0.07393	0.04922	0.00000	0.00000
35	0.00000	0.00000	0.10901	0.09136	0.00000	0.00000
36	0.30029	0.04010	0.00000	0.00000	-0.09478	0.39059

.....

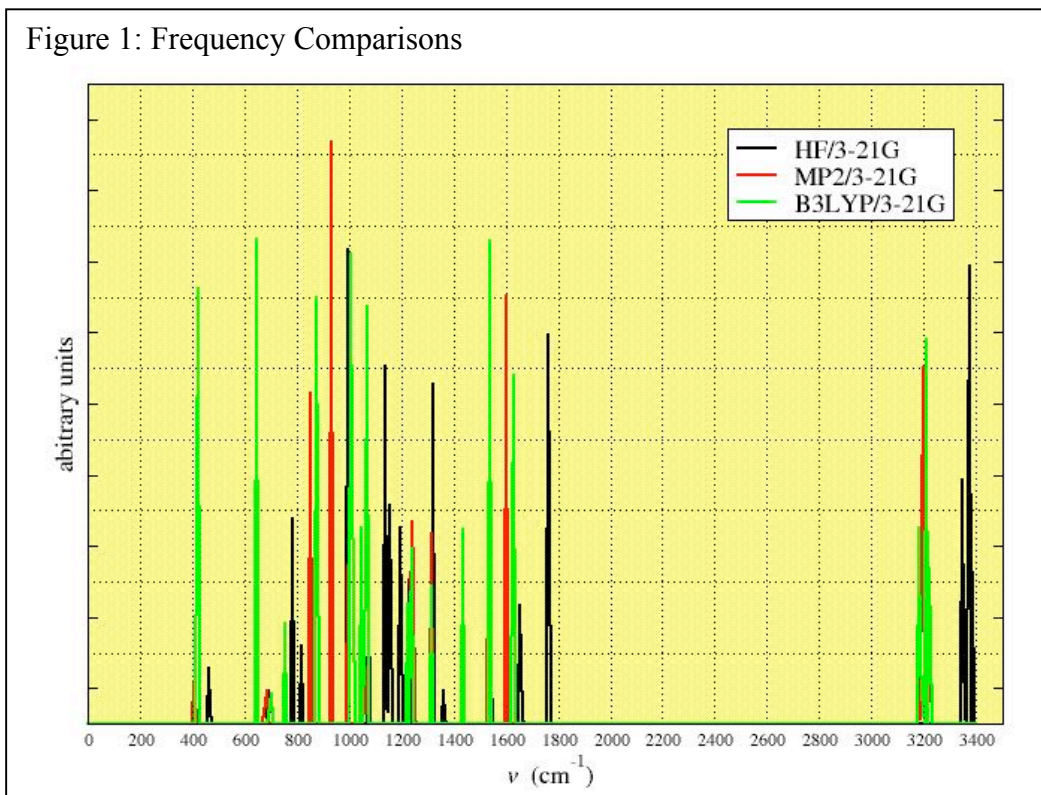
Table of frequencies and IR intensities

Normal Mode	Eigenvalue [cm** <sup>-1</sup> ]	Projected Infra Red Intensities			
		[atomic units]	[(debye/angs)**2]	[(KM/mol)]	[arbitrary]
1	0.000	0.000000	0.000	0.000	0.000
2	0.000	0.000000	0.000	0.000	0.000
3	0.000	0.000000	0.000	0.000	0.000
4	0.000	0.000000	0.000	0.000	0.000
5	0.000	0.000000	0.000	0.000	0.000
6	0.000	0.000000	0.000	0.000	0.000
7	411.974	0.000000	0.000	0.000	0.000
8	411.974	0.000000	0.000	0.000	0.000
9	645.424	0.000000	0.000	0.000	0.000
10	645.424	0.000000	0.000	0.000	0.000
11	678.011	0.000000	0.000	0.000	0.000
12	685.337	0.125792	2.902	122.628	200.643
13	853.000	0.000000	0.000	0.000	0.000
14	853.000	0.000000	0.000	0.000	0.000
15	932.389	0.000000	0.000	0.000	0.000
16	932.389	0.000000	0.000	0.000	0.000
17	934.382	0.000000	0.000	0.000	0.000
18	993.427	0.000000	0.000	0.000	0.000
19	1058.856	0.003450	0.080	3.363	5.503
20	1058.856	0.003450	0.080	3.363	5.503
21	1067.299	0.000000	0.000	0.000	0.000
22	1239.142	0.000000	0.000	0.000	0.000
23	1249.108	0.000000	0.000	0.000	0.000
24	1249.108	0.000000	0.000	0.000	0.000
25	1316.086	0.000000	0.000	0.000	0.000
26	1439.509	0.000000	0.000	0.000	0.000
27	1535.167	0.011662	0.269	11.369	18.602
28	1535.167	0.011662	0.269	11.369	18.602
29	1600.393	0.000000	0.000	0.000	0.000
30	1600.393	0.000000	0.000	0.000	0.000
31	3184.758	0.000000	0.000	0.000	0.000
32	3194.410	0.000000	0.000	0.000	0.000
33	3194.410	0.000000	0.000	0.000	0.000
34	3213.586	0.034841	0.804	33.965	55.573
35	3213.586	0.034841	0.804	33.965	55.573
36	3224.993	0.000000	0.000	0.000	0.000

The animation frames will be saved into your permanent directory. To view the animation corresponding to mode 7 (the true vibrational mode in this particular case) you can concatenate all animation frames into a single file,

```
cat freq.m-007.s-0*xyz > freq.m7.xyz
```

and load it into your favorite visualization program.



## Example IV: Comparisons between three different MP2 programs in NWChem

In this example we will calculate the ground state energy of the benzene molecule employing the MP2 (second order Moller-Plesat perturbation theory, and using the indirect MP2, direct MP2, and tce modules in NWChem with a RHF reference  $|\Phi\rangle$ .

Table II: Energy and Timing Comparisons

Modules	MP2/3-21G Energies	Timings (Seconds)
Semi-direct MP2	-229.947620238232	23.6
Direct MP2	-229.947620238108	6.9
TCE	-229.947620235370	70.1

Input Deck:

```
echo
title "Comparisons of MP2 and TCE modules for the total energy calculations of
benzene at the MP2/3-21G level"

start c6h6-mp2-compare

memory 900 mb

scratch_dir ./perm
permanent_dir ./perm

geometry units angstroms print xyz autosym
  symmetry d6h
  C      0.99261      0.99261      0.00000
  H      1.75792      1.75792      0.00000
end

basis
* library 3-21G
end
```

```
# *** Semi-direct ***
```

```
# Semi-direct -- this is recommended for most large applications  
# (up to about 2800 basis functions), especially on the IBM SP and  
# other machines with significant disk I/O capability. Partially  
# transformed integrals are stored on disk, multi-passing as necessary.  
# RHF and UHF references may be treated including computation of analytic  
# derivatives. This is selected by specifying mp2 on the task directive,  
# e.g.
```

```
mp2  
end  
task mp2 energy
```

```
# *** Fully-direct ***
```

```
# Fully-direct -- this is of utility if only limited I/O resources are  
# available (up to about 2800 functions). Only RHF references and energies  
# are available. This is selected by specifying direct_mp2 on the task directive,  
# e.g.
```

```
mp2  
end  
task direct_mp2 energy
```

```
# *** TCE implementation ***
```

```
# While the MBPT (MP) models implemented in the TCE module give identical  
# correlation energies as conventional implementation for a canonical HF  
# reference of a closed-shell system, the former are intrinsically more general  
# and theoretically robust for other less standard reference wave functions  
# and open-shell systems. This is because the zeroth order of Hamiltonian is  
# chosen to be the full Fock operator (not just the diagonal part), and no  
# further approximation was invoked. So unlike the conventional implementation  
# where the Fock matrix is assumed to be diagonal and a correlation energy is  
# evaluated in a single analytical formula that involves orbital energies  
# (or diagonal Fock matrix elements), the present tensor MBPT requires the  
# iterative solution of amplitude equations and subsequent energy evaluation  
# and is generally more expensive than the former. For example, the operation  
# cost of many conventional implementation of MBPT(2) scales as the fourth  
# power of the system size, but the cost of the present tensor MBPT(2) scales  
# as the fifth power of the system size, as the latter permits non-canonical  
# HF reference and the former does not (to reinstate the non-canonical HF  
# reference in the former makes it also scale as the fifth power of the system  
# size).
```

```
## Note that only non-abelian symmetries are allowed with TCE
```

```
geometry  
C      0.99261000      0.99261000      0.00000000  
C     -1.35593048      0.36332048      0.00000000
```

C	0.36332048	-1.35593048	0.00000000
C	-0.99261000	-0.99261000	0.00000000
C	1.35593048	-0.36332048	0.00000000
C	-0.36332048	1.35593048	0.00000000
H	1.75792000	1.75792000	0.00000000
H	-2.40136338	0.64344338	0.00000000
H	0.64344338	-2.40136338	0.00000000
H	-1.75792000	-1.75792000	0.00000000
H	2.40136338	-0.64344338	0.00000000
H	-0.64344338	2.40136338	0.00000000

symmetry Cs

end

tce

mp2

end

task tce energy