

TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

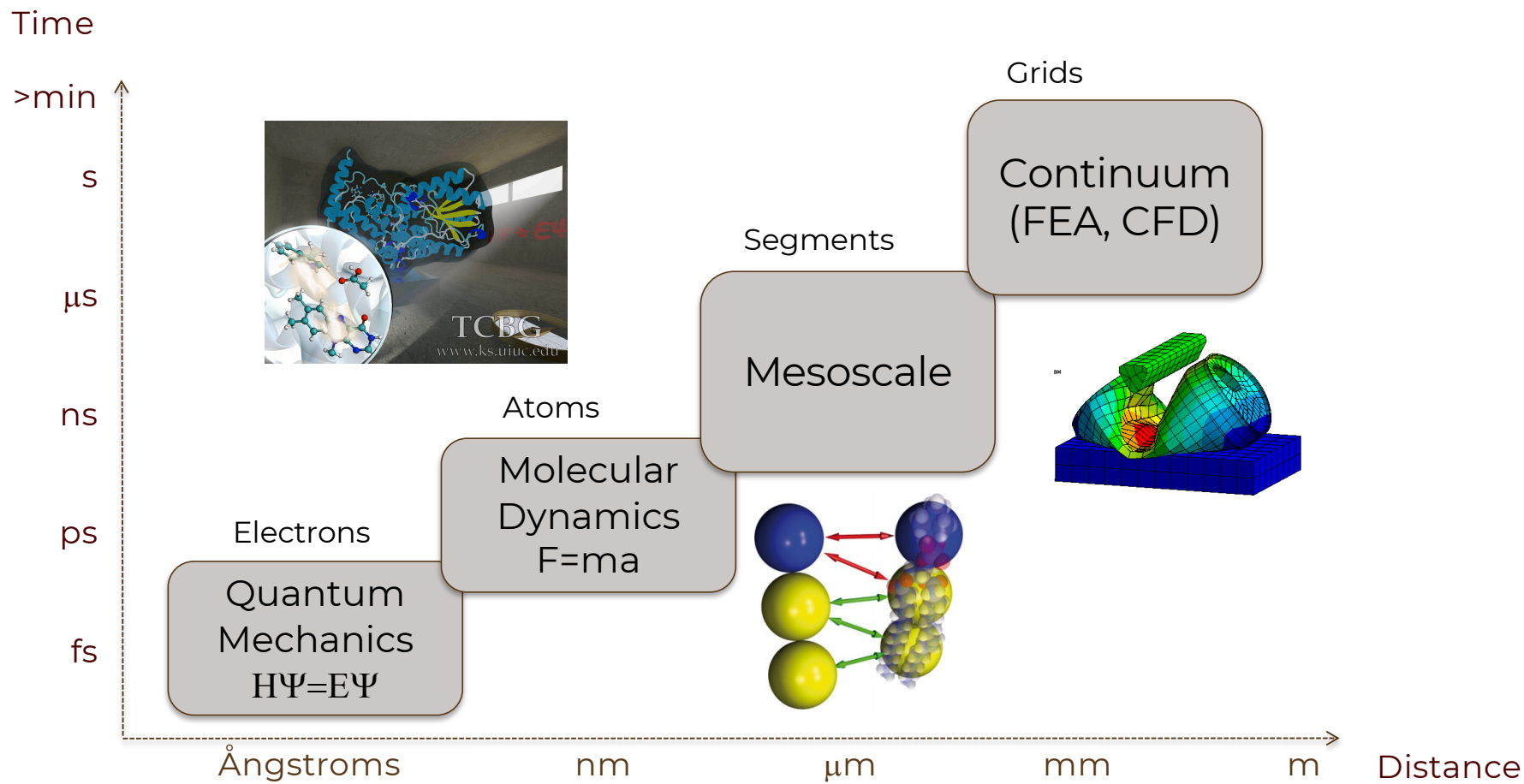
Lecture 1 of 6



TEXAS A&M UNIVERSITY
Division of Research



Microscopic \leftrightarrow Macroscopic



Quantum Mechanics

Time-independent Schrödinger Equation

$$\hat{H}\psi = E\psi$$

\hat{H} Hamiltonian Operator

ψ Wavefunction (eigenfunction)

E Energy of the system (eigenvalue)



Quantum Mechanics

Approximations made in the Hamiltonian

- 1) Neglect relativistic effect
- 2) Neglect coupling of electronic states (adiabatic approximation)
- 3) Neglect coupling of the electronic and nuclear motion (Born-Oppenheimer approximation)



Quantum Mechanics

Born-Oppenheimer Approximation

- 1) The electronic Schrödinger equation:
 $H_e \psi = E_e \psi$ is solved for a set of nuclear coordinates.
- 2) The nuclear motion is treated classically.



Getting Started

- Molecular Coordinates

- atomic coordinates for ALL atoms (including hydrogens)

- ✦ cartesian coordinates

- ✦ internal coordinates

- z-matrix

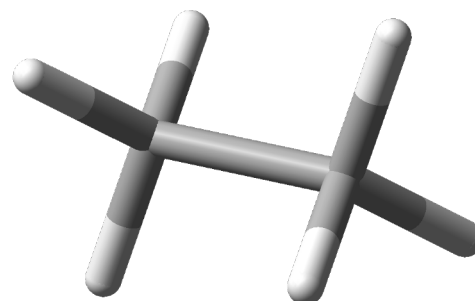
- Internal redundant coordinates

- etc

- Symmetry (Point Group)

- Charge (overall charge of the molecular system)

- Multiplicity (number of unpaired electrons)



C_2H_6

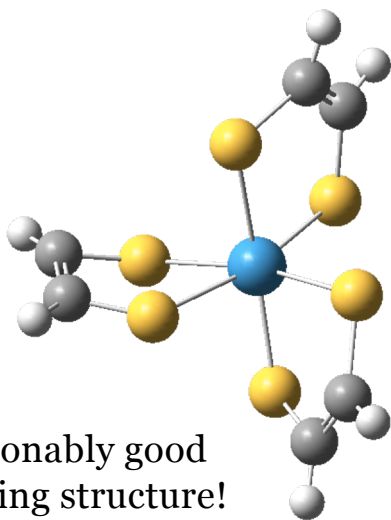
D_{3d}

Charge = 0

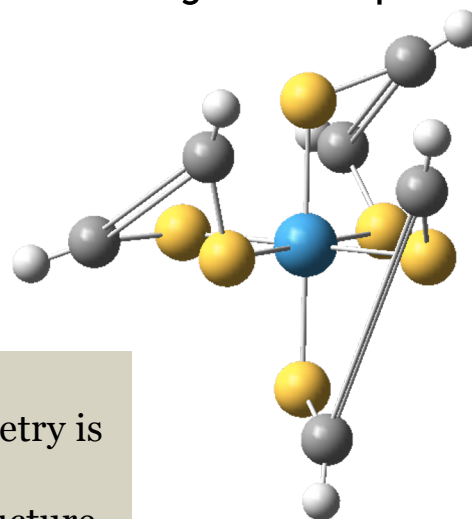
Multiplicity = 1

Getting Started – Atomic Coordinates

- Atomic (nuclear) coordinates are required for all atomistic calculations.
- A reasonably good starting geometry is required for electronic structure calculations.



A reasonable starting geometry is required for electronic structure calculations.



Will most likely fail with an SCF convergence failure or possibly optimize to an excited state or high energy structure.

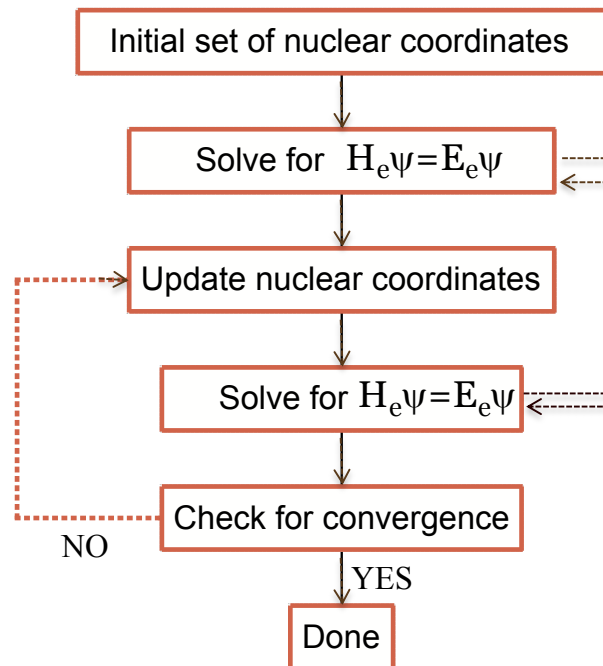
Getting Started

- **Choose a level of theory**
 - The level of theory determines the Hamiltonian (H) used to solve the Schrödinger equation ($H\Psi = E\Psi$)
 - HF, MP2, MP3, DFT (B3LYP, BP86, etc), CCSD, etc
- **Choose a basis set**
 - The basis set is a set of coefficient and exponents for the functions used to describe the atomic orbitals that will be using to describe the wavefunction (Ψ)
 - 6-31G(d), SDD, LANL2DZ, etc
- **Calibrate**
 - against experimental data
 - against benchmark calculations (CCSD(T), MRCI, etc)

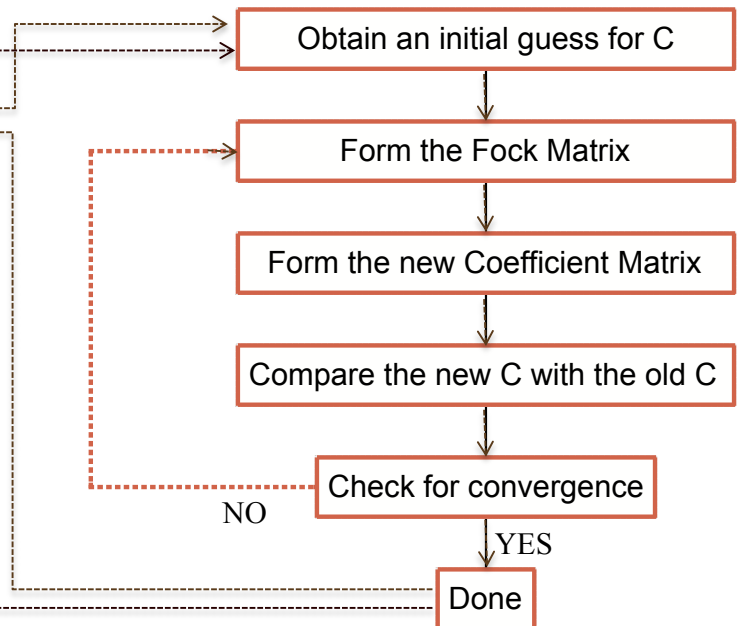


Geometry Optimization

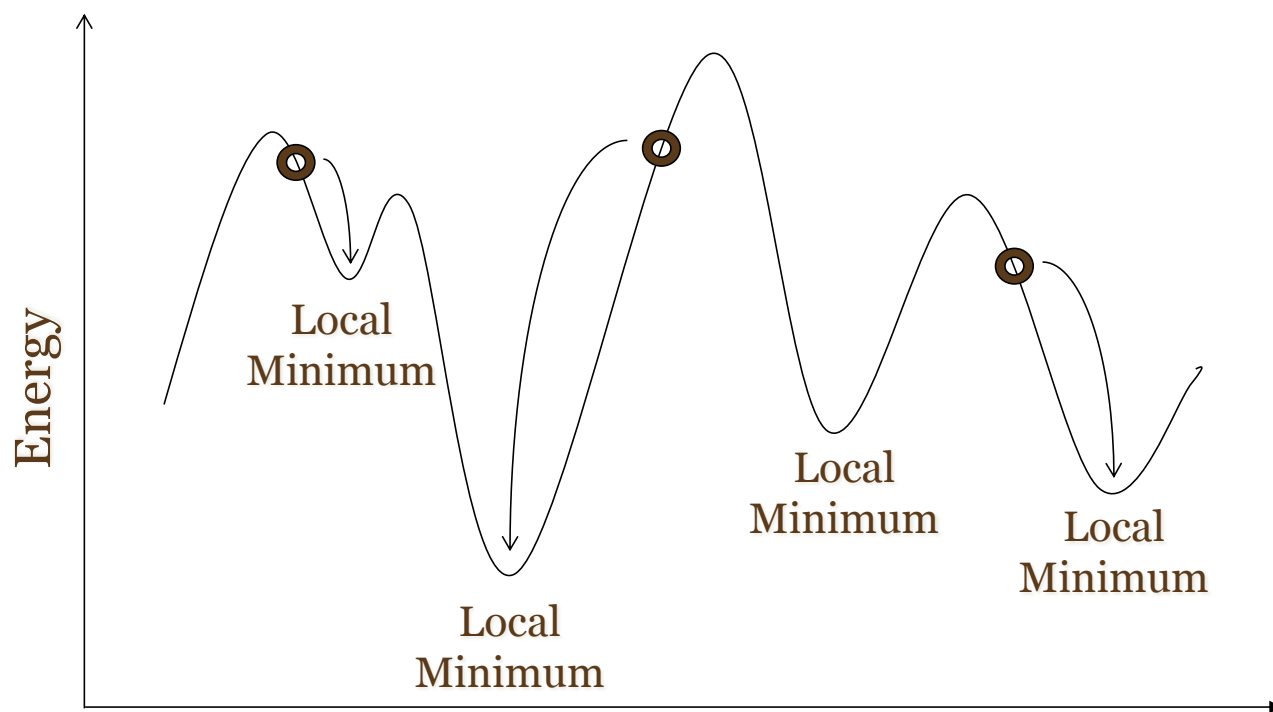
Iterative Geometry Optimization Steps



SCF (Self Consistent Field) iterative process to solve the non-linear Roothan Equations

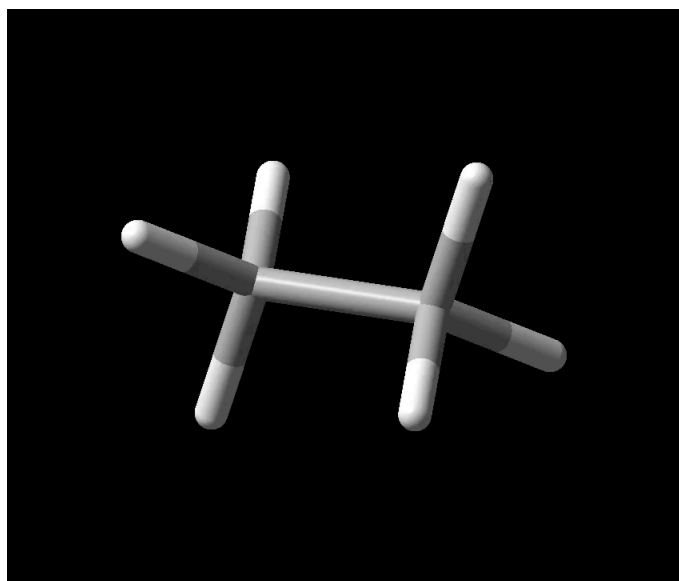


Geometry Optimization

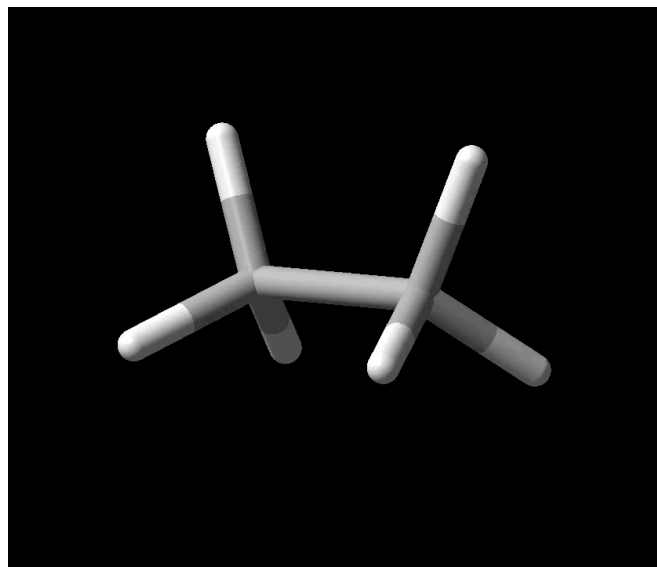


Symmetry

- Does your molecule have symmetry?



D_{3d}

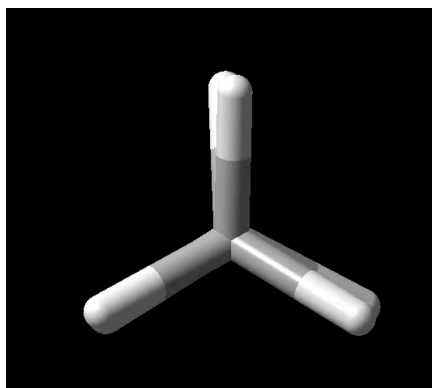


D_{3h}

on-line symmetry tutorial - <http://symmetry.otterbein.edu/tutorial/pointgroups.html>



Stationary Points



Stationary Point: Gradients with respect to all internal coordinates are zero.

Vibrational modes

All real = minimum

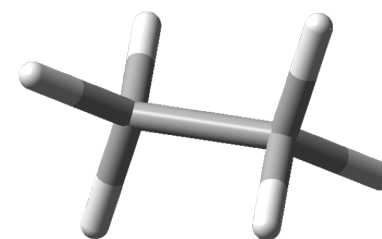
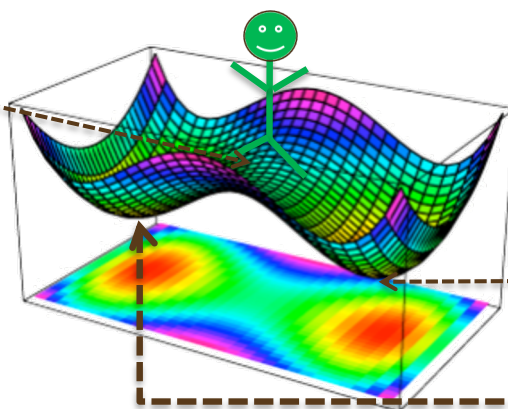
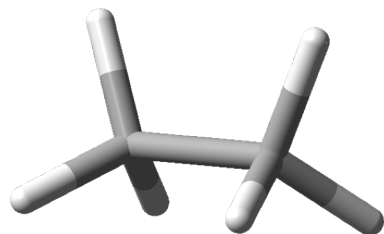
1 imaginary = 1st order saddle point (sp) (transition state)

2 imaginary = 2nd order sp

3 imaginary = 3rd order sp

etc

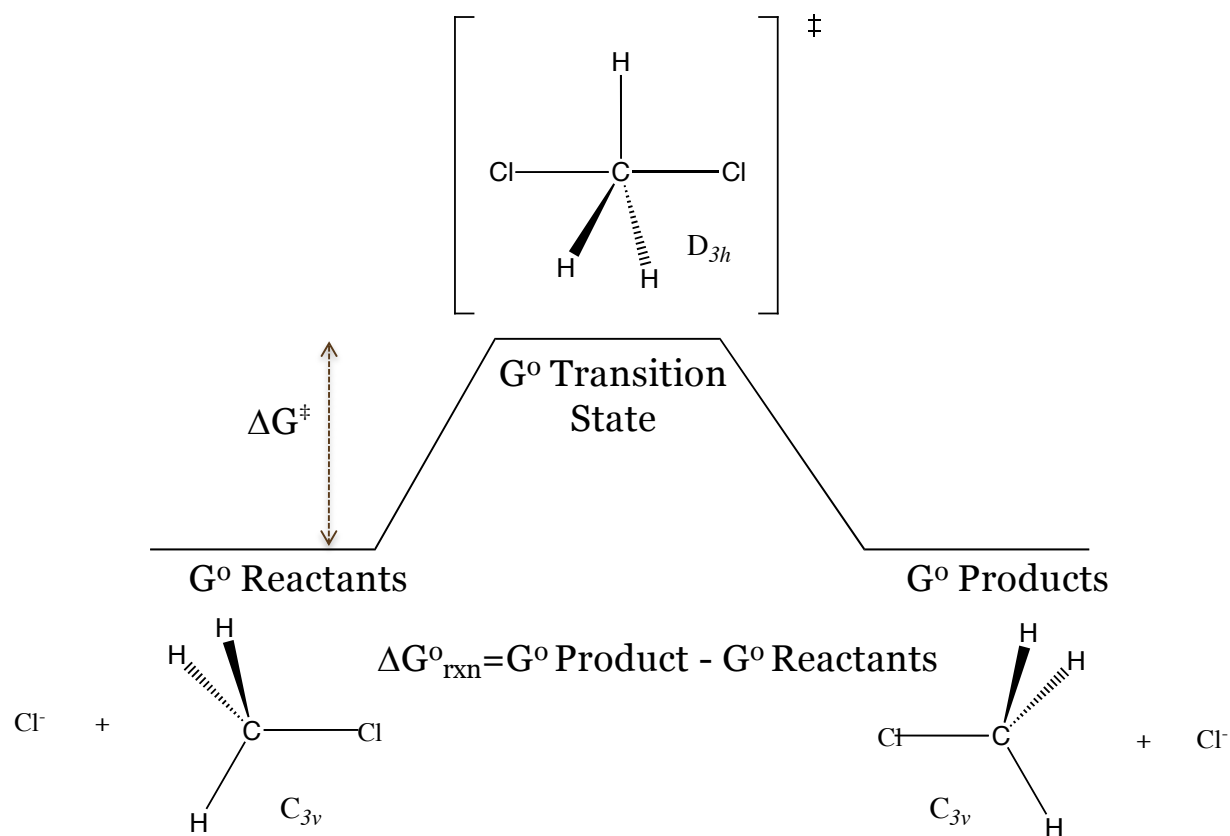
Imaginary mode $294.0i \text{ cm}^{-1}$
1st order saddle point
transition state



Minimum (D_{3d})



Use of Symmetry in TS Searches



Vibrational Analysis

2.5 Calculate the frequencies

At this point, the eigenvalues need to be converted frequencies in units of reciprocal centimeters. First we change from frequencies (ν_i) to wavenumbers ($\tilde{\nu}_i$), via the relationship $\nu_i = \tilde{\nu}_i c$, where c is the speed of light. Solving $\lambda = 4\pi^2 \tilde{\nu}^2 c^2$ for $\tilde{\nu}_i^2$ we get

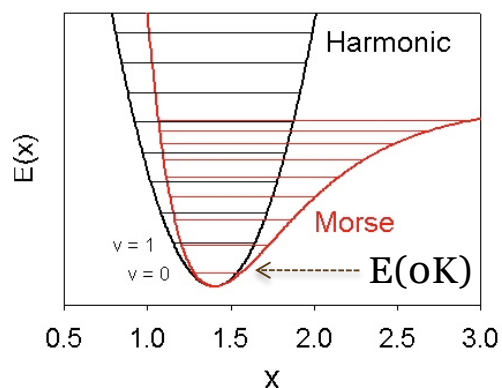
$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}} \quad (8)$$

The rest is simply applying the appropriate conversion factors: from a single molecule to a mole, from hartrees to joules, and from atomic mass units to kilograms. For negative eigenvalues, we calculate $\tilde{\nu}_i$ using the absolute value of λ_i , then multiply by -1 to make the frequency negative (which flags it as imaginary). After this conversion, the frequencies are ready to be printed out.

http://www.gaussian.com/g_whitepap/vib.htm



Frequency Calculation



Calculation uses the
Harmonic Oscillator
Approximation

"The essential message is this: the basic equations used to calculate thermochemical quantities in Gaussian are based on those used in standard texts. Since the vibrational partition function depends on the frequencies, you must use a structure that is either a **minimum** or a **saddle point**. For electronic contributions to the partition function, it is assumed that the first and all higher states are inaccessible at the temperature the calculation is done at. The data generated by Gaussian can be used to calculate heats and free energies of reactions as well as absolute rate information."

Zero-point correction=	0.010473 (Hartree/Particle)
Thermal correction to Energy=	0.012833
Thermal correction to Enthalpy=	0.013777
Thermal correction to Gibbs Free Energy=	-0.000995
Sum of electronic and zero-point Energies=	-1.122035 E(0K)
Sum of electronic and thermal Energies=	-1.119674 E(298K)
Sum of electronic and thermal Enthalpies=	-1.118730 H°(298K)
Sum of electronic and thermal Free Energies=	-1.133503 G°(298K)



```

Low frequencies ----1173.8833 -12.8219 -10.7863 0.0005 0.0007 0.0010
Low frequencies --- 10.2288 2227.9437 2879.5324
***** 1 imaginary frequencies (negative Signs) *****
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:

```

1			2			3				
A'			A'			A'				
Frequencies --	-1173.8833		2227.9437			2879.5324				
Red. masses --	1.1748		12.1728			1.0640				
Frc consts --	0.9539		35.5998			5.1980				
IR Inten --	90.0380		6.4894			149.2555				
Raman Activ --	6.8213		23.9012			48.8471				
Depolar (P) --	0.6392		0.1013			0.2434				
Depolar (U) --	0.7799		0.1840			0.3915				
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.08	0.05	0.00	-0.01	0.73	0.00	-0.07	0.01	0.00
2	1	0.07	-0.99	0.00	-0.12	0.21	0.00	1.00	0.03	0.00
3	7	-0.07	0.03	0.00	0.02	-0.64	0.00	-0.01	-0.01	0.00

Vibrational modes

All real = minimum

1 Imaginary = 1st order saddle point (TS)

2 Imaginary = 2nd order saddle point

3 Imaginary = 3rd order saddle point

etc

Calculation uses Harmonic Oscillator Approximation

- Thermochemistry -

```

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Atom 1 has atomic number 6 and mass 12.00000
Atom 2 has atomic number 1 and mass 1.00783
Atom 3 has atomic number 7 and mass 14.00307
Molecular mass: 27.01090 amu.

```

1 imaginary frequencies ignored.

```

Zero-point vibrational energy 30549.5 (Joules/Mol)
7.30150 (Kcal/Mol)

```

```

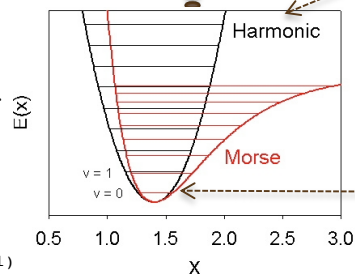
Vibrational temperatures: 3205.51 4143.00
(Kelvin)

```

```

Zero-point correction= 0.011636 (Hartree/Particle)
Thermal correction to Energy= 0.014468
Thermal correction to Enthalpy= 0.015413
Thermal correction to Gibbs Free Energy= -0.009352
Sum of electronic and zero-point Energies=
Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies=
Sum of electronic and thermal Free Energies=

```

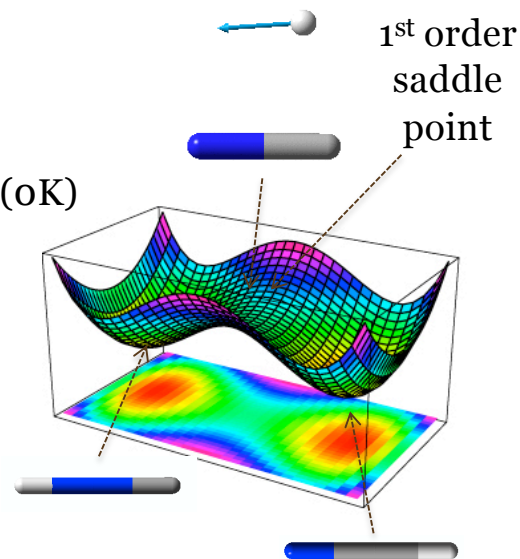


E(oK)

```

-92.797961 E(0K)
-92.795128 E(298K)
-92.794184 H°(298K)
-92.818948 G°(298K)

```



Frequency Calculation

KE= 1.128388355094D+00 PE=-3.640638664551D+00 EE= 6.600019613873D-01

Item	Value	Threshold	Converged?
Maximum Force	0.000124	0.000450	YES
RMS Force	0.000124	0.000300	YES
Maximum Displacement	0.000154	0.001800	YES
RMS Displacement	0.000218	0.001200	YES

Predicted change in Energy=-1.679765D-08

Optimization completed.

-- Stationary point found.

1
SGG
Frequencies -- 4597.0225
Red. masses -- 1.0078
Frc consts -- 12.5484
IR Inten -- 0.0000
Raman Activ -- 106.2495

Zero-point correction= 0.010473 (Hartree/Particle)
Thermal correction to Energy= 0.012833
Thermal correction to Enthalpy= 0.013777
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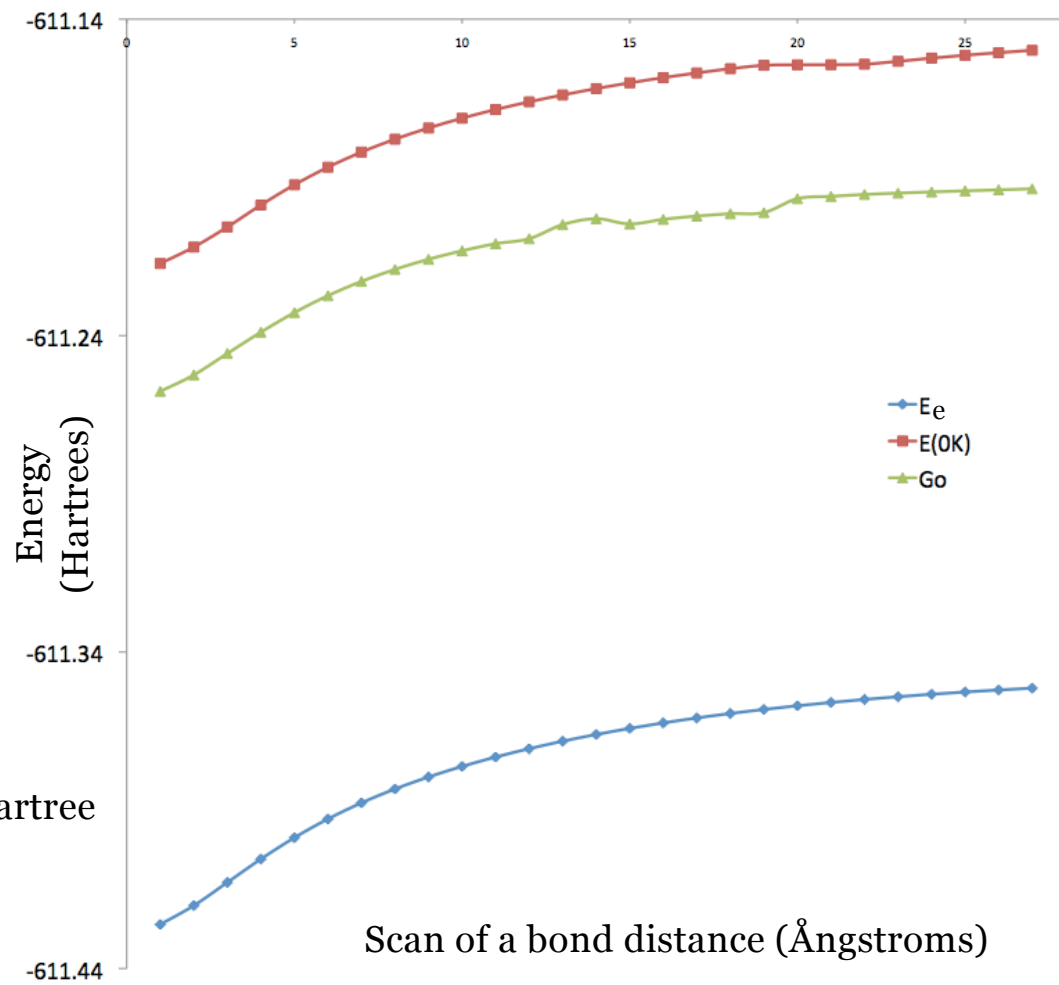


Thermodynamics

“The essential message is this: the basic equations used to calculate thermochemical quantities in Gaussian are based on those used in standard texts. Since the vibrational partition function depends on the frequencies, you must use a structure that is either a minimum or a saddle point. For electronic contributions to the partition function, it is assumed that the first and all higher states are inaccessible at the temperature the calculation is done at. The data generated by Gaussian can be used to calculate heats and free energies of reactions as well as absolute rate information.”

http://www.gaussian.com/g_whitepap/thermo.htm



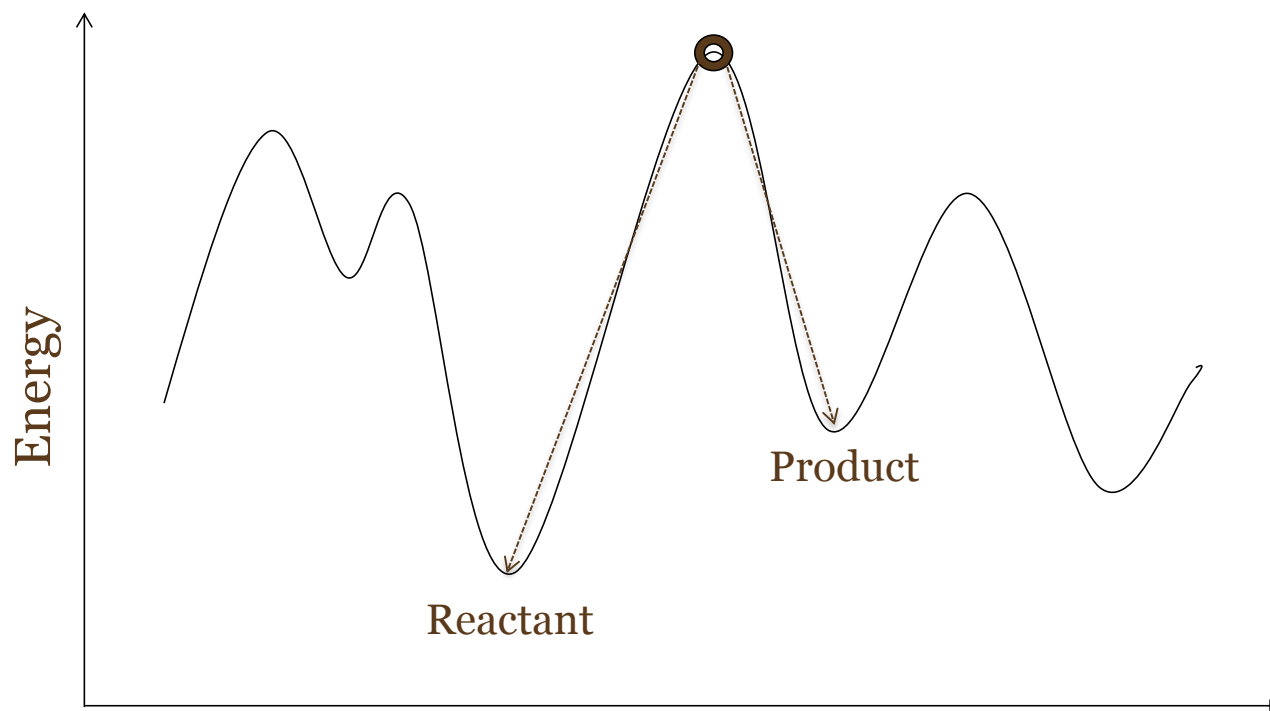


627.5095 kcal mol⁻¹/Hartree



Intrinsic Reaction Coordinate (IRC)

IRC will try to follow the imaginary mode backward or forward to the minimum.



Charge, Spin, and Multiplicity

- Charge of the Molecule
- Spin State – How many unpaired electrons?
- Spin Multiplicity = $2S+1$ where S is the total Spin

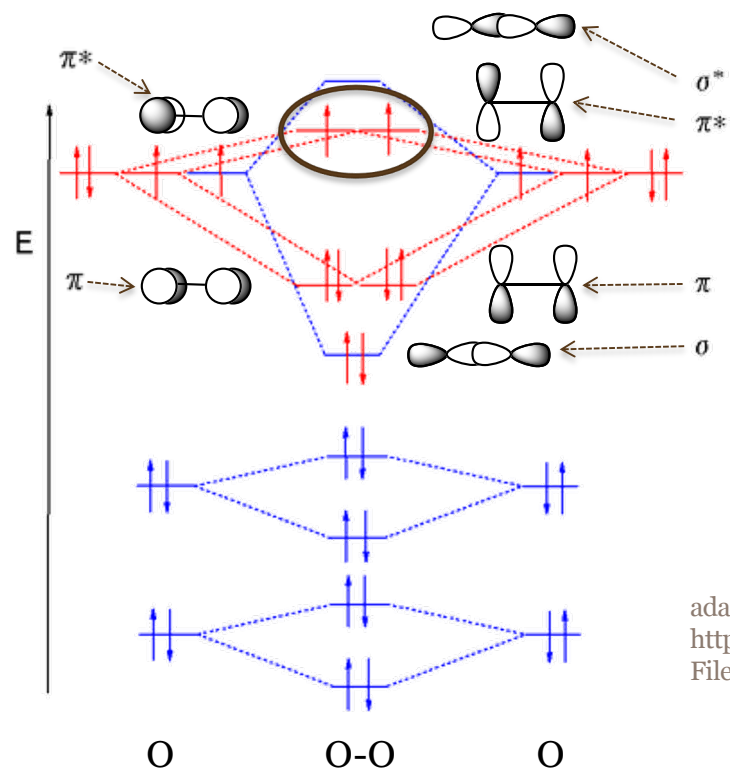
$$S = \sum m_s \quad m_s = 1/2 \text{ spin up, alpha} \quad m_s = -1/2 \text{ spin down, beta}$$

Number of unpaired e ⁻	Spin	Spin Multiplicity	
0	$S=0$	1	Singlet
1	$S=1/2$	2	Doublet
2	$S=1$	3	Triplet
3	$S=3/2$	4	Quartet
4	$S=2$	5	Quintet



Getting Started

Molecular Oxygen (O_2)
has
2 unpaired electrons
 $S = 1/2 + 1/2 = 1$
Multiplicity $(2S+1) = 3$
triplet



adapted from
[https://commons.wikimedia.org/wiki/
File:MO_diagram_dioxygen.png](https://commons.wikimedia.org/wiki/File:MO_diagram_dioxygen.png)

Molecular Oxygen Molecular Orbital Diagram

Restricted vs. Unrestricted Calculations

\uparrow $m_s = 1/2$ spin up, alpha
 \downarrow $m_s = -1/2$ spin down, beta

$$S^2 = S(S+1)$$

