



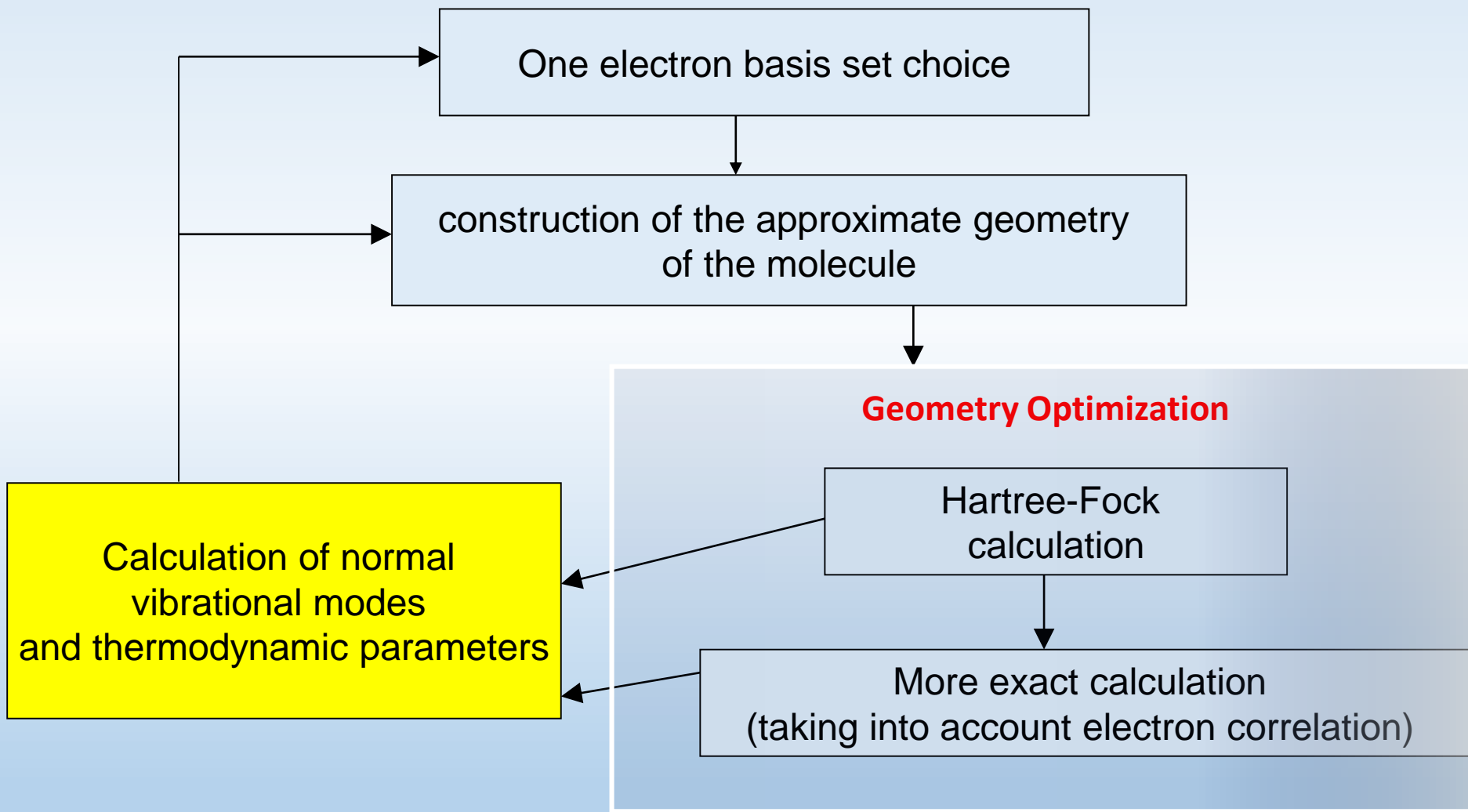
Lecture 5

ThermoChemical Calculations

Materials Chemistry Department
V. N. Karazin Kharkiv National University
61077, Kharkiv, **Ukraine**

E-mail: vivanov@karazin.ua

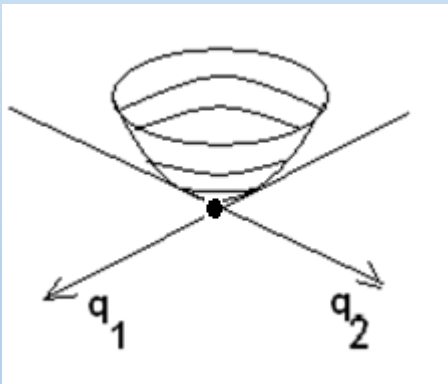
A typical scheme of quantum chemical calculations (ab initio)



Critical Points of Potential Energy surface

$$H = \begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & 0 \\ 0 & \frac{\partial^2 E}{\partial q_2^2} \end{pmatrix}$$

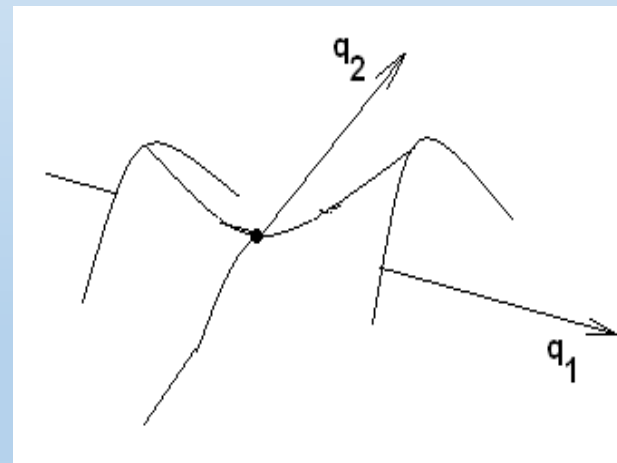
Optimal Geometry



$$\frac{\partial^2 E}{\partial q_1^2} > 0$$

$$\frac{\partial^2 E}{\partial q_2^2} > 0$$

Transition State



$$\frac{\partial^2 E}{\partial q_1^2} > 0$$

$$\frac{\partial^2 E}{\partial q_2^2} < 0$$

Topography of PES

$$E = E(q_1, q_2, \dots, q_{3N-6})$$

Critical Points of PES:

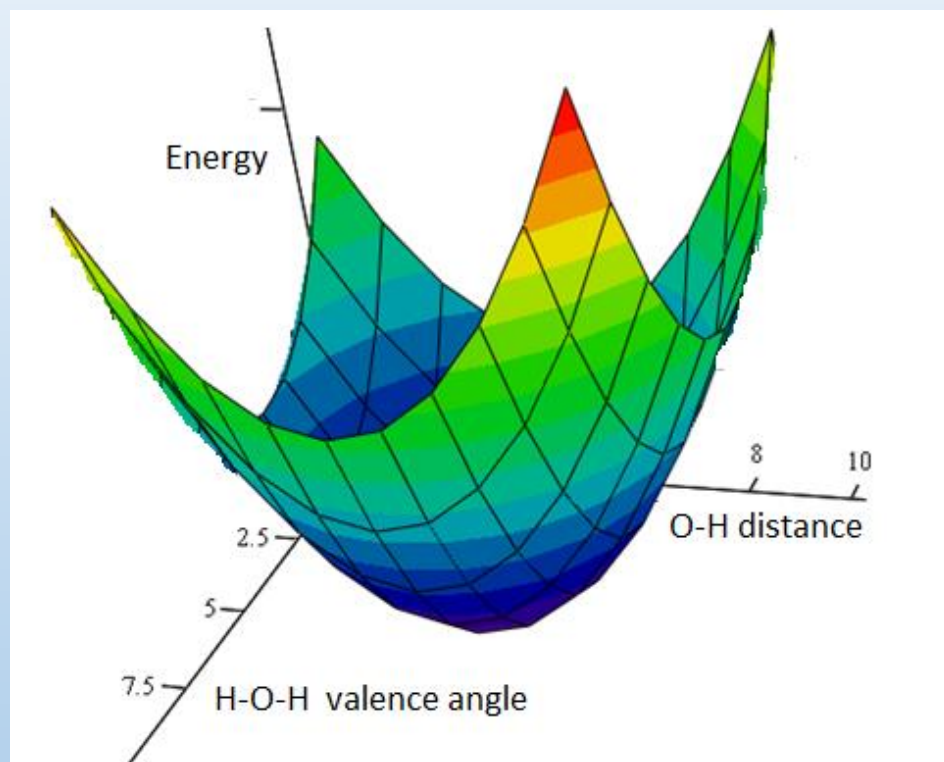
$$\text{grad}(E) = \left(\frac{\partial E}{\partial q_1}, \frac{\partial E}{\partial q_2}, \dots, \frac{\partial E}{\partial q_{3N-6}} \right) = 0$$

Characteristics of Critical points of PES (Hess matrix):

$$H = \begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & \frac{\partial^2 E}{\partial q_1 \partial q_2} & \dots & \frac{\partial^2 E}{\partial q_1 \partial q_{3N-6}} \\ \frac{\partial^2 E}{\partial q_2 \partial q_1} & \frac{\partial^2 E}{\partial q_2^2} & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \frac{\partial^2 E}{\partial q_{3N-6} \partial q_1} & \dots & \dots & \frac{\partial^2 E}{\partial q_{3N-6}^2} \end{pmatrix}$$

Fragment of PES for water molecule

$$E[q(\text{OH}); q(\text{HOH})]$$



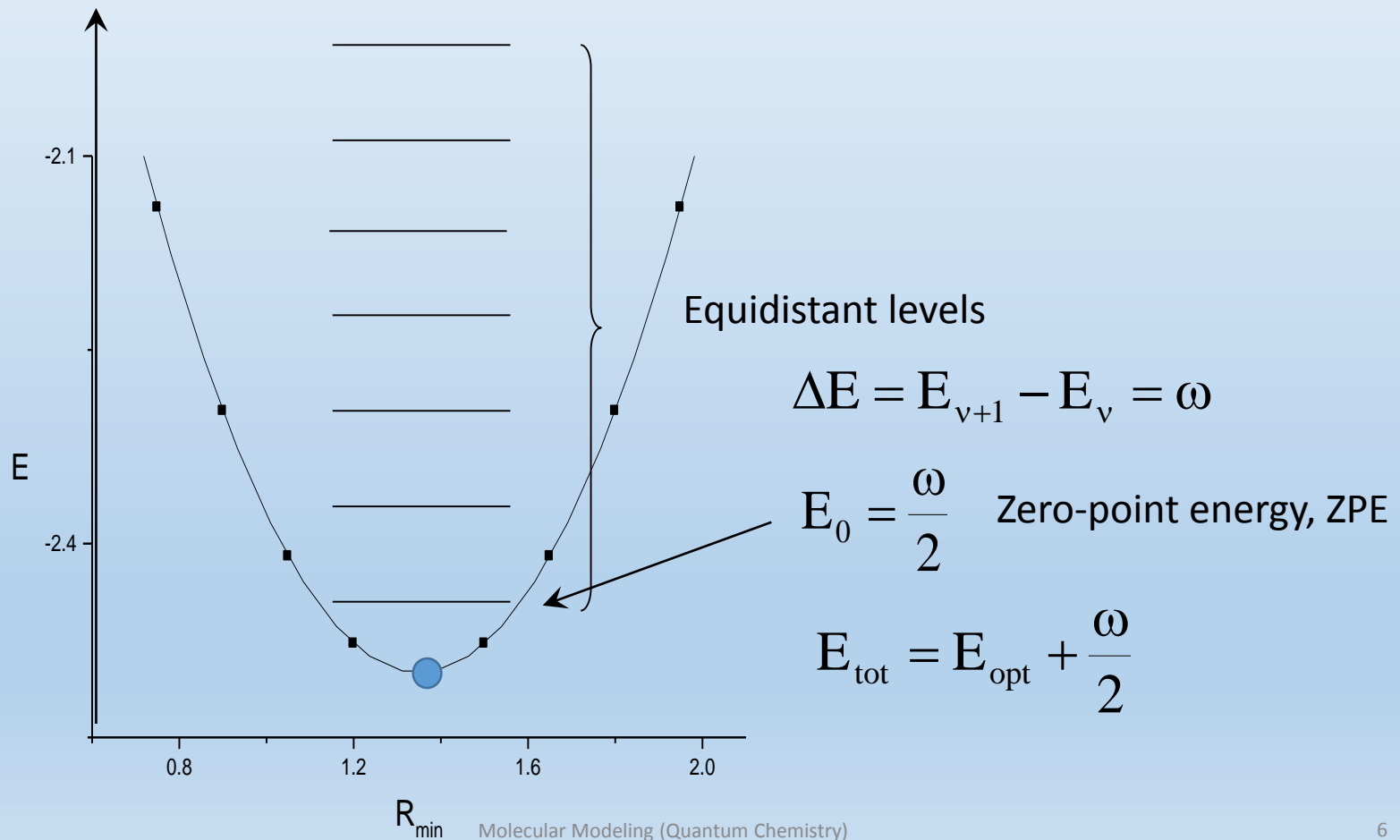
$$3N - 6 = 3 \cdot 3 - 6 = 3$$

$$E = E(\theta_{\text{HOH}}, r_{\text{OH}_1}, r_{\text{OH}_2})$$

Quantum Theory of vibrations

Harmonic approximation

$$E_v = \omega \left(v + \frac{1}{2} \right) \quad v\text{- Quantum Number}$$

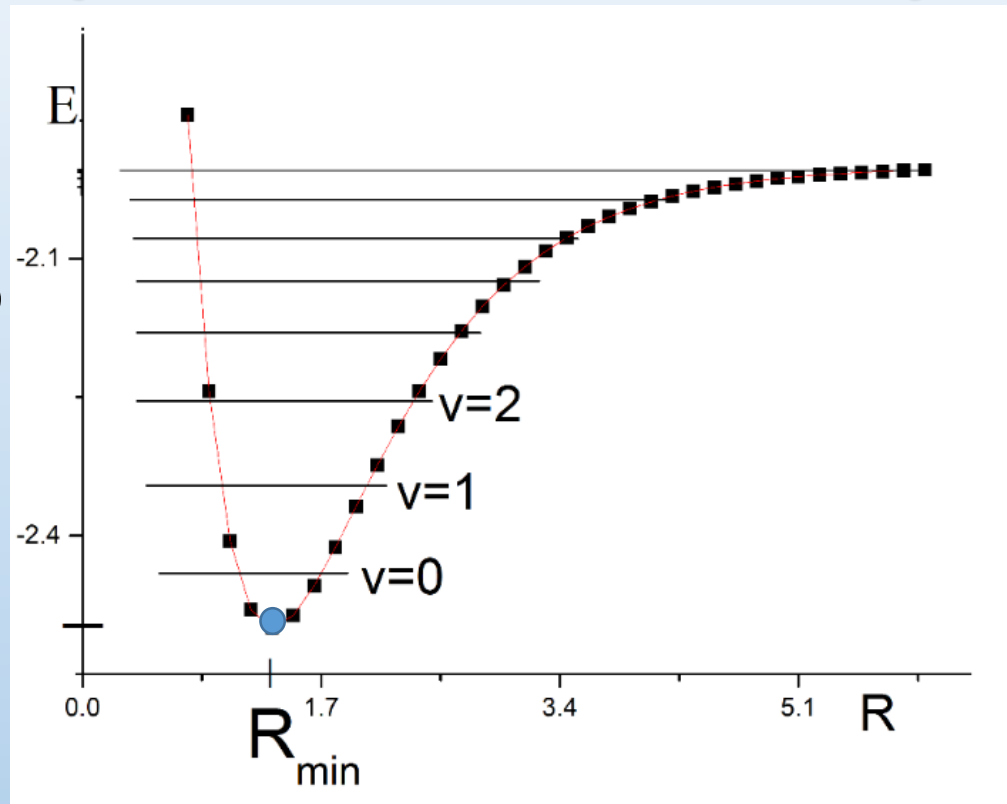


Total energy of system (account vibrations)

$$E_v = \omega \left(v + \frac{1}{2} \right) \quad (\text{a.u.})$$

Zero-point energy, ZPE

$$E_{v=0} = \frac{\omega}{2}$$

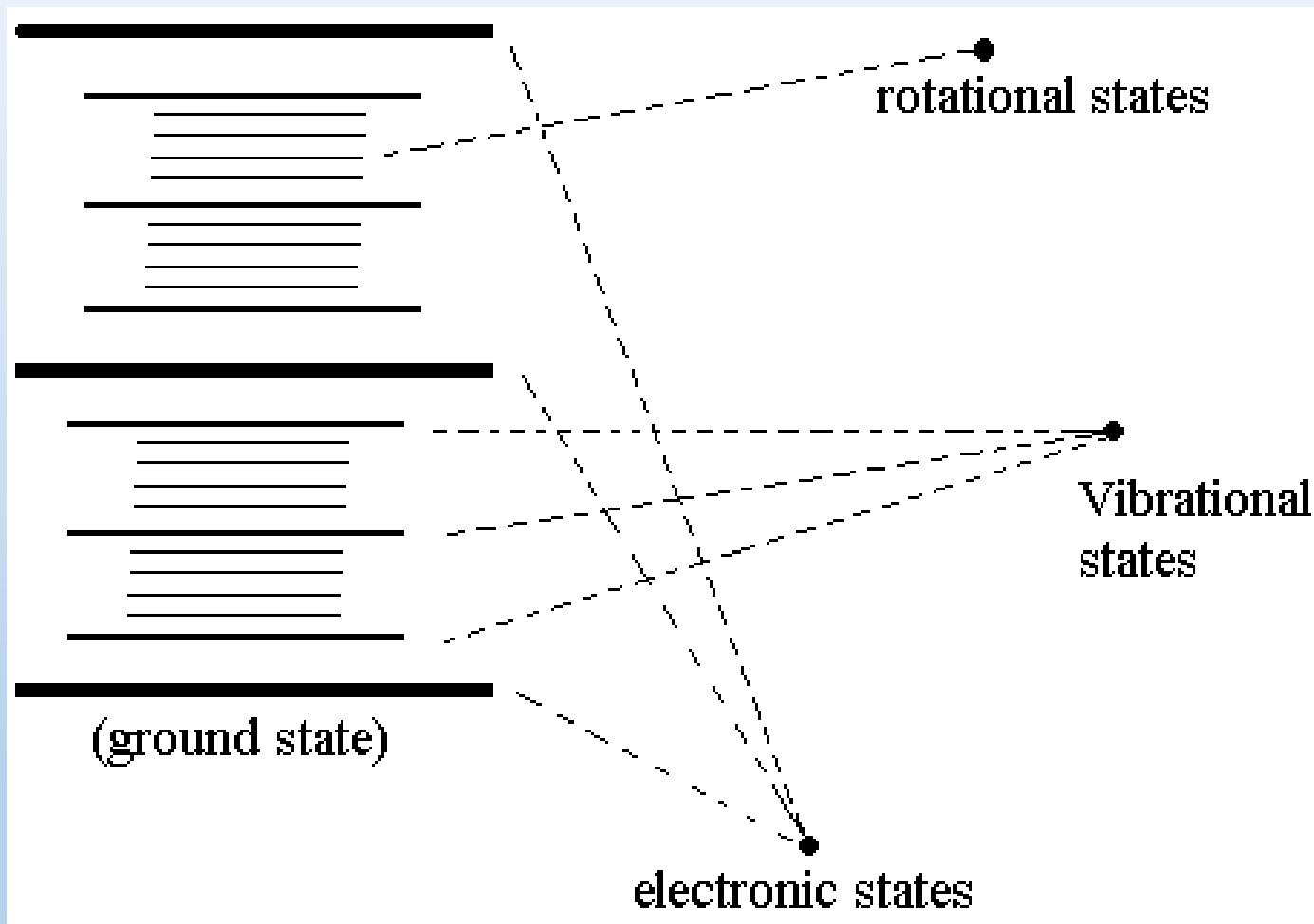


$$E_{\text{electr}} \quad E_{\min} = E_{\text{electr-electr}} + E_{\text{electr-nucl}} + E_{\text{nucl-nucl}} + E_{\text{кинет}}$$

$$E_{v=0} = \frac{1}{2} \sum_i^{3N-6} \omega_i, \quad (\text{a.u.})$$

$$E_{\text{total}} = E_{\min} + E_{v=0}$$

Accounting for vibrational, rotational, and translational states



$$E_{\text{total}} = E_{\text{min}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

Thermochemical calculations

Main thermochemical parameters

- Internal energy U and its changes ΔU throughout a chemical transformation.
- Enthalpy $H=U+PV$. Its changes ΔH are characteristics of thermal effects.
- Entropy S .
- Gibbs free energy $G = H-TS$ $\Delta G = \Delta H-T\Delta S$
 $\Delta G < 0$ – spontaneous reaction (process).

Thermochemical Characteristics

$$H_{\text{tot}} = H_{\text{electr}} + H_{\text{vib}} + H_{\text{rot}} + H_{\text{trans}}$$

$$\Delta H(T) = \Delta H_{\text{electr}} + \Delta H_{\text{vib}}(T) + \Delta H_{\text{rot}}(T) + \Delta H_{\text{trans}}(T) + \Delta nRT$$

$$S_{\text{tot}} = S_{\text{elec}} + S_{\text{vibr}} + S_{\text{rot}} + S_{\text{trans}}$$

At T=0 K

ZPE – zero point energy

$$H(0) = \frac{1}{2} \sum_i^{3N-6} \omega_i$$

Thermal Correction:

$$\Delta H_{\text{vib}}(T) = H_{\text{vib}}(T) - H_{\text{vib}}(0) = N \sum_i^{3N-6} \frac{\omega_i}{\exp(\omega_i / k_B T) - 1}$$

$$H_{\text{rot}}(T) = \frac{3}{2} RT \quad (= RT \text{ for linear molecules})$$

$$H_{\text{trans}}(T) = \frac{3}{2} RT$$

Elements of statistical Mechanics

Partition function $q = \sum_i^{\text{all states}} g_i \exp(-E_i / k_B T)$

q is a measure of the number of states accessible to the molecule at a particular temperature.

g_i – degeneracy,

k_B – **Boltzmann constant**, $1.380649 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$

T – temperature

i – number of quantum state

$$P(E_i) = \exp(-E_i / k_B T) / q$$

$$E_{tot} = E_{elec} + E_{vibr} + E_{rot} + E_{trans}$$

$$q_{tot} = q_{elect} q_{vib} q_{rot} q_{trans}$$

Thermodynamic parameters in statistical physics

$$Q = q_{tot}^N / N !$$

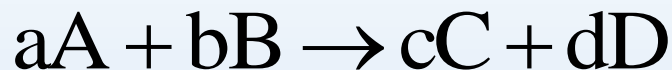
$$H = U + PV = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V$$

$$S = \frac{U - A}{T} = kT \left(\frac{\partial \ln Q}{\partial T} \right)_V + k \ln Q$$

$$G = H - TS = kTV \left(\frac{\partial \ln Q}{\partial T} \right)_T - kT \ln Q$$

Heat effect of the reaction



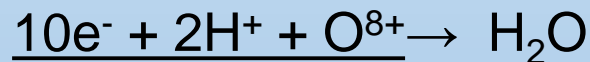
$$\Delta H = c\Delta H_f (C) + d\Delta H_f (D) - (a\Delta H_f (A) + b\Delta H_f (B))$$

ΔH_f - Enthalpy of formation

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta nRT$$

- In **Physical Chemistry** we are computing H_f relative to the elements in their standard states. For instance graphene for C, O₂ for oxygen etc.
- In **Quantum Chemistry** we are computing H relative to infinitely separated electrons and nuclei.

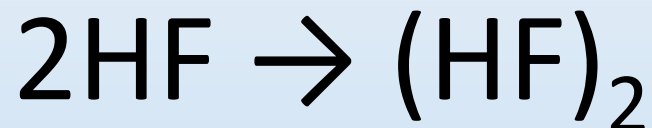
$$\text{HF/6-31G } E(\text{H}_2\text{O}) = -75.985359 \text{ a.u.}$$



$$\Delta H_{\text{reaction}} = \underbrace{\Delta H_f (\text{product}) - \Delta H_f (\text{reagents})}_{\text{Physical Chemistry}} = \underbrace{H(\text{product}) - H(\text{reagents})}_{\text{Quantum Chemistry}}$$

Hydrogen Bond energy HF....HF

Hartree-Fock calculation 6-31(d,p)



- 1) Calculate HF molecule (optimization geometry and vibrations !)
- 2) Calculate dimer $(\text{HF})_2$ (optimization geometry and vibrations !)
- 3) Calculate the enthalpy:

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H_{\text{H-bond}} = (E(\text{dimer}) - 2E(\text{HF})) + (E_{\text{vrt}}(\text{dimer}) - 2E_{\text{vrt}}(\text{HF})) + (1-2)RT$$

HF molecule

NSERCH= 4 ENERGY= -100.0116908

GRADIENT (HARTREE/BOHR)

ATOM	ZNUC	DE/DX	DE/DY	DE/DZ
1 F	9.0	-0.0000017	0.0000000	0.0000000
2 H	1.0	0.0000017	0.0000000	0.0000000

MAXIMUM GRADIENT = 0.0000017 RMS GRADIENT = 0.0000010

***** EQUILIBRIUM GEOMETRY LOCATED *****

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
F	9.0	-9.7723451483	3.5314400000	0.0000000000
H	1.0	-8.8718148517	3.5314400000	0.0000000000

INTERNUCLEAR DISTANCES (ANGS.)

	1 F	2 H
1 F	0.0000000	0.9005303 *
2 H	0.9005303 *	0.0000000

* ... LESS THAN 3.000

HF molecule

	E	H	G	CV	CP	S
	KJ/MOL	KJ/MOL	KJ/MOL	J/MOL-K	J/MOL-K	J/MOL-K
ELEC.	0.000	0.000	-0.000	0.000	0.000	0.000
TRANS.	3.718	6.197	-37.366	12.472	20.786	146.111
ROT.	2.479	2.479	-5.591	8.314	8.314	27.068
VIB.	26.872	26.872	26.872	0.000	0.000	0.000
TOTAL	33.069	35.548	-16.085	20.786	29.100	173.179

$E(T)-E(\theta) = H(T)-H(\theta) = 0.000$

	E	H	G	CV	CP	S
	KCAL/MOL	KCAL/MOL	KCAL/MOL	CAL/MOL-K	CAL/MOL-K	CAL/MOL-K
ELEC.	0.000	0.000	-0.000	0.000	0.000	0.000
TRANS.	0.889	1.481	-8.931	2.981	4.968	34.921
ROT.	0.592	0.592	-1.336	1.987	1.987	6.469
VIB.	6.423	6.423	6.423	0.000	0.000	0.000
TOTAL	7.904	8.496	-3.844	4.968	6.955	41.391

$E(T)-E(\theta) = H(T)-H(\theta) = 0.000$

.....END OF NORMAL COORDINATE ANALYSIS.....

STEP CPU TIME = 0.02 TOTAL CPU TIME = 0.2 (0.0 MIN)

TOTAL WALL CLOCK TIME= 0.7 SECONDS, CPU UTILIZATION IS 33.92%

994248 WORDS OF DYNAMIC MEMORY USED

EXECUTION OF GAMESS TERMINATED NORMALLY Mon Oct 31 16:54:02 2022

DDI: 262808 bytes (0.3 MB / 0 MWords) used by master data server.

CPU timing information for all processes

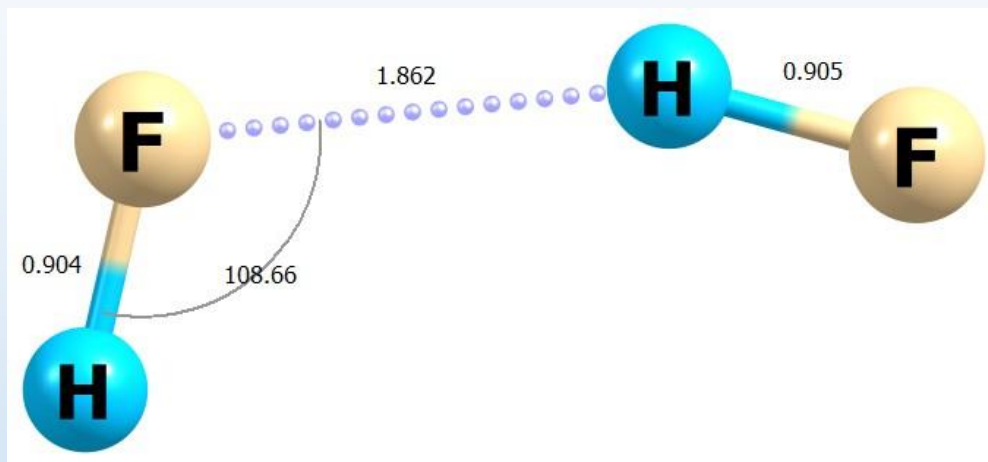
=====

0: 0.202000 + 0.078000 = 0.280000

1: 0.000000 + 0.015000 = 0.015000

ddikick.x: exited gracefully.

----- accounting info -----



TOTAL WALL CLOCK TIME= 5.7 SECONDS, CPU UTILIZATION IS 98.41%

NSERCH= 37 ENERGY= -200.0329032

GRADIENT (HARTREE/BOHR)

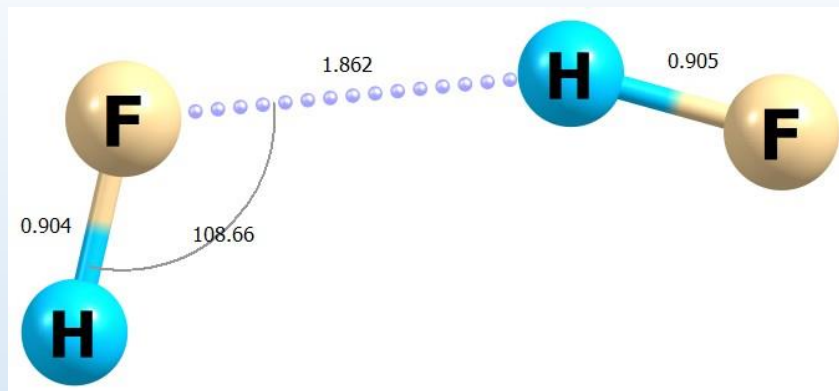
ATOM	ZNUC	DE/DX	DE/DY	DE/DZ
1 F	9.0	0.0000005	-0.0000013	-0.0000011
2 H	1.0	0.0000004	0.0000016	0.0000014
3 F	9.0	-0.0000035	-0.0000066	0.0000016
4 H	1.0	0.0000026	0.0000063	-0.0000018

MAXIMUM GRADIENT = 0.0000066 RMS GRADIENT = 0.0000031

***** EQUILIBRIUM GEOMETRY LOCATED *****

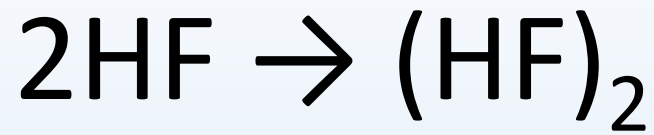
COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
F	9.0	-7.8016825507	2.6417823864	0.2472952307
H	1.0	-6.0631056724	2.3610608822	0.0100783362



	E	H	G	CV	CP	S
	KJ/MOL	KJ/MOL	KJ/MOL	J/MOL-K	J/MOL-K	J/MOL-K
ELEC.	0.000	0.000	-0.000	0.000	0.000	0.000
TRANS.	3.718	6.197	-39.943	12.472	20.786	154.755
ROT.	3.718	3.718	-21.125	12.472	12.472	83.325
VIB.	65.678	65.678	58.085	25.502	25.502	25.467
TOTAL	73.114	75.593	-2.983	50.445	58.759	263.547
E(T)-E(θ) = H(T)-H(θ) = 4241.524						

	E	H	G	CV	CP	S
	KCAL/MOL	KCAL/MOL	KCAL/MOL	CAL/MOL-K	CAL/MOL-K	CAL/MOL-K
ELEC.	0.000	0.000	-0.000	0.000	0.000	0.000
TRANS.	0.889	1.481	-9.547	2.981	4.968	36.987
ROT.	0.889	0.889	-5.049	2.981	2.981	19.915
VIB.	15.697	15.697	13.883	6.095	6.095	6.087
TOTAL	17.475	18.067	-0.713	12.057	14.044	62.989
E(T)-E(θ) = H(T)-H(θ) = 1013.749						
.....END OF NORMAL COORDINATE ANALYSIS.....						



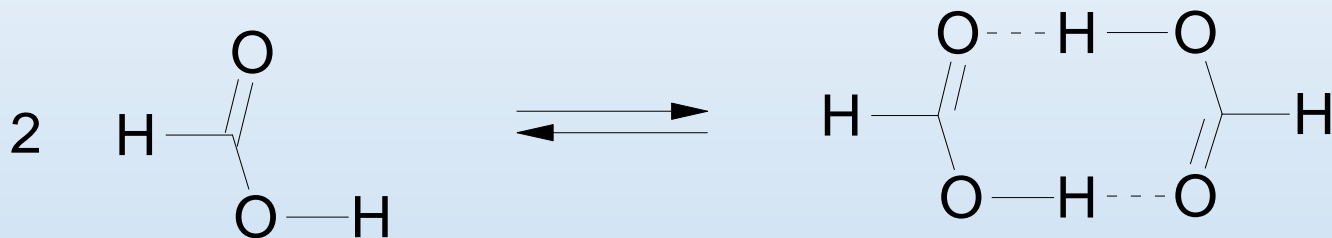
	E(a.u)	E_{vrt} (kcal/mol)
HF	-100.011691	8.496
$(\text{HF})_2$	-200.032903	18.067
ΔE	-0.009521	

RT=0.592 kcal/mol

$$\Delta H_{\text{H-bond}} = (E(\text{dimer}) - 2E(\text{HF}))627.50 + (E_{\text{vrt}}(\text{dimer}) - 2E_{\text{vrt}}(\text{HF})) + (1-2)RT$$

(kcal/mol)	$E(\text{dimer}) - 2E(\text{HF})$	$E_{\text{vrt}}(\text{dimer}) - 2E_{\text{vrt}}(\text{HF})$
ΔE	-5.97	1.075
$\Delta H_{\text{H-bond}}$	-5.49	
$\Delta H_{\text{H-bond}}$ (Experim)	-4.81 ± 0.2	

Enthalpy of dimerization of formic acid



$$\Delta H^{298.15} \text{ (ккал} \cdot \text{моль}^{-1}\text{)}$$

HF	HF	B3LYP	MP2	Experim
3-21G	6-31+G(d)	6-31+G(d)	6-31+G(d)	
-26.6	-12.8	-14.8	-14.8	-14.7

To be continued

Methods for accounting of electron correlation effects