Final report

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Problem 1: N, O, F atoms

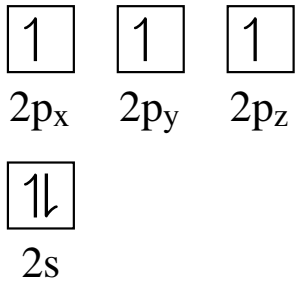

Figure 1: Electron configuration of nitrogen (N) atom

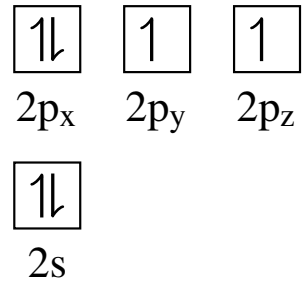

Figure 2: Electron configuration of oxygen (O) atom

- Nitrogen (N) atom
  - Electron configuration $2s^2 2p^3$
  - Main term ^4S
- Oxygen (O) atom
  - Electron configuration $2s^2 2p^4$
  - Main term ^3P
- Fluorine (F) atom
  - Electron configuration $2s^2 2p^5$
  - Main term ^2P

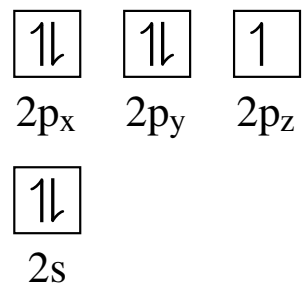

Figure 3: Electron configuration of fluorine (F) atom

Determinig the point group of a molecule

Let's calculate the ground states of our atoms. At the beginning, we need to determine a molecule's point group.

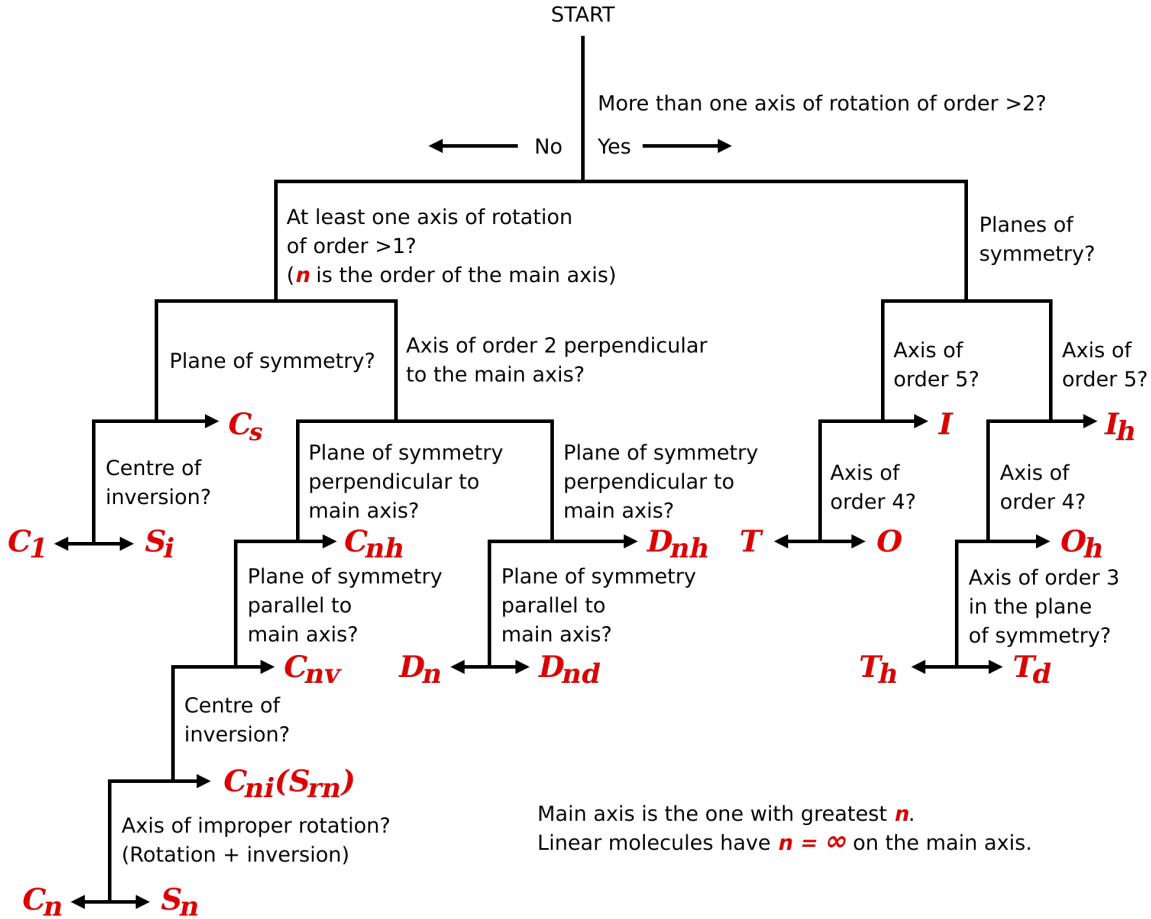

Figure 4: Flowchart for determining the point group of a molecule

It's difficult to determine point group of atom with this table, but MOLPRO says, that point group for N, O and F is D_{2h}.

Character table

MOLPRO writes irreducible representations of point groups in a different order, than in the reference materials. Let's show the table for D_{3h} as MOLPRO imagines it.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B_{3u}	1	−1	−1	1	−1	1	1	−1
B_{2u}	1	−1	1	−1	−1	1	−1	1
B_{1g}	1	1	−1	−1	1	1	−1	−1
B_{1u}	1	1	−1	−1	−1	−1	1	1
B_{2g}	1	−1	1	−1	1	−1	1	−1
B_{3g}	1	−1	−1	1	1	−1	−1	1
A_u	1	1	1	1	−1	−1	−1	−1

Table 1: Character table for D_{2h} point group

As we can see, the 1s and 2s states are described by A_g irreducible representation, $2p_x$ is described by B_{3u}, $2p_y$ is described by B_{2u}, $2p_z$ is described by B_{1u}.

Determining irreducible representation for nitrogen N ground state

For nitrogen (N) atom we have

$$B_{3u} \otimes B_{2u} \otimes B_{1u}$$

We calculate this case in detail.

B_{3u}	1	-1	-1	1	-1	1	1	-1
B_{2u}	1	-1	1	-1	-1	1	-1	1
$B_{3u} \otimes B_{2u}$	1	1	-1	-1	1	1	-1	-1

As we can see, $B_{3u} \otimes B_{2u} = B_{1g}$

B_{1g}	1	1	-1	-1	1	1	-1	-1
B_{1u}	1	1	-1	-1	-1	-1	1	1
$B_{1g} \otimes B_{1u}$	1	1	1	1	-1	-1	-1	-1

As we can see, $B_{3u} \otimes B_{2u} \otimes B_{1u} = B_{1g} \otimes B_{1u} = A_u$.

MOLPRO code for ground state of nitrogen (N) atom

```
1 ***, Nitrogen
2
3 geometry={n}
4 basis=vdz
5 {hf
6 wf, 7, 8, 3};
7 {casscf
8 wf, 7, 8, 3};
```

- 7 is the number of electrons
- 8 is the number (in character table) of the irreducible representation for the state we are considering
- 3 defines the spin symmetry

Ground states for fluorine (F) and oxygen (O) atoms

Analogically for oxygen (O) we have

$$B_{3u} \otimes B_{3u} \otimes B_{2u} \otimes B_{1u} = B_{3g}$$

For fluorine (F) we have

$$B_{3u} \otimes B_{3u} \otimes B_{2u} \otimes B_{2u} \otimes B_{1u} = B_{1u}$$

```
***, Oxygen

geometry={o}
basis=vdz
{hf
wf, 8, 7, 2};
{casscf
wf, 8, 7, 2};
```

```
***, Fluorine

geometry={f}
basis=vdz
{hf
wf, 9, 5, 1};
{casscf
wf, 9, 5, 1};
```

Excited states for nitrogen N atom

```
***, Nitrogen

geometry={n}
basis=vdz
{hf
wf, 7, 3, 1};
{casscf
wf, 7, 3, 1};
```

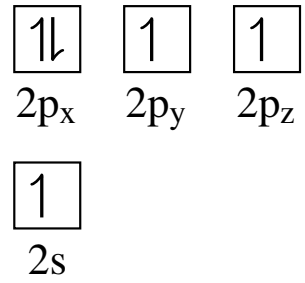

Figure 5: First excited state

```
***, Nitrogen

geometry={n}
basis=vdz
{hf
wf, 7, 7, 3};
{casscf
wf, 7, 7, 3};
```

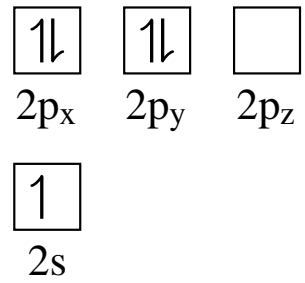

Figure 6: Second excited state

```
***, Nitrogen

geometry={n}
basis=vdz
{hf
wf, 7, 1, 1};
{casscf
wf, 7, 1, 1};
```

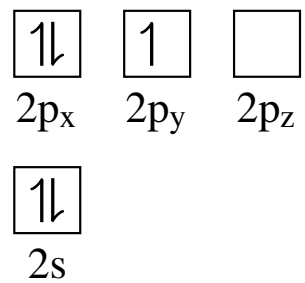

Figure 7: Third excited state

Excited states for oxygen O atom

```
***, Oxygen

geometry={o}
basis=vdz
{hf
wf, 8, 1, 0};
{casscf
wf, 8, 1, 0};
```

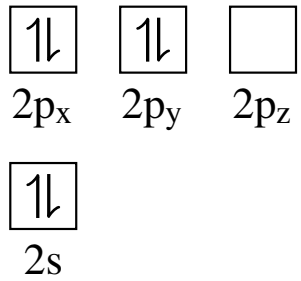

Figure 8: First excited state

```
***, Oxygen

geometry={o}
basis=vdz
{hf
wf, 8, 5, 2};
{casscf
wf, 8, 5, 2};
```

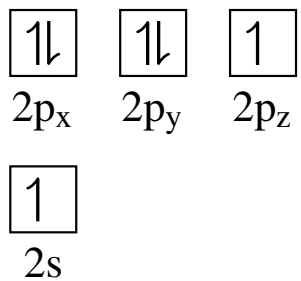

Figure 9: Second excited state

Excited states for fluorine F atom

```
***, Fluorine

geometry={f}
basis=vdz
{hf
wf, 9, 1, 1};
{casscf
wf, 9, 1, 1};
```

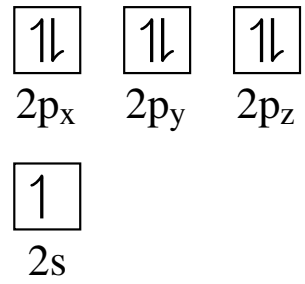

Figure 10: First excited state

```
***, Fluorine

geometry={f}
basis=vdz
{hf
wf, 9, 7, 3;
occ, 3, 1, 1, 0, 1, 0, 0, 0};
{casscf
occ, 3, 1, 1, 0, 1, 0, 0, 0;
wf, 9, 7, 3}
```

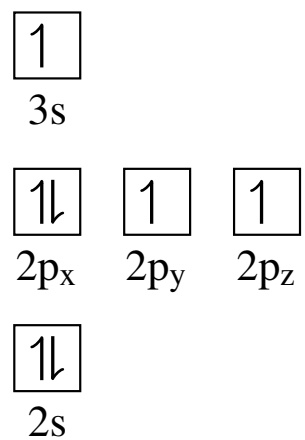

Figure 11: Second excited state

Excited states for fluorine F atom

```
***, Fluorine

geometry={f}
basis=vdz
{hf
wf, 9, 8, 3;
occ, 3, 1, 1, 0, 1, 0, 0, 0};
{casscf
occ, 3, 1, 1, 0, 1, 0, 0, 0;
wf, 9, 8, 3}
```

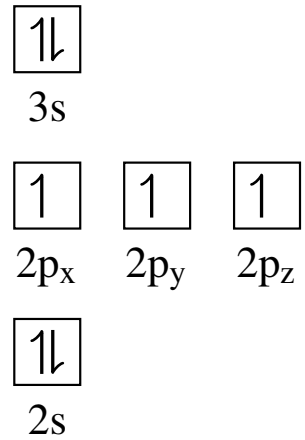

Figure 12: Third excited state

Calculated energies

- Basis: VDZ
- Method: CASSCF

N	Energy (eV)
Ground state ($2s^2 2p_x^1 2p_y^1 2p_z^1$ or ^4S)	0
First excited state ($2s^2 2p_x^2 2p_y^1$ or ^2S)	2.876692
Second excited state ($2s^1 2p_x^2 2p_y^1 2p_z^1$ or ^4P)	11.240083
Third excited state ($2s^1 2p_x^2 2p_y^2$ or ^2S)	16.965493

O	Energy (eV)
Ground state ($2s^2 2p_x^2 2p_y^1 2p_z^1$ or ^3P)	0
First excited state ($2s^2 2p_x^2 2p_y^2$ or ^1S)	2.231114
Second excited state ($2s^1 2p_x^2 2p_y^2 2p_z^1$ or ^3P)	17.129585

F	Energy (eV)
Ground state ($2s^2 2p_x^2 2p_y^2 2p_z^1$ or ^2P)	0
First excited state ($2s^1 2p_x^2 2p_y^2 2p_z^2$ or ^2S)	24.098432
Second excited state ($2s^2 2p_x^2 2p_y^1 2p_z^1 3s^1$ or ^4P)	45.079899
Third excited state ($2s^2 2p_x^1 2p_y^1 2p_z^1 3s^2$ or ^4S)	93.413827

Problem 2 - diatomic molecules

Let's start with a simple case. For example, consider a nitrogen molecule N_2.

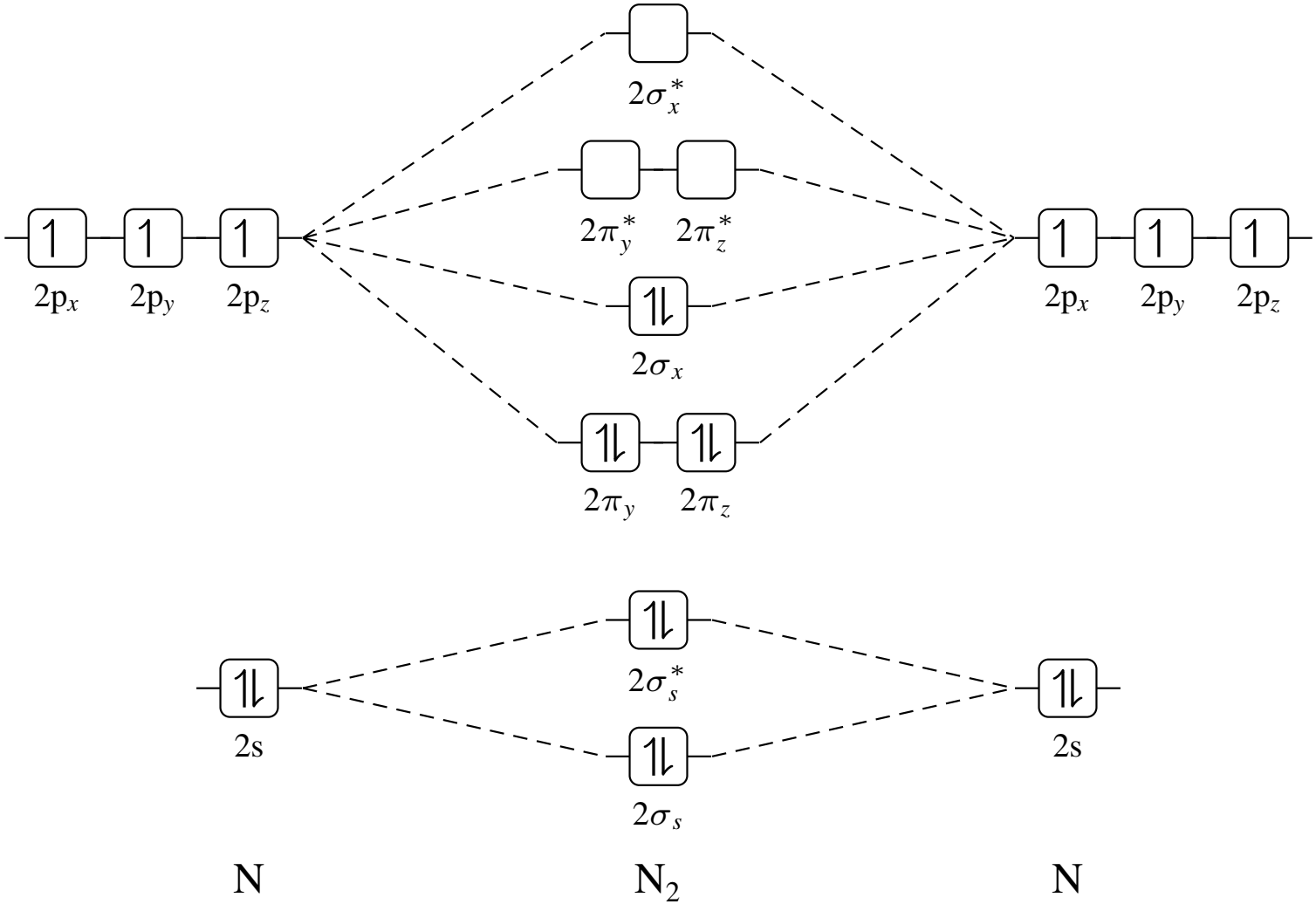

Figure 13: N_2 molecular orbital diagram - ground state

Nitrogen molecule N_2

Each linear molecule has a C_{2v} symmetry point group. But Molpro defines symmetry as D_{2h}. We can write the ground state of nitrogen molecule N_2 as

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 1\pi_{u,y}^2$$

And, for example, consider excited state

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 3\sigma_u^2 1\pi_{g,x}^1 1\pi_{g,y}^2$$

```
do i = 1, #rs
  r = rs(i) Ang
  {hf
  wf, 14, 1, 0};
  e_hf(i) = energy
  {casscf
  wf, 14, 1, 0};
  e_cas(i) = energy
enddo

{table,rs,e_hf,e_cas
head,r,HF,CASSCF
save, N2_molecule_term_data.dat}
```

```
do i = 1, #rs
  r = rs(i) Ang
  {hf
  wf, 14, 6, 2};
  e_hf(i) = energy
  {casscf
  wf, 14, 6, 2};
  e_cas(i) = energy
enddo

{table,rs,e_hf,e_cas
head,r,HF,CASSCF
save,
N2_molecule_term_eighth_excited_data.dat
     }
```

Nitrogen molecule N_2

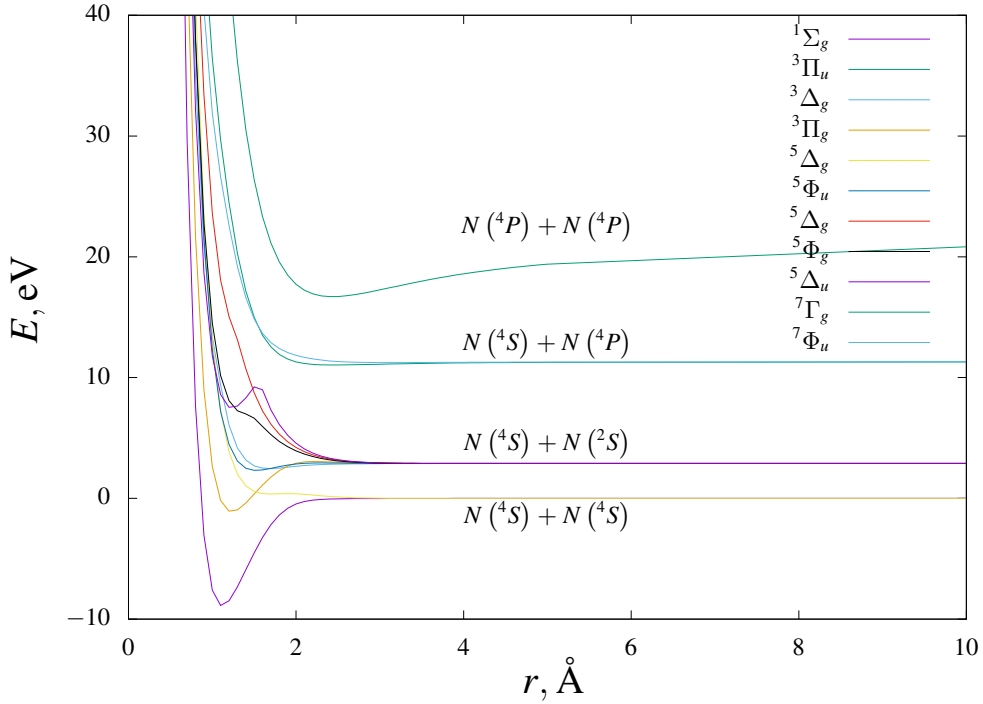

Figure 14: N_2 molecule terms

	r, Å	E, eV
$1\Sigma_g$	1.116	0
$1\Sigma_g$, exp.	1.098	0
$3\Delta_g$	1.682	11.35
$3\Delta_g$, exp.	1.611	10.90
$3\Pi_g$	1.233	7.78
$3\Pi_g$, exp.	1.213	7.39

Table 2: Calculated and experimental results for N_2 molecule

	Energy $(r \to \infty)$, eV	Total atomic energy, eV
$N\left(^4S\right) + N\left(^4S\right)$	0	0
$N\left(^4S\right) + N\left(^2S\right)$	2.892592	2.876692
$N\left(^4S\right) + N\left(^4P\right)$	11.295647	11.240083
$N\left(^4P\right) + N\left(^4P\right)$	22.129523	22.480166

Table 3: Comparison of the energy of a term at infinity with the energy of atoms

Nitric oxide molecule NO

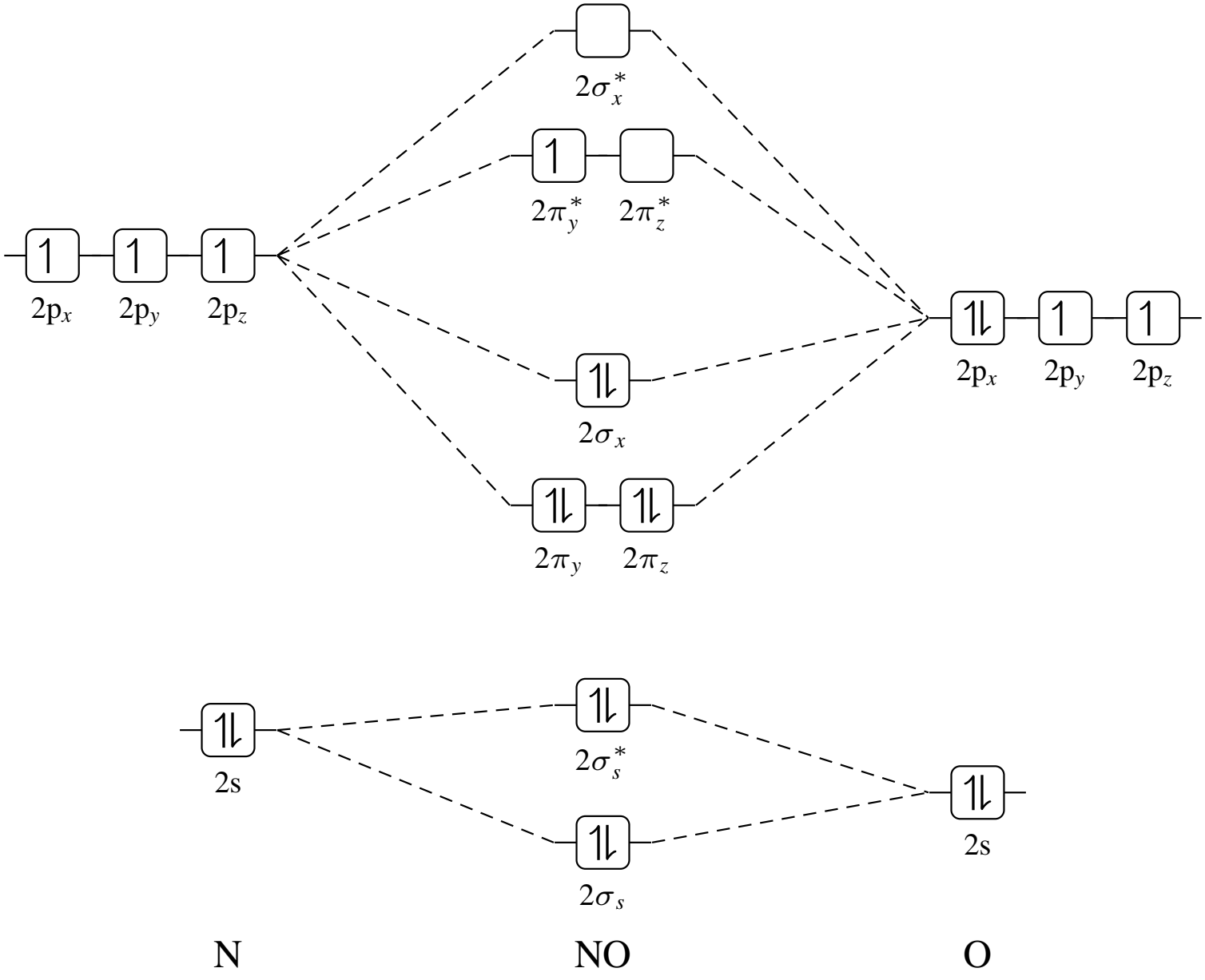

Figure 15: NO molecular orbital diagram - ground state

Nitric oxide molecule NO

This molecule has a C_{2v} symmetry point group. Let's consider two states: ground and excited. We can write the ground state of nitric oxide molecule NO as

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 1\pi_{u,y}^2 1\pi_{g,x}^1$$

And, for example, excited state

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_{u,x}^2 1\pi_{u,y}^2 1\pi_{g,x}^1 1\pi_{g,y}^1$$

```
do i = 1, #rs
  r = rs(i) Ang
  {hf
  wf, 15, 2, 1};
  e_hf(i) = energy
  {casscf
  wf, 15, 2, 1};
  e_cas(i) = energy
enddo

{table, rs, e_hf, e_cas
head, r, HF, CASSCF
save, NO_molecule_term_data.dat}
```

```
do i = 1, #rs
  r = rs(i) Ang
  {hf
  wf, 15, 4, 3};
  e_hf(i) = energy
  {casscf
  wf, 15, 4, 3};
  e_cas(i) = energy
enddo

{table, rs, e_hf, e_cas
head, r, HF, CASSCF
save,
NO_molecule_term_second_excited_data.dat
     }
```

Nitric oxide molecule NO

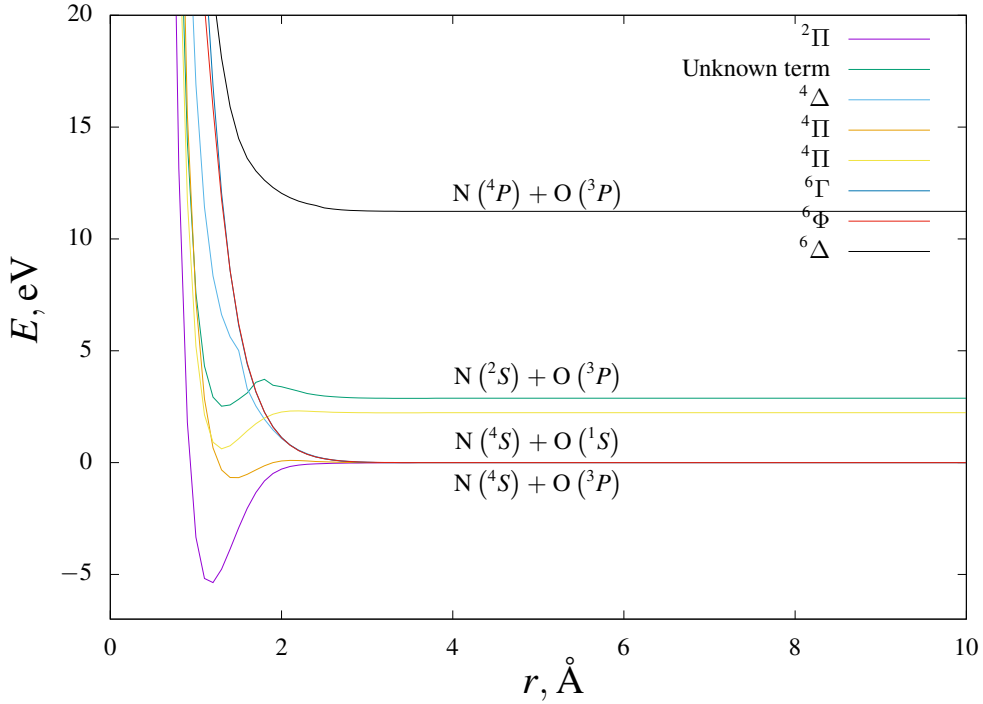

Figure 16: NO molecule terms

	r, Å	E, eV
$^2\Pi$	1.164	0
$^2\Pi$, exp.	1.151	0
U.term	1.328	7.928
U.term, exp.	1.302	7.484
$^4\Pi$	1.305	6.042
$^4\Pi$, exp.	–	–

Table 4: Calculated and experimental results for NO molecule

	Energy $(r \to \infty)$, eV	Total atomic energy, eV
N (^4S) + O (^3P)	0	0
N (^4S) + O (^1S)	2.229535	2.231114
N (^2S) + O (^3P)	2.876692	2.876692
N (^4P) + O (^3P)	11.231929	11.240083

Table 5: Comparison of the energy of a term at infinity with the energy of atoms

Water molecule H_2O

- Bond length $r = 0.967$Å
- First angle $\theta = 102.50383°$
- Symmetry group: C_{2v}

```
1  ***, H2O molecule
2
3  basis=avdz
4
5  geometry=
6  {O;
7   H1,O,R;
8   H2,O,R,H1,THETA}
9
10 R=0.96 Ang
11 Theta=104
12
13 hf;
14 mp4;
15 optg;
16
17 frequencies;
```

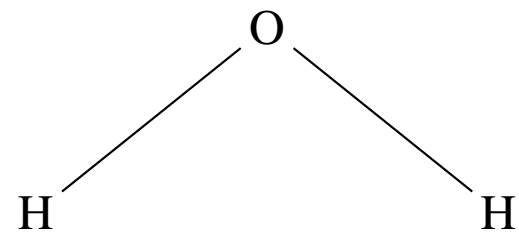

Figure 17: Water molecule (H_2O)

Water molecule H_2O

Let's find the vibrational modes of the water molecule H_2O. First, we write a table for C_{2v} group, then we find the number of atoms that do not change their position during symmetry transformations, and multiply the character of the element by the number of unchanged atoms.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
χ	3	-1	1	1
$\Gamma = \chi \cdot N$	9	-1	3	1

Table 6: Character table for C_{2v} point group

Let us find a decomposition in terms of irreducible representations:

$$N_\mu = \frac{1}{h} \sum_{\mathbf{R}} \chi_\mu(\mathbf{R})\, \chi(\mathbf{R}) = \frac{1}{h} \sum_{\mathbf{C}} g(\mathbf{C})\, \chi_\mu(\mathbf{C})\, \chi(\mathbf{C})$$

Water molecule H_2O

$$N_\mu = \frac{1}{4}(1\cdot 1\cdot 9 + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot 3 + 1\cdot 1\cdot 1)A_1 +$$
$$+ \frac{1}{4}(1\cdot 1\cdot 9 + 1\cdot 1\cdot(-1) + 1\cdot(-1)\cdot 3 + 1\cdot(-1)\cdot 1)A_2 +$$
$$+ \frac{1}{4}(1\cdot 1\cdot 9 + 1\cdot(-1)\cdot(-1) + 1\cdot 1\cdot 3 + 1\cdot(-1)\cdot 1)B_1 +$$
$$+ \frac{1}{4}(1\cdot 1\cdot 9 + 1\cdot(-1)\cdot(-1) + 1\cdot(-1)\cdot 3 + 1\cdot 1\cdot 1)B_2 =$$
$$= 3A_1 + A_2 + 3B_1 + 2B_2$$

As a result we have

All motions	Translation	Rotation	Vibration
$3A_1$	A_1		$2A_1$
A_2		A_2	
$3B_1$	B_1	B_1	B_1
$2B_2$	B_2	B_2	

Table 7: Distribution of representations by motion type for water molecule H_2O

Methane molecule CH_4

- Bond length $r = 1.11$Å
- First angle $\theta = 109.47122^\circ$
- Second angle $\phi = 120^\circ$
- Symmetry group: T_d

```
geometry=
{H1;
 C1, H1, R;
 H2, C1, R, H1, THETA;
 H3, C1, R, H1, THETA, H2, PHI;
 H4, C1, R, H1, THETA, H3, PHI;
}

R = 1.09 Ang
Theta = 109.471220
Phi = 120;
```

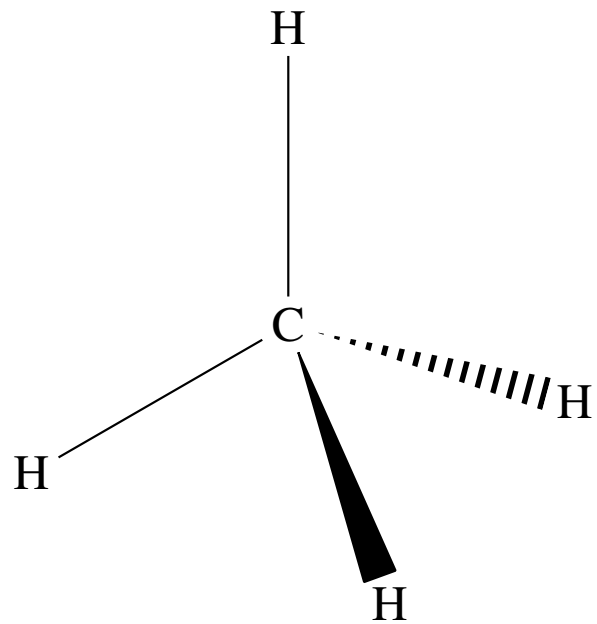

Figure 18: Methane molecule (CH_4)

Methane molecule CH_4

Let's find the vibrational modes of the water molecule H_2O. First, we write a table for C_{2v} group, then we find the number of atoms that do not change their position during symmetry transformations, and multiply the character of the element by the number of unchanged atoms.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1
χ	3	0	-1	-1	1
$\Gamma = \chi \cdot N$	15	0	-1	-1	3

Table 8: Character table for C_{2v} point group

Let us find a decomposition in terms of irreducible representations:

$$N_\mu = \frac{1}{h} \sum_{\mathbf{R}} \chi_\mu(\mathbf{R})\, \chi(\mathbf{R}) = \frac{1}{h} \sum_{\mathbf{C}} g(\mathbf{C})\, \chi_\mu(\mathbf{C})\, \chi(\mathbf{C})$$

Methane molecule CH_4

$$N_\mu = \frac{1}{24}(1\cdot 1\cdot 15 + 8\cdot 1\cdot 0 + 3\cdot 1\cdot(-1) + 6\cdot 1\cdot(-1) + 6\cdot 1\cdot 3)\,A_1 +$$
$$+ \frac{1}{24}(1\cdot 1\cdot 15 + 8\cdot 1\cdot 0 + 3\cdot 1\cdot(-1) + 6\cdot(-1)\cdot(-1) + 6\cdot(-1)\cdot 3)\,A_2 +$$
$$+ \frac{1}{24}(1\cdot 2\cdot 15 + 8\cdot(-1)\cdot 0 + 3\cdot 2\cdot(-1) + 6\cdot 0\cdot(-1) + 6\cdot 0\cdot 3)\,E +$$
$$+ \frac{1}{24}(1\cdot 3\cdot 15 + 8\cdot 0\cdot 0 + 3\cdot(-1)\cdot(-1) + 6\cdot 1\cdot(-1) + 6\cdot(-1)\cdot 3)\,T_1 +$$
$$+ \frac{1}{24}(1\cdot 3\cdot 15 + 8\cdot 0\cdot 0 + 3\cdot(-1)\cdot(-1) + 6\cdot(-1)\cdot(-1) + 6\cdot 1\cdot 3)\,T_2 =$$
$$= A_1 + E + T_1 + 3T_2$$

All motions	Translation	Rotation	Vibration
A_1			A_1
E			E
T_1		T_1	
T_2	T_2		$2T_2$

Table 9: Distribution of representations by motion type for methane molecule CH_4

Frequency results for water H_2O and methane CH_4

Symmetry	A_1	A_1	B_2
Frequency, cm^{-1}	1630.75	3778.17	3901.53
Frequency(fund. exp. data), cm^{-1}	1595	3657	3756
Frequency(harm. exp. data), cm^{-1}	1649	3832	3943

Table 10: Harmonic frequencies for water molecule H_2O

Symmetry	A_1	E	T_2	T_2
Frequency, cm^{-1}	3023.17	1537.98	3155.23	1320.55
Frequency(fund. exp. data), cm^{-1}	2917	1534	3019	1306
Frequency(harm. exp. data), cm^{-1}	3025.5	1582.7	3156.8	1367.4

Table 11: Harmonic frequencies for methane molecule CH_4