Computational Chemistry

How Maths Develop Models to Understand Chemistry

Dr. José A. Gámez | Advanced Workshop on Modelling and Simulation of Complex Systems | 29/05/2024

Outlook

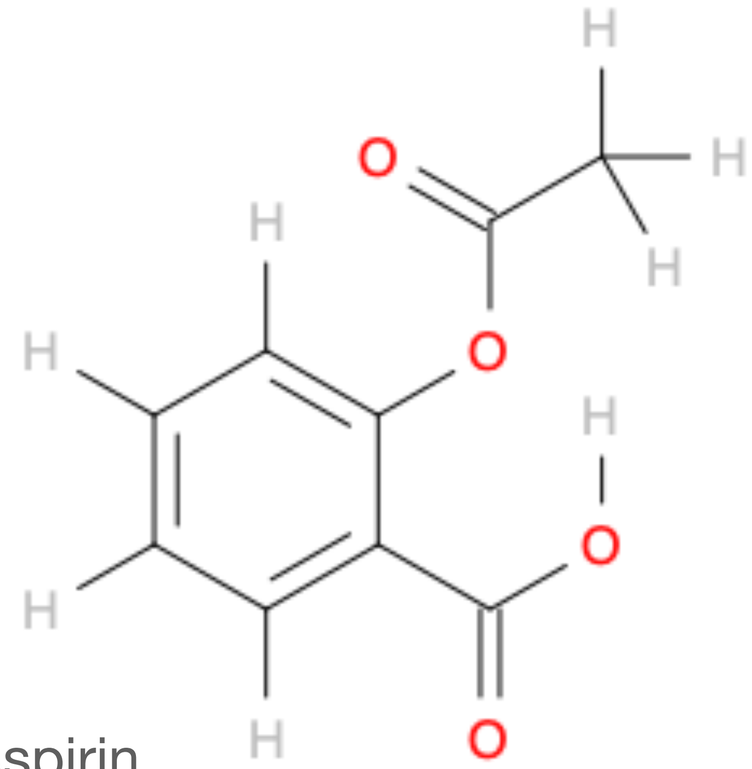
1. Fundamentals on Quantum Mechanics
2. A practical solution to the Schrödinger equation
3. The Potential Energy Surface
    1. The Harmonic Approach
    2. Getting Reaction Parameters: Optimisation
4. Computational Chemistry at work

Fundamentals on Quantum Mechanics

What is a Molecule?

For a Mathematician

- A molecule is a collection of atoms:
  - Carbon (C), omitted
  - Oxygen (O)
  - Hydrogen (H)
- Which are chemically bond:
  - Simple sticks
  - Double sticks

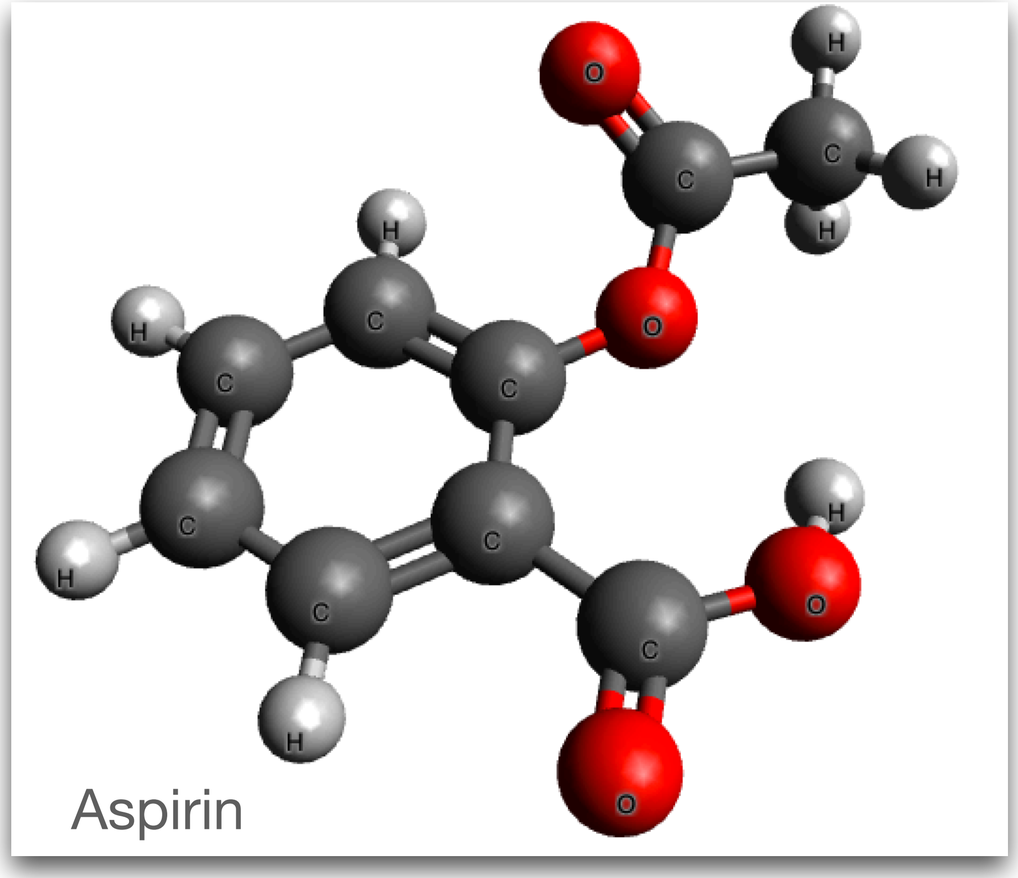


Aspirin

What is a Molecule?

For a Mathematician

- A molecule is then a collection of:
  - Atoms, atomic nuclei
  - Electrons, which may not be bound to a single nucleus
- These two elements have very different properties
  - Charge: nuclei (+) vs. electrons (–)
  - Mass: m(H-nucleus) ≈ 1840 m(electron)



How to Describe a Molecule Mathematically? (I)

Quantum Mechanics in a Nutshell

- Nuclei and electrons are quantum particles, so they follow Quantum Mechanics
- Quantum particles have also wave properties, known a wave-particle duality
- "*One may say that the potential possibility exists for atomic objects to appear or as a particle, or as a wave on dependence of the outer condition*", V. Fock
- To prove that, let's see when an electron goes through two slits

How to Describe a Molecule Mathematically? (II)

The Wavefunction

Classical Particles

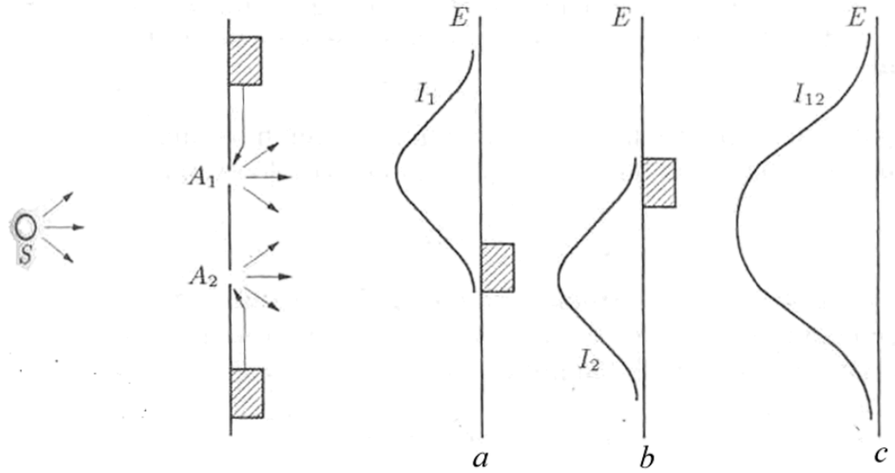


Figure 7-10. Transition of a beam of classical particles trough two slits A_1 and A_2 (S - source, E - screen, I - intensity): a) the slit A_2 is closed; b) the slit A_1 is closed; c) the both slits are opened - their intensities add, i.e. the total intensity is $I_{12} = I_1 + I_2$.

Waves

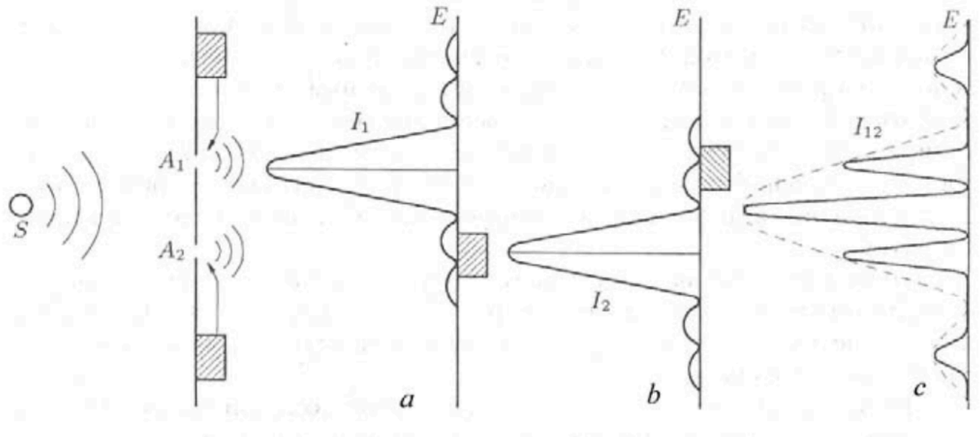


Figure 7-11. Transition of a wave trough two slits A_1 and A_2: a) the slit A_2 is closed; b) the slit A_1 is closed; c) the both slits are opened the interference-diffraction picture is not the sum of the both diffraction picture, i. e. the total intensity is not a sum of the separate intensities $I_{12} = I_1 + I_2$.

S. Ivanov, Theoretical and Quantum Mechanics, 1st Edition, Springer, Dordrecht, p.172

How to Describe a Molecule Mathematically? (III)

The Wavefunction

- A 2 slit can be reproduce with a monocristal
- Davisson and Gremer shot a beam of electrons against a monocrystal and saw the diffraction pattern
- The diffraction patter of an electron is that of a wave

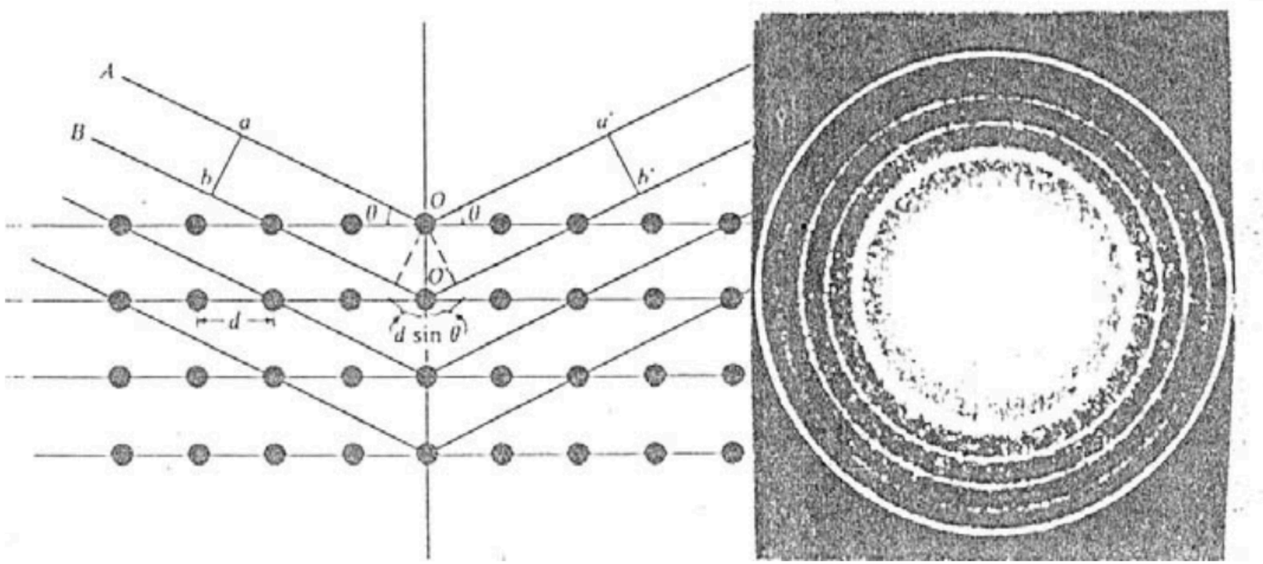


Figure 7-14. The experiment of Davisson and Germer: a beam of electrons incidents on at monocrystal (a); The electrons reflected from successive atomic layers with a path-length $\Delta = 2d\sin\theta$ interfere according to the de Broglie hypothesis and as a result one get the diffraction picture (b).

S. Ivanov, Theoretical and Quantum Mechanics, 1st Edition, Springer, Dordrecht, p.178

How to Describe a Molecule Mathematically? (IV)

The Wavefunction

- Consequently, a wavefunction can be associated to each quantum system (1st postulate of Quantum Mechanics)

$$\Psi(x, y, z, t) = \Psi(\mathbf{r}, t)$$

- For a free particle, the wavefunction is easy to determine

$$\Psi(\mathbf{r}, t) = A \exp\left[-\frac{i}{\hbar}\left(Et - \mathbf{pr}\right)\right]$$

- The value of $\left|\Psi(\mathbf{r}, t)\right|^2 dV$ is proportional to the probability of finding that particle in dV

How to Describe a Molecule Mathematically? (IV)

The Wavefunction

- $\Psi(\mathbf{r})$ can be a complex function, $\left|\Psi(\mathbf{r},t)\right|^2 = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)$
- Indeed, you can think of a wavefunction (wfn) in terms of a probability function.
  - The wfn of the electrons of a molecule integrate to the total number of electrons of that molecule $\int_V \Psi_e(\mathbf{r})^*\Psi_e(\mathbf{r})d\mathbf{r} = N$
  - The wfn of two non interacting, independent particles is the product of the wfn of each of the particles: $\Psi(\mathbf{r_1},\mathbf{r_2}) = \Psi(\mathbf{r_1}) \cdot \Psi(\mathbf{r_2})$
- Indeed, by knowing the wavefunction of a system, you can calculate ANY property of it

How to Describe a Molecule Mathematically? (V)

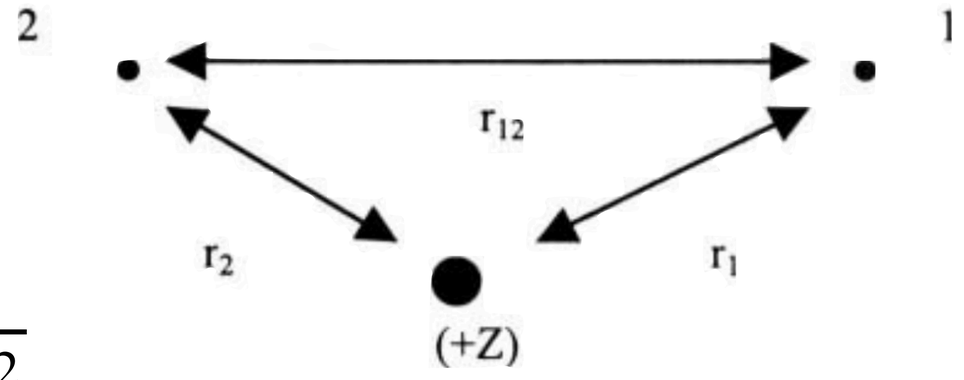
Operators

- For each magnitude which can be measured (observable) an operator (mathematical operation) can be built (second postulate of Quantum Mechanics)
- The wavefunction is an eigenvector to that operator, the eigenvalue being what would be obtained if the magnitude were actually measured in the lab:
  - For the momentum: $\frac{\partial}{\partial \mathbf{r}}$, $\int_V \Psi^*(\mathbf{r},t)\frac{\partial}{\partial \mathbf{r}}\Psi(\mathbf{r},t)d\mathbf{r} = \left\langle \Psi^*(\mathbf{r},t) \middle| \frac{\partial}{\partial \mathbf{r}} \middle| \Psi(\mathbf{r},t) \right\rangle = p\Psi(\mathbf{r},t)$
  - For dipole moment: $q\mathbf{r}$, $\int_V \Psi^*(\mathbf{r},t)\cdot q\mathbf{r}\cdot\Psi(\mathbf{r},t)d\mathbf{r} = \left\langle \Psi^*(\mathbf{r},t) \middle| q\mathbf{r} \middle| \Psi(\mathbf{r},t) \right\rangle = \mathbf{d}\Psi(\mathbf{r},t)$
  - For energy, Hamiltonian: $\hat{H}$, $\int_V \Psi^*(\mathbf{r},t)\hat{H}\Psi(\mathbf{r},t)d\mathbf{r} = \left\langle \Psi^*(\mathbf{r},t) \middle| \hat{H} \middle| \Psi(\mathbf{r},t) \right\rangle = E\Psi(\mathbf{r},t)$

How to Describe a Molecule Mathematically? (VI)

The Hamiltonian

- The Hamiltonian ($\hat{H}$) is the operator to calculate the total energy of a system
- Let's write $\hat{H}$ for a molecule
  - Kinetic energy operator:
    - $$\hat{T}_N = \frac{1}{2m_N}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = \sum_N \frac{\hbar}{2m_N}\frac{\partial^2}{\partial R^2}$$
    - $$\hat{T}_e = \sum_i \frac{\hbar}{2m_e}\frac{\partial^2}{\partial r^2}$$



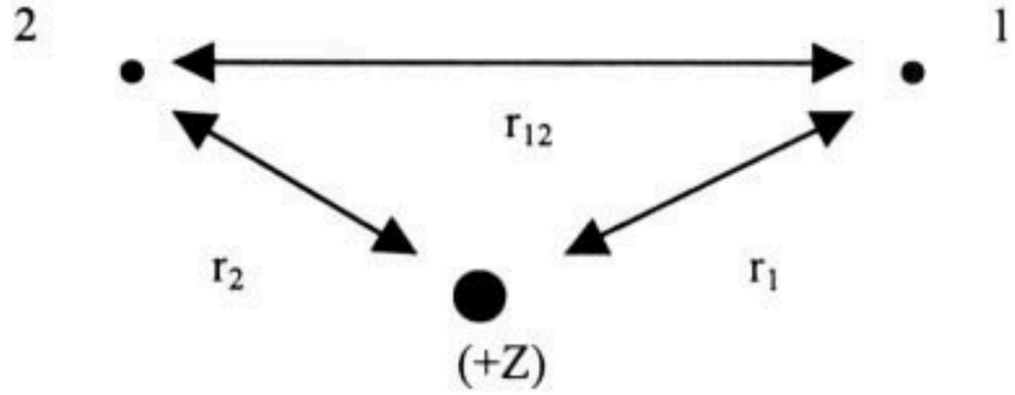
R: nuclear coordinates
N: index running on nuclei
m_M: mass of each nucleus
Z_N: atomic number of nucleus

r: electronic coordinates
i: index running on electrons
m_e: mass of the electron
e: charge of the electron

How to Describe a Molecule Mathematically? (VII)

The Hamiltonian

- Potential energy:
  - $V_{eN} = -\sum_N \sum_i \frac{q_N e}{r_i} = -\sum_N \sum_i \frac{Z_N e^2}{r_i}$
  - $V_{ee} = \sum_i \sum_{j>i} \frac{e^2}{r_j - r_i} = \sum_i \sum_{j>i} \frac{e^2}{r_{ij}}$



- Summing up together we have the final expression of the Hamiltonian:
  - $\hat{H} = \sum_N \frac{\hbar}{2m_N} \frac{\partial^2}{\partial R^2} + \sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} - \sum_i \sum_N \frac{Z_N e^2}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}}$

R: nuclear coordinates
N: index running on nuclei
m_M: mass of each nucleus
Z_N: atomic number of nucleus
r: electronic coordinates
i: index running on electrons
m_e: mass of the electron
e: charge of the electron

How to Describe a Molecule Mathematically? (VIII)

The Schrödinger Equation

- The Hamiltonian also allows us to calculate the wavefunction.
- The wavefunction must fulfil the **Time Dependent Schrödinger Equation (TDSE)**:

$$\hat{H}\Psi(\mathbf{r},\mathbf{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t)$$

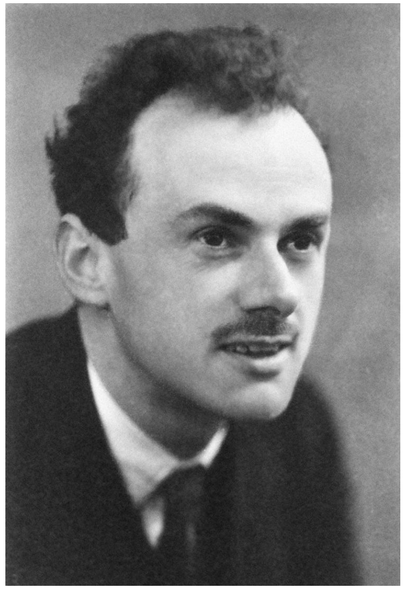
- Which for the previous molecular Hamiltonian turns into:

$$\left(\sum_N \frac{\hbar}{2m_N}\frac{\partial^2}{\partial R^2} + \sum_i \frac{\hbar}{2m_e}\frac{\partial^2}{\partial r^2} - \sum_i\sum_N \frac{Z_N e^2}{r} + \sum_i\sum_{j>i}\frac{e^2}{r_{ij}}\right)\Psi(\mathbf{r},\mathbf{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t)$$

From Theory to Reality

Let’s be practical

- The TDSE is a second order partial differential equation on different variables with crossed terms.
- “*The underlying physical laws necessary for the mathematical theory of […] the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble*”, Paul Dirac
- Firstly, let’s asume an ansatz for the function solution



A Practical Solution to the Schrödinger Equation

Solving the TD Schrödinger Equation (I)

Quantum Mechanics in a Nutshell

- **Born-Huang Ansatz**: Ψ is expressed in a basis of nuclear and electronic wavefunctions:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i \chi_i(\mathbf{R}, t)\Phi_i(\mathbf{r}; \mathbf{R})$$

- Nuclear and electronic coordinates are now separated in $\chi_i(\mathbf{R}, t)$ and $\Phi_i(\mathbf{r}; \mathbf{R})$

- $\chi_i(\mathbf{R}, t)$ and $\Phi_i(\mathbf{r}; \mathbf{R})$ constitute an orthonormal basis:

$$\left\langle \varphi_i \varphi_i \right\rangle = 1; \left\langle \varphi_i \varphi_j \right\rangle = 0;$$ TOP

Solving the TD Schrödinger Equation (II)

Quantum Mechanics in a Nutshell

- Now Now TDSE turns into:

$$\left(\hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}\right)\Psi(\mathbf{r},\mathbf{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t)$$

- Inserting the Born-Huang ansatz into the TDSE:

$$\left[\hat{T}_N(\mathbf{R}) + T_e(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right]\sum_i \chi_i(\mathbf{R},t)\Phi_i(\mathbf{r};\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\sum_i \chi_i(\mathbf{R},t)\Phi_i(\mathbf{r};\mathbf{R})$$

- And multiplying by $\left\langle \Phi_j(\mathbf{r},\mathbf{R}) \right|$

$$\left[\hat{T}_N + \mathrm{E}_j\right]\chi_j - \sum_i \Lambda_{ji}\chi_i = i\hbar\frac{\partial}{\partial t}\chi_j$$

Solving the TD Schrödinger Equation (IV)

Quantum Mechanics in a Nutshell

- Let's explain the last step: $\left[\hat{T}_N + \mathrm{E}_j\right]\chi_j - \sum_i \Lambda_{ji}\chi_i = i\hbar\frac{\partial}{\partial t}\chi_j$
- **Dirac brackets:** $\left\langle \Phi_j(\mathbf{r},\mathbf{R}) \right|$ is a hand short notation for $\int \Phi_j^*(\mathbf{r},\mathbf{R})dr$
- Right hand side of the equation:
  - As the Born-Huang ansatz leads to an orthonormal basis, only j term survives:

$$\int \Phi_j^*(\mathbf{r},\mathbf{R})\left(\frac{\partial}{\partial t}\sum_i \chi_i(\mathbf{R},t)\right)\Phi_i(\mathbf{r};\mathbf{R})dr = \left(\frac{\partial}{\partial t}\sum_i \chi_i(\mathbf{R},t)\right)\int \Phi_j^*(\mathbf{r},\mathbf{R})\Phi_i(\mathbf{r};\mathbf{R})dr = \chi_i(\mathbf{R},t)$$

Solving the TD Schrödinger Equation (V)

Quantum Mechanics in a Nutshell

- Left hand side: $\left[\hat{T}_N + \mathrm{E}_j\right]\chi_j - \sum_i \Lambda_{ji}\chi_i$
  - Kinetic energy of nucleus N: $\hat{T}_N$
  - Energy of electron j: $\mathrm{E}_j = \left\langle \Phi_j \middle| \hat{T}_e \middle| \Phi_i \right\rangle + \left\langle \Phi_j \middle| \hat{V}_{eN} \middle| \Phi_i \right\rangle \left\langle \Phi_j \middle| \hat{V}_{ee} \middle| \Phi_i \right\rangle$
  - Coupling of nuclear and electronic degrees of freedom:
    $\Lambda_{ji} = \frac{\hbar}{2m_N e^2}\left[\left\langle \Phi_j \middle| \nabla_R \Phi_i \right\rangle \nabla_R + \left\langle \Phi_j \middle| \nabla_R^2 \Phi_i \right\rangle\right]$

Born-Oppenheimer Approximation (I)

Using Physics to Simplify

- So far, no approximation has been made.
- Let's introduce the first one: **Born-Oppenheimer Approximation:**
  - The electronic Φ_i varies little with nuclear coordinates, $\nabla_R \Phi_i(\mathbf{r};\mathbf{R}) \approx 0$, as $m_e << m_N$
- That produces a <u>decoupling of the TDSE into one equation depending only on nuclear coordinates and another equation depending of electronic coordinates</u>:

$$\text{Electronic Schrödinger Equation: } \bar{H}_e \Phi_j(t,\mathbf{r};\mathbf{R}) = i\hbar \frac{\partial}{\partial t} \Phi_j(t,\mathbf{r};\mathbf{R})$$

$$\text{Nuclear Schrödinger Equation: } \left[\hat{T}_N(\mathbf{R}) + E_j(\mathbf{R})\right] \chi_j(\mathbf{R},t) = i\hbar \frac{\partial}{\partial t} \chi_j(\mathbf{R},t)$$

Born-Oppenheimer Approximation (II)

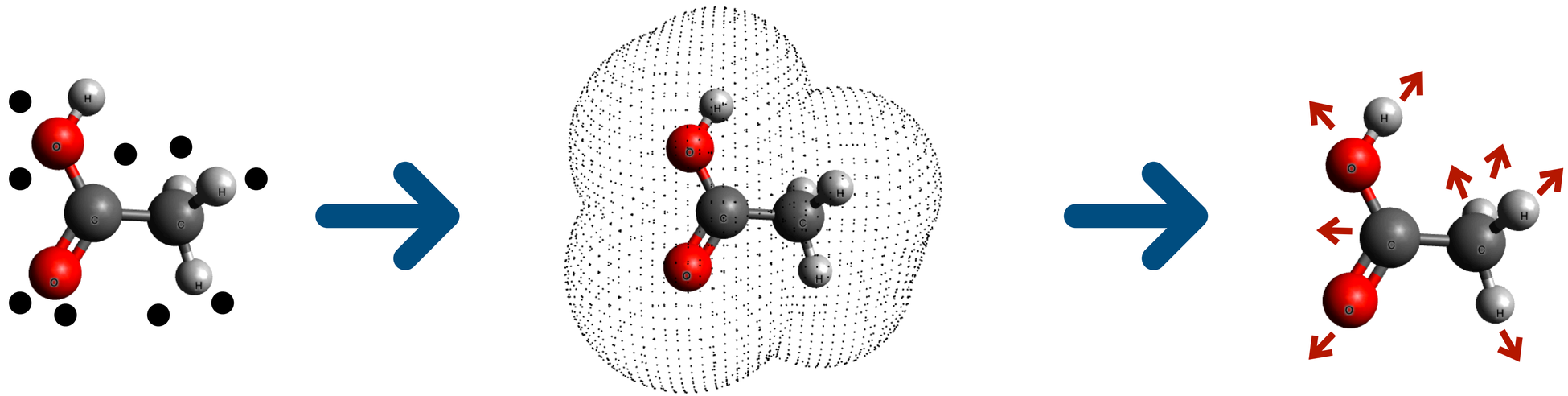
Using Physics to Simplify

- The Born-Oppenheimer Approximation simplifies the solution of the TDSE
- Instead of crossed terms, now there are equations, depending on a set of coordinates each
- Physical Meaning: Electronic cloud adjust instantaneously to changes in the nuclear configuration. **Electrons behaves as potential for nuclei**.
- The small derivative coupling $\nabla_R \Phi_i(\mathbf{r};\mathbf{R})$ is essential for the validity of the BO approximation

Born-Oppenheimer Approximation (III)

Using Physics to Simplify

- With the Born-Oppenheimer Approximation we don't treat the electrons as isolated particles but rather as a potential in which the nuclei move



From particles, e^-

To Potential, $V(\mathbf{r})$

& nuclear forces, $F(\mathbf{r}) = \nabla V(\mathbf{r})$

The Stationary State (I)

Simplifying Even More

- In a majority of cases, in chemistry we are only interested in stable molecules, i. e. molecules in which the nuclei don't move, stay still with time
- Forget about the nuclear SE! $\left[\hat{T}_N(\mathbf{R}) + E_j(\mathbf{R})\right]\chi_j(\mathbf{R}) = i\hbar\frac{\partial}{\partial t}\chi_j(\mathbf{R}, t)$
- The electronic part becomes simpler: $\hat{H}_e\Phi_j(t, \mathbf{r}; \mathbf{R}) = i\hbar\frac{\partial}{\partial t}\Phi_j(t, \mathbf{r}; \mathbf{R})$
  - As the nuclei are fixed on time, the hamiltonian is constant in time $\hat{H}(\mathbf{r}; \mathbf{R})$
  - We can then assume that $\Phi_j(t, \mathbf{r}; \mathbf{R}) = \Phi_j(t) \cdot \phi_j(\mathbf{r}; \mathbf{R})$

The Stationary State (II)

Simplifying Even More

- If we devide both sides of the equation by $\Phi_j(t)\phi_j(\mathbf{r};\mathbf{R})$

$$i\hbar\frac{\frac{\partial\phi(t)}{\partial t}}{\phi_j(t)} = \frac{\hat{H}\Phi(\mathbf{r})}{\Phi(\mathbf{r})}$$

- What results in:

$$i\hbar\frac{\partial\phi(t)}{\partial t} = const\cdot\phi_j(t)$$

$$\hat{H}\Phi_j(\mathbf{r};\mathbf{R}) = const\cdot\Phi_j(\mathbf{r};\mathbf{R})$$

- The latter is an equation for the eigenfunctions of the operator $\hat{H}$, so the constant is the electronic energy E_j

The Stationary State (II)

Simplifying Even More

- What can be plugged into the time equation

$$i\hbar\frac{\partial\phi(t)}{\partial t} = E_j\phi_j(t)$$

- Integration leads that the time part is of an exponential form: $\Phi_j(t) = A_j e^{-i\frac{E_j}{\hbar}t}$
- This phase term is usually dropped, as is doesn't depend on $\mathbf{r}$
- What leads to the Time Independent Electronic Schrödinger Equation:

$$\left(\sum_i \frac{\hbar}{2m_e}\frac{\partial^2}{\partial r^2} + \sum_i\sum_N \frac{q_N e}{r} + \sum_i\sum_{j>i}\frac{e^2}{r_{ij}}\right)\Phi_j(\mathbf{r};\mathbf{R}) = E\Phi_j(\mathbf{r};\mathbf{R})$$

Recapping

- With two assumptions, we went from

$$\left(\sum_N \frac{\hbar}{2m_N} \frac{\partial^2}{\partial R^2} + \sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} + \sum_i \sum_N \frac{q_N e}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \right) \Psi(\mathbf{r}, \mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t)$$

$$\left(\sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} + \sum_i \sum_N \frac{q_N e}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \right) \Phi_j(\mathbf{r}; \mathbf{R}) = E \Phi_j(\mathbf{r}; \mathbf{R})$$

- We removed 2 variables, $\mathbf{R}$ and t, the latter depending only on $\mathbf{r}$
- And that's enough because <u>chemistry is only about the behaviour of electrons</u>

Getting Inspired by Atoms

$$\left(\sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} + \sum_i \sum_N \frac{q_N e}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \right) \Phi_j(\mathbf{r};\mathbf{R}) = E\Phi_j(\mathbf{r};\mathbf{R})$$

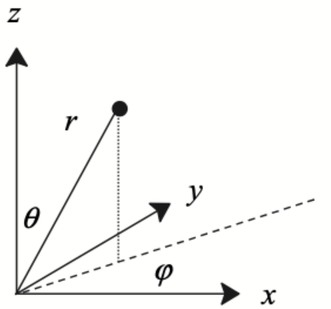
- This equation still does't have an analytic solution due to the term $\sum_i \sum_{j>i} \frac{e^2}{r_{ij}}$
- For atoms with 1 electron, like Hydrogen atom, this term disappears and there is an analytic solution.

Getting Inspired by Atoms (I)

How to Represent an Electronic Wavefunction in a Practical Way

- Atoms are convenient, because in there the Hamiltonian is that of a central symmetric field.
  - It's central because all forces point a single point
  - It's symmetric because there's angular symmetry
- Under a central symmetric field is more convenient to represent the atomic wave function in polar coordinates $\Phi_i(\mathbf{r}) = R_i(r)Y_i(\theta,\phi)$

$$\left(-\frac{\hbar}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2m_e}\frac{\nabla^2_{\theta,\phi}}{r^2} + \frac{q_N e}{r}\right) R_i(r)Y_i(\theta,\phi) = E_i R_i(r)Y_i(\theta,\phi)$$



$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$

Getting Inspired by Atoms (II)

How to Represent an Electronic Wavefunction in a Practical Way

$$\left(-\frac{\hbar}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{\hbar^2}{2m_e}\frac{\Delta_{\theta,\phi}}{r^2}+\frac{q_N e}{r}\right)R_i(r)Y_i(\theta,\phi)=E_i R_i(r)Y_i(\theta,\phi)$$

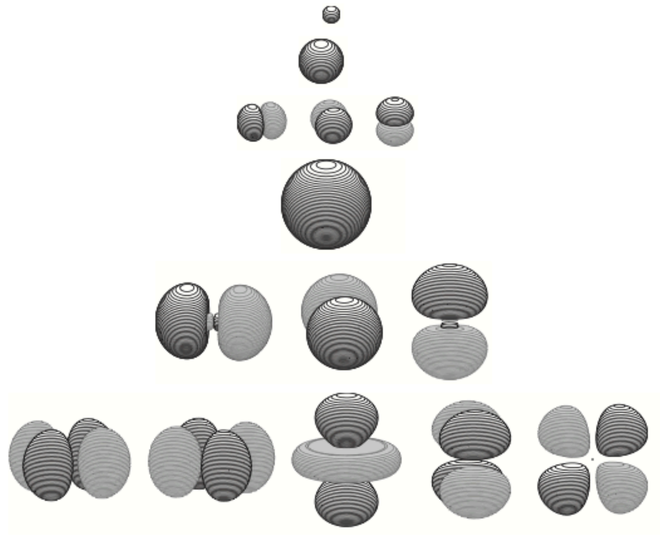
- The solution of this is:
  - For the radial part, the Leguerre polynomials: $R(r)=L_n(r)=e^r\frac{d^n}{dr^n}\left(r^n e^{-r}\right)$
  - For the angular part, the Legendre polynomials (*spherical harmonics*):
    $Y(\theta,\phi)=Y_{lm}(\theta,\phi)\frac{1}{\sqrt{2\pi}}A_l^{|m|}P_l^{|m|}(cos\theta)e^{im\phi}$

Getting Inspired by Atoms (II)

How to Represent an Electronic Wavefunction in a Practical Way

- The wave function of an electron is called **orbital**; depends only on the coordinates of 1 electron.

Hydrogenic orbitals obtained from solving the Schrödinger equation

n	l	m	$\Psi_{n,l,m}(r,\theta,\varphi)$	Shape and size
1	0	0	$Y_{0,0}(\theta,\varphi)e^{-Zr}$	
2	0	0	$Y_{0,0}(\theta,\varphi)(2-Zr)e^{-Zr/2}$	
	1	$\pm1, 0$	$Y_{1,m}(\theta,\varphi)Zre^{-Zr/2}$	
3	0	0	$Y_{0,0}(\theta,\varphi)(27-18Zr+2Z^2r^2)e^{-Zr/3}$	
	1	$\pm1, 0$	$Y_{1,m}(\theta,\varphi)Zr(6-Zr)e^{-Zr/3}$	
	2	$\pm2, \pm1, 0$	$Y_{2,m}(\theta,\varphi)Z^2r^2e^{-Zr/3}$	

F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed.

Getting Inspired by Atoms (III)

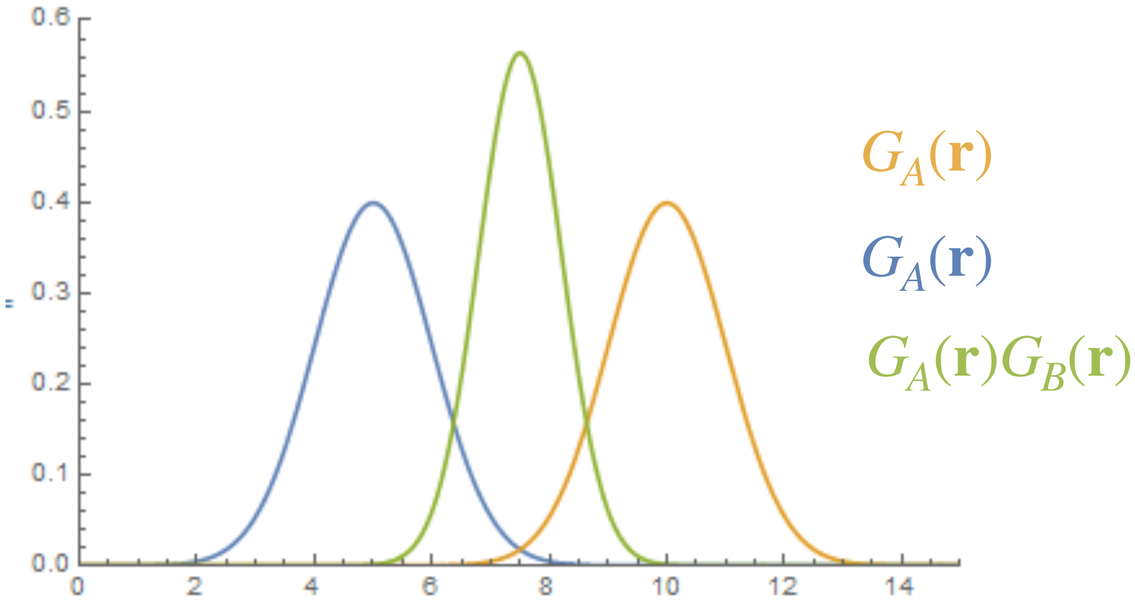
How to Represent an Electronic Wavefunction in a Practical Way

- The radial part is always of the form $R_1(r) = ke^{-\frac{Zr}{n}}$, Z being the atomic number
- However, in quantum mechanics quite often this integral is solved, $\left\langle R \middle| R \right\rangle = \int R(r)^* R(r) dr$, difficult to solved with $R(r) = k_1 e^{-k_2 r}$
- Gaussian functions offer a nice alternative to it:
  - The product of two Gaussian functions is another Gaussian function
  - If $R(r) = Ae^{br^2}$, then $\left\langle R \middle| R \right\rangle = \int Ae^{br^2}$, which is still easy to integrate

Getting Inspired by Atoms (IV)

Product of Gaussian Functions

- $G_A(\mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha\left(\mathbf{r}+\mathbf{R}_A\right)^2}$, and
- $G_B(\mathbf{r}) = \left(\frac{2\beta}{\pi}\right)^{\frac{3}{4}} e^{-\beta\left(\mathbf{r}+\mathbf{R}_B\right)^2}$
- $G_A(\mathbf{r})G_B(\mathbf{r})$ is another gaussian function
- $G_A(\mathbf{r})G_B(\mathbf{r}) = Ke^{-\gamma\left(\mathbf{r}+\mathbf{R}_C\right)^2}$;
- $\gamma = \alpha+\beta;\ \mathbf{R}_c = \frac{\alpha\mathbf{R}_A\beta\mathbf{R}_B}{\alpha+\beta};\ K = \left(\frac{2}{\pi}\right)^2 (\alpha\beta)^{\frac{3}{4}} e^{-\frac{\alpha\beta}{\alpha+\beta}\left(\mathbf{R}_A-\mathbf{R}_B\right)^2}$



Getting Inspired by Atoms (V)

How to Represent an Electronic Wavefunction in a Practical Way

- It is therefore most common to represent the radial part as an expansion of Gaussian functions to fit the e^{-ar} exponential:

$$R(r) = \sum_i a_i e^{-b_i r^2}$$

- The coefficients a_i and b_i are optimised for each atom to reproduce their properties

- The set of Gaussians is call **basis set**, as form a basis on which $R(r)$ is spanned

Getting Inspired by Atoms (VI)

How to Represent an Electronic Wavefunction in a Practical Way

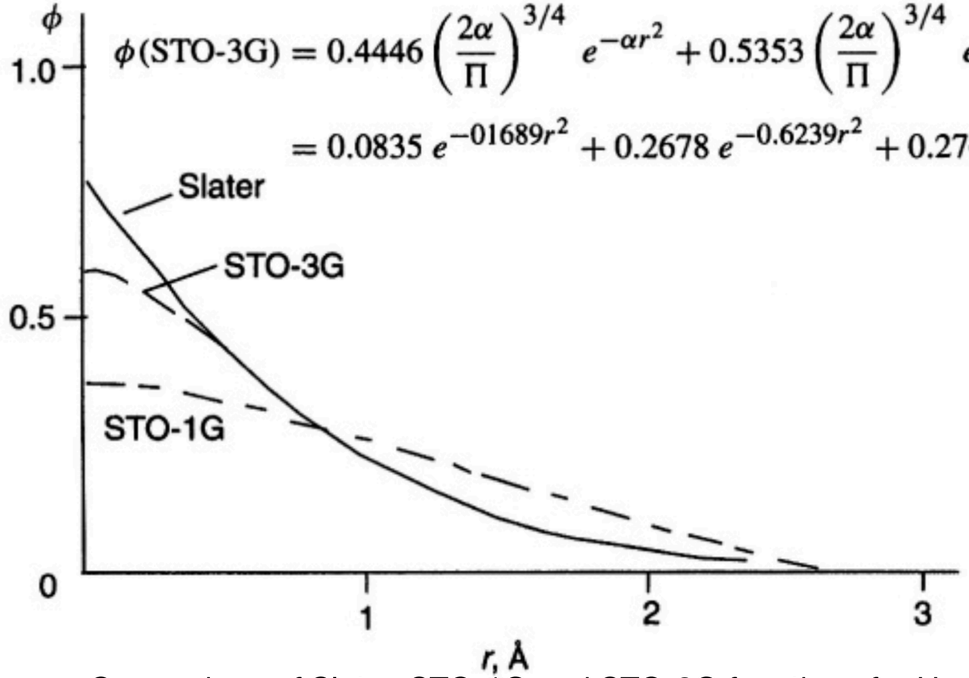
- The more number of basis functions, the more accurate
- The more number of basis functions, the more $\left\langle G_A \middle| G_B \right\rangle$ integrals to solve
- Experience show that 6 Gaussians are accurate enough

$$\phi(\text{Slater}) = \left(\frac{\zeta^3}{\Pi}\right)^{1/2} e^{-\zeta r} = 0.7790\, e^{-1.24r}$$

$$\phi(\text{STO-1G}) = \left(\frac{2\alpha}{\Pi}\right)^{3/4} e^{-\alpha r^2} = 0.3696\, e^{-0.4166 r^2}$$

$$\phi(\text{STO-3G}) = 0.4446\left(\frac{2\alpha}{\Pi}\right)^{3/4} e^{-\alpha r^2} + 0.5353\left(\frac{2\alpha}{\Pi}\right)^{3/4} e^{-\alpha r^2} + 0.1543\left(\frac{2\alpha}{\Pi}\right)^{3/4} e^{-\alpha r^2}$$

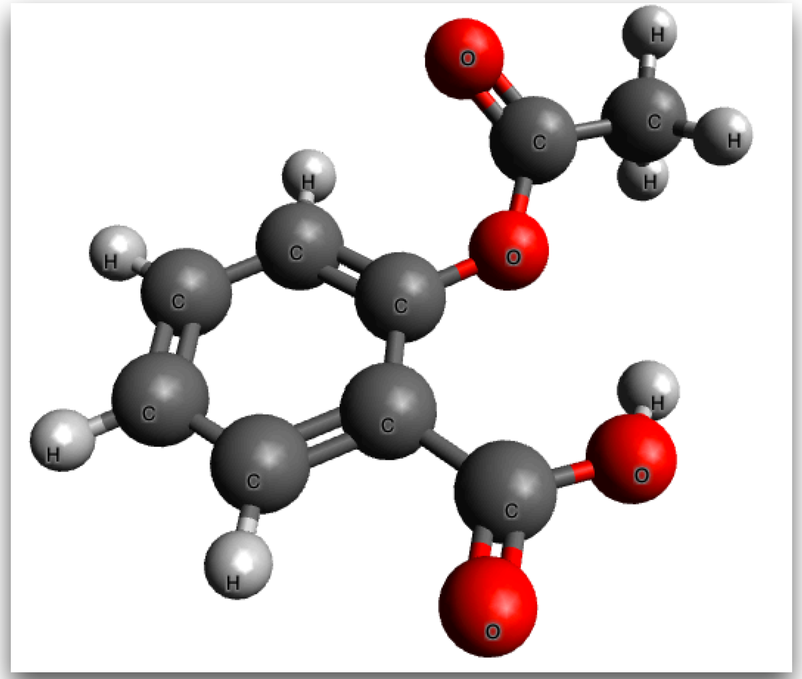
$$= 0.0835\, e^{-01689 r^2} + 0.2678\, e^{-0.6239 r^2} + 0.2769\, e^{-3.4253 r^2}$$



Comparison of Slater, STO-1G and STO-3G functions for Hydrogen, taken from E. Lewars, *Computational Chemistry,* 1st Ed., Kuwler, New York, p. 213

From Atoms to Molecules (I)

- In the same way that molecules are made by atoms, we can build a molecular wave function from atomic orbitals:
  - Wave function, 3N-dimensional function, N being the number of atoms
  - Orbital, 3-dimensional function
- The orbital ansatz reduces the dimensionality of the equations to solve



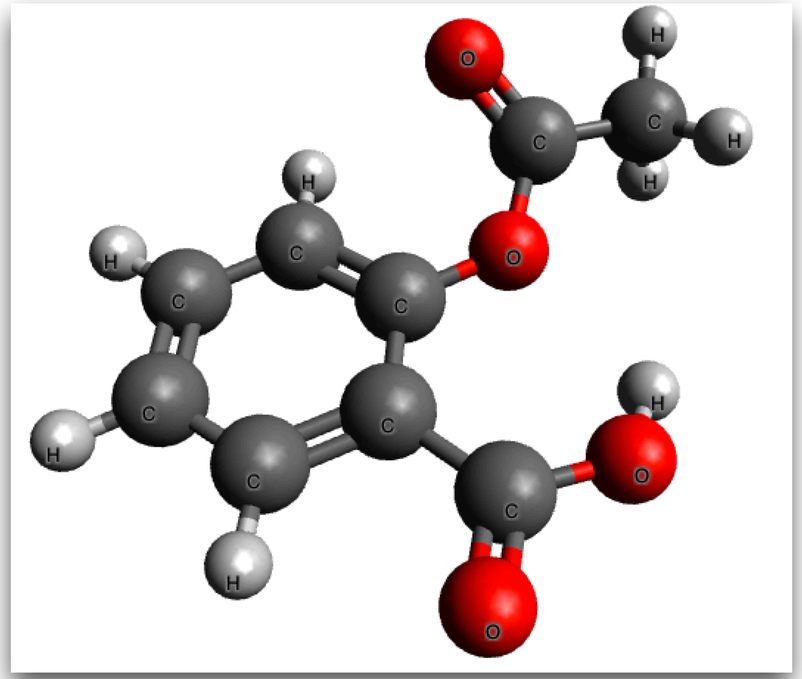
From Atoms to Molecules (II)

- We first define a molecular orbital φ_i, a function describing an electron in a molecule
- As molecules are made by atoms, a molecular orbital can be expressed as linear combination of atomic orbitals:

$$\varphi_i = \sum_{\alpha} c_{\alpha,i}\chi_{\alpha}$$

- Considering the electrons as non interacting, a molecular wave function can be express as product of molecular orbitals:

$$\Phi(\mathbf{r}) = \Pi\varphi_i(r_i)$$



From Atoms to Molecules (III)

- And we plug this molecular wave function into the Schrödinger equation

$$\left(\sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} + \sum_i \sum_N \frac{q_N e}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \right) \Phi(\mathbf{r}; \mathbf{R}) = E\Phi(\mathbf{r}; \mathbf{R})$$

- Remember that we said “assuming non-interacting electrons”?
- This is contradictory as the term $\frac{e^2}{r_{ij}}$ measures the interaction of electron i with electron j.
- We had said that this term makes the equation impossible to solve.

From Atoms to Molecules (IV)

- Indeed, the $\frac{e^2}{r_{ij}}$ is approximated so that, within the framework of non interacting particles, the interaction between them can still be described as precise as possible

- The two main approximations with this ansatz are

  Hartree-Fock Density Functional Theory

- These two are different ways of describing the electronic repulsion within the framework of non-interacting electrons

Recapping

Practical Guide for Computing Wavefunctions of Electrons

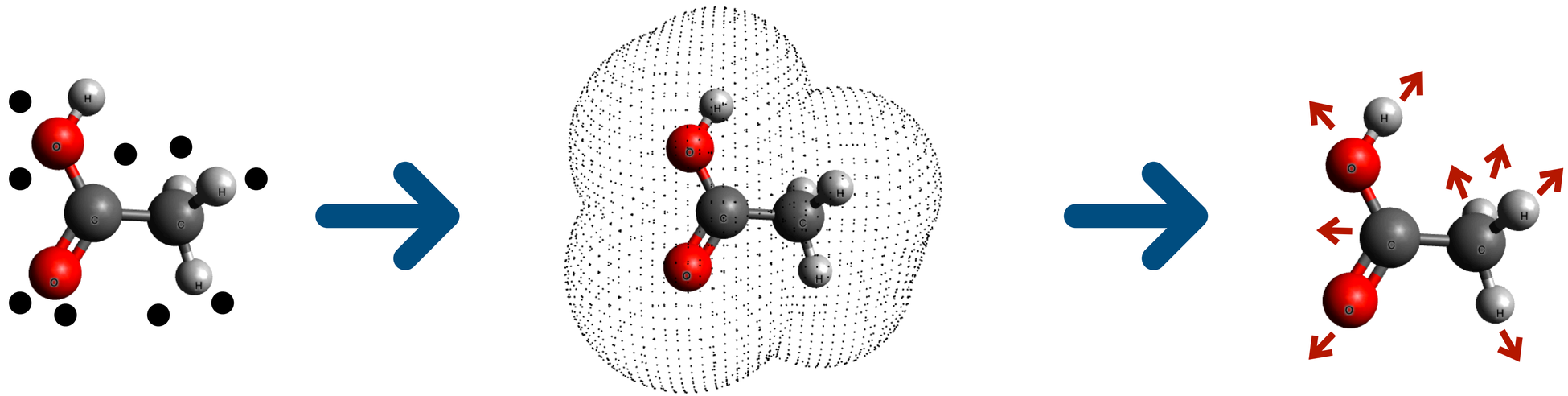
1. We start with the electronic Schrödinger equation:
$$\left(\sum_i \frac{\hbar}{2m_e} \frac{\partial^2}{\partial r^2} + \sum_i \sum_N \frac{q_N e}{r} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} \right) \Phi_e(\mathbf{r};\mathbf{R}) = E_e \Phi_e(\mathbf{r};\mathbf{R})$$
2. We use a set of Gaussian functions to represent atomic orbitals, namely basis set: $\phi_k(r) = \sum_n a_i e^{-b_n r^2}$
3. We linearly combine these atomic orbitals to make the molecular orbitals $\varphi_l(r) = \sum_k \phi_k(r)$
4. We make an assumption to describe the electronic repulsion term $\sum_i \sum_{j>i} \frac{e^2}{r_i j}$
5. We solve the resulting equation and obtain the molecular wavefunction, $\Phi_e(\mathbf{r})$, and its energy, E_e

The Potential Energy Surface

Born-Oppenheimer Approximation

Using Physics to Simplify

- With the Born-Oppenheimer Approximation we don't treat the electrons as isolated particles but rather as a potential in which the nuclei move



From particles, e^-

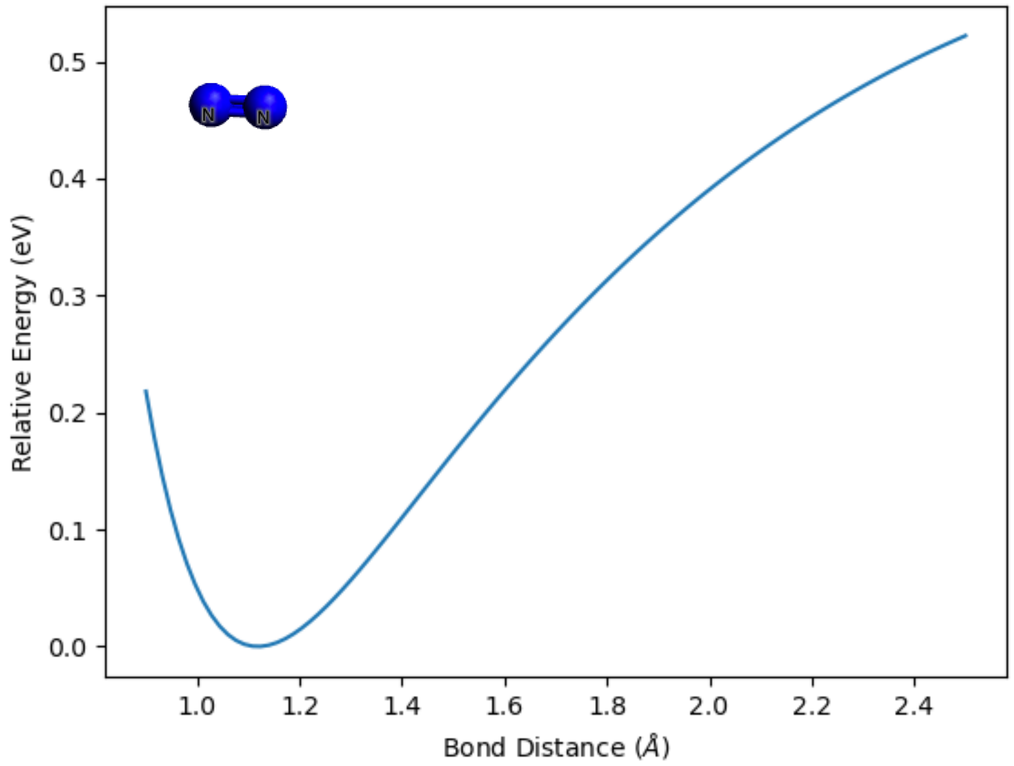
To Potential, $V(\mathbf{r})$

& nuclear forces, $F(\mathbf{r}) = \nabla V(\mathbf{r})$

The Potential Energy Surface

- Remember!, the outcome of the electronic Schrödinger Equation is the potential in which the nuclei are embedded (Born-Oppenheimer Approximation)
- The solution is also called Potential Energy (Hyper)Surface (PES)
- For a diatomic molecule, it depends only on 1 coordinate: the bond distance between the nuclei
- It follows the form of a Morse potential:

$$V(r) = D_e \left(1 - e^{-\alpha(r - r_{eq})}\right)^2$$



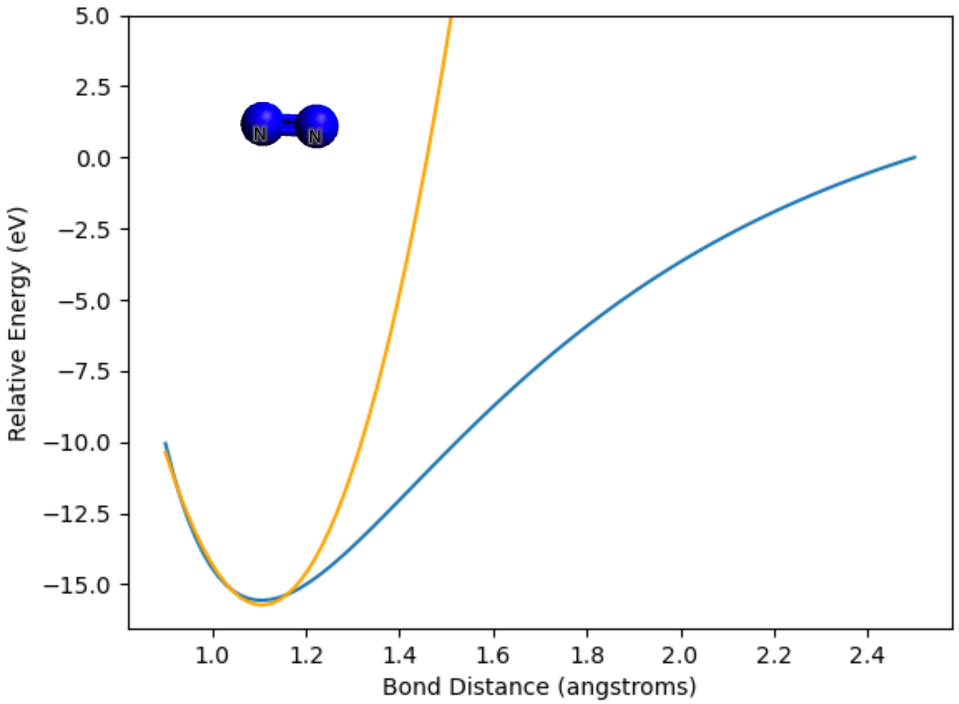
The Harmonic Approach (I)

Getting Molecular Frequencies

- Around the minimum, the potential can be approximated to a parabola
- It's equivalent to making a second order Taylor expansion around the minimum
- There's another system in physics with a quadratic potential: the Harmonic Oscillator

$$V(x) = k\left(x - x_o\right)^2; k = \frac{(2\pi\nu)^2}{\mu}; \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- k is the oscillator strength, ν is the frequency, μ is the reduced mass and m_1 and m_2 atomic masses.



The Harmonic Approach (II)

Getting Molecular Frequencies

- Therefore, around the minimum, a molecule can be approximated as a collection of harmonic oscillators of k_i
- k_i, the force constant, measures the stiffness of the molecule towards that vibration.
- k is obtained by the second derivative of the second derivative of the energy
- Indeed, diagonialisation of the Hessian renders the force constants of all the vibration modes

$$\mathbf{H} = \begin{bmatrix} \partial^2 E/\partial q_1 q_1 & \partial^2 E/\partial q_1 q_2 & \dots & \partial^2 E/\partial q_1 q_9 \\ \partial^2 E/\partial q_2 q_1 & \partial^2 E/\partial q_2 q_2 & \dots & \partial^2 E/\partial q_2 q_9 \\ \vdots & \vdots & \dots & \vdots \\ \partial^2 E/\partial q_9 q_1 & \partial^2 E/\partial q_9 q_2 & \dots & \partial^2 E/\partial q_9 q_9 \end{bmatrix}$$

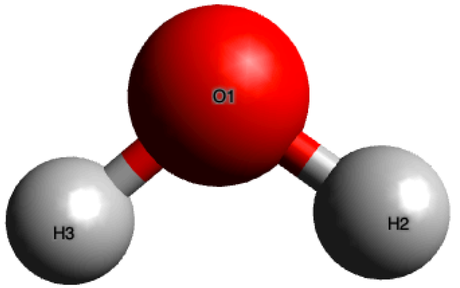
$$= \underbrace{\begin{bmatrix} q_{11} & q_{12} & \cdots & q_{19} \\ q_{21} & q_{22} & \cdots & q_{29} \\ \vdots & & & \\ q_{91} & q_{92} & \cdots & q_{99} \end{bmatrix}}_{\mathbf{P}} \underbrace{\begin{bmatrix} k_1 & 0 & \cdots & 0 \\ 0 & k_2 & \cdots & 0 \\ \vdots & & & \\ 0 & 0 & \cdots & k_9 \end{bmatrix}}_{\mathbf{k}} \mathbf{P}^{-1}$$

Diagonalisation of the Hessian matrix of a triatomic molecule, $\mathbf{H} = \mathbf{PkP}^{-1}$. Each atom is described by 3 Cartesian coordinates, hence the Hessian depends on 9 coordinates, $q_{1\text{-}9}$. Taken from E. Lewars, *Computational Chemistry,* 1st Ed., Kuwler, New York, p. 31.

The Harmonic Approach (III)

Internal Coordinates

- In the the Jupyter Notebook we've seen that:
  - 6 (or 5) eigenvalues of the Hessian matrix are 0, corresponding to rotation and translation
  - Only molecular vibrations change $V(r)$
  - As eigenvectors are orthogonal, vibrations constitute a new basis set to represent a molecule
- Vibrations as coordinates are powerful: define the direction where $V(\mathbf{r})$ really changes
- We did that unconsciously when representing N_2 just with the bond distance
- These are also known as **internal coordinates** or **Z-matrix**

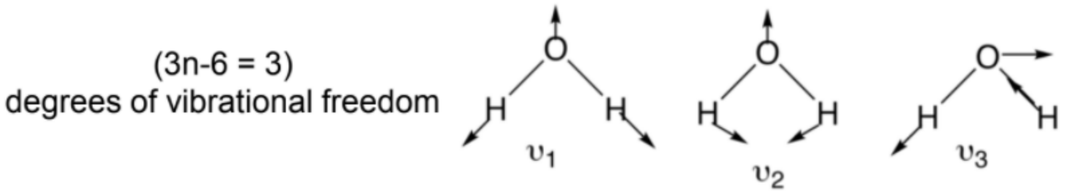


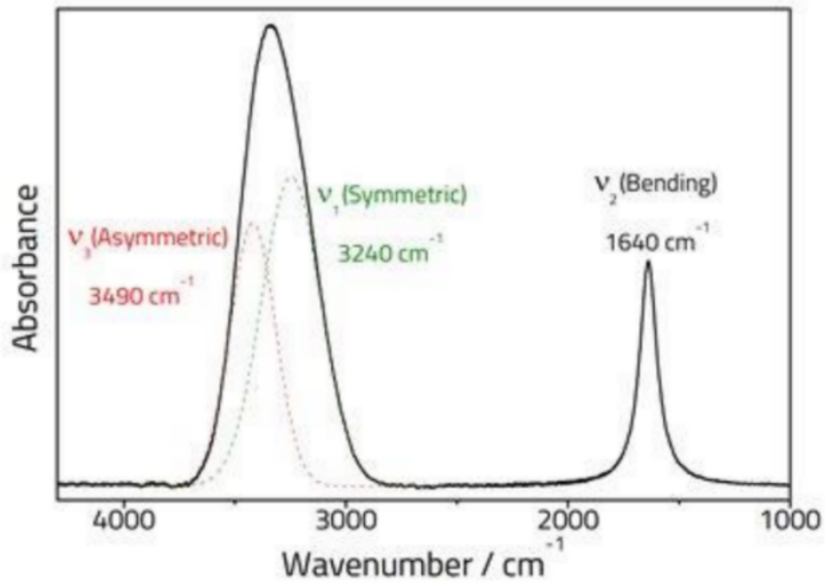
O
H 1 r
H 1 r 2 a
r = 0.975 Å
a = 105°

The Harmonic Approach (IV)

Infrared Spectra

- Molecular Vibrations constitute the Infrared (IR) spectrum of the molecule
- Position of the band: ν_i
- Intensity of the band: $I_i = \frac{\partial \mu}{\partial \nu_i}$, μ is the molecular dipole moment



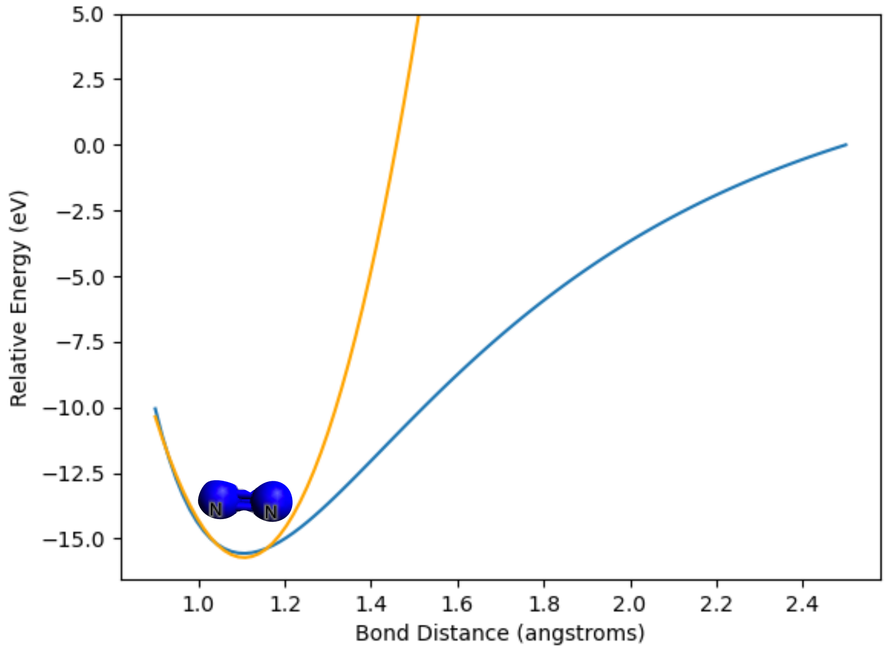


Taken from https://chemistry.stackexchange.com/questions/162316/why-is-this-graph-of-vibration-spectroscopy-like-this

The Harmonic Approach (V)

Zero Point Energy

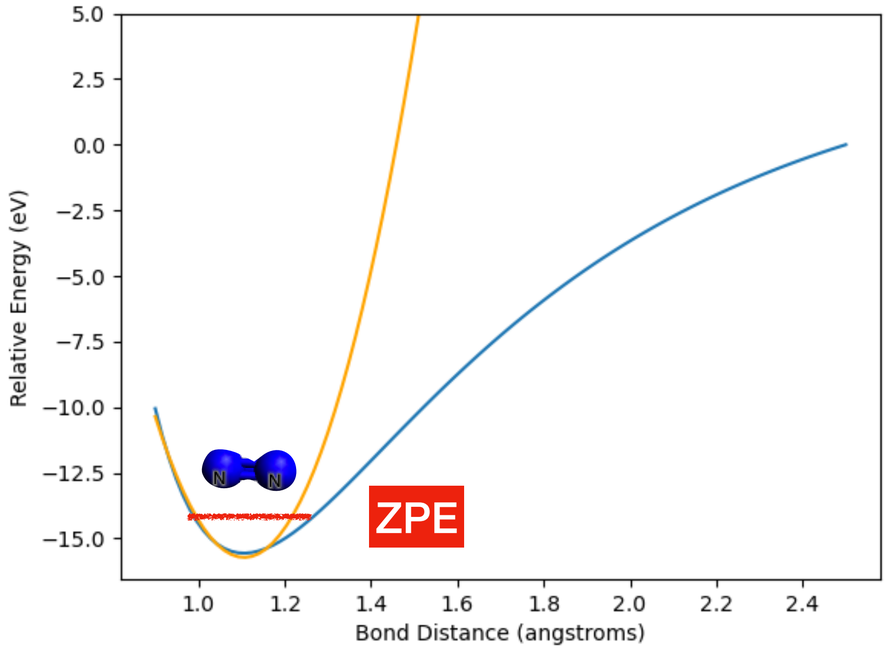
- Heisenberg's Uncertainty Principle: "*there is inherent uncertainty in the act of measuring a position and velocity simultaneously*": $\Delta x \Delta p \geq \frac{\hbar}{2}$
- Temperature is the measure of the movement of the atoms.
- If in 0K the molelcule would reach the bottom of the well, $x = 0$ and $p = 0$, what's not allowed
- Molecules never reach the bottom of the potential $\Rightarrow$ they're always moving



The Harmonic Approach (VI)

Zero Point Energy

- Through the partition function, each vibrational mode contributes to the internal energy of the molecule:
- $$E_{vib} = \sum_{i=1}^{3N-6(5)} \left(n_i + \frac{1}{2} \right) h\nu_i$$
- n_i is the vibrational quantum number, the vibrational state of the molecule.
- At $T = 0K$, $n_i = 0$ and $E_{vib}(T = 0) = \frac{1}{2} \sum_{i=1}^{3N-6(5)} h\nu_i$
- $E_{vib}(T = 0)$ is known as the Zero Point Energy (ZPE), an energy the molecule ALWAYS has, even at 0K.



From Vibrations to Thermodynamics (I)

Calculation of Real Chemistry

- The partition function makes the link between properties of a molecule and properties of a macromolecular system.
- It therefore establish a relation to calculate the enthalpy of a system:
- $H_{trans} = \frac{5}{2}RT$
- $H_{rot} = \frac{3}{2}RT$
- $H_{vib} = R \sum_{i}^{3N-6(5)} \left(\frac{h\nu_i}{2k} + \frac{h\nu_i}{k} \frac{1}{e^{h\nu_i/kT} - 1} \right)$
- $H = H_{trans} + H_{rot} + H_{vib}$

From Vibrations to Thermodynamics (II)

Calculation of Real Chemistry

- Entropy can be calculated in an analogous way:
- $$S_{trans} = \frac{5}{2}R + R\ln\left(\frac{V}{N_A}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}\right)$$
- $$S_{rot} = R\left(\frac{3}{2} + \ln\left(\frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{\frac{3}{2}}\sqrt{I_1 I_2 I_3}\right)\right)$$
- $$S_{vib} = R\sum_{i}^{3N-6(5)}\left(\frac{h\nu_i}{kT}\frac{1}{e^{h\nu_i/kT}-1} - \ln\left(1-e^{-\frac{h\nu_i}{kT}}\right)\right)$$

- $S_{elec} = R\ln g_o$
- And the total entropy is built:
- $S = S_{trans} + S_{rot} + S_{vib} + S_{elec}$
- This is already programmed

```
# Electronic part
results['S_elec' ] = (R_Eh * numpy.log(mol.multiplicity), 'Eh/K')
results['Cv_elec'] = results['Cp_elec'] = (0, 'Eh/K')
results['E_elec' ] = results['H_elec' ] = (E0, 'Eh')

# Translational part. See also https://cccbdb.nist.gov/thermo.asp for the
# partition function q_trans
mass_tot = mass.sum() * nist.ATOMIC_MASS
q_trans = ((2.0 * numpy.pi * mass_tot * kB * temperature / h**2)**1.5
           * kB * temperature / pressure)
results['S_trans' ] = (R_Eh * (2.5 + numpy.log(q_trans)), 'Eh/K')
results['Cv_trans'] = (1.5 * R_Eh, 'Eh/K')
results['Cp_trans'] = (2.5 * R_Eh, 'Eh/K')
results['E_trans' ] = (1.5 * R_Eh * temperature, 'Eh')
results['H_trans' ] = (2.5 * R_Eh * temperature, 'Eh')

# Rotational part
rot_const = rotation_const(mass, atom_coords, 'GHz')
results['rot_const'] = (rot_const, 'GHz')
rotor_type = _get_rotor_type(rot_const)

sym_number = rotational_symmetry_number(mol)
results['sym_number'] = (sym_number, '')

# partition function q_rot (https://cccbdb.nist.gov/thermo.asp)
if rotor_type == 'ATOM':
    results['S_rot' ] = (0, 'Eh/K')
    results['Cv_rot'] = results['Cp_rot'] = (0, 'Eh/K')
    results['E_rot' ] = results['H_rot' ] = (0, 'Eh')
```

From Vibrations to Thermodynamics (III)

Calculation of Real Chemistry

- And with H and S, calculation of Gibb's free energy is possible:
- $G = H - TS$
- And with that, you can calculate the ΔG of a reaction:
- $\Delta G_{\text{reaction}} = G_{\text{product}} - G_{\text{reactant}}$

Recapping

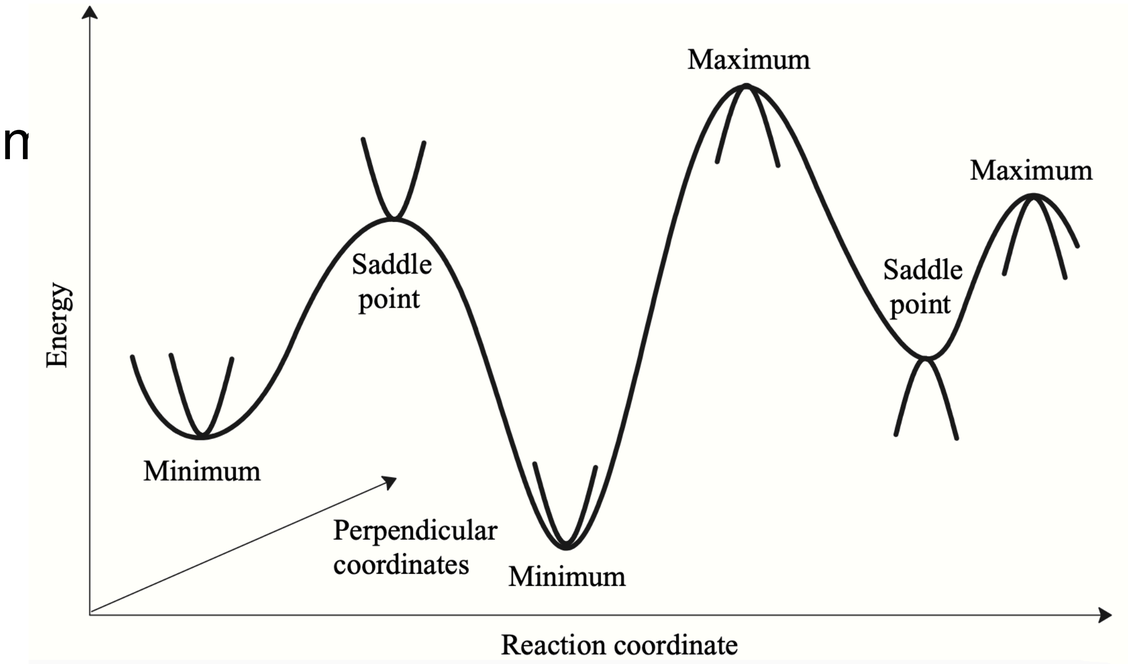
Calculating Thermodynamics of Molecules and Reactions

- Around the minimum, the Potential Energy Surface can be approximated by a harmonic (quadratic) potential
- Under this harmonic approximation, the molecular degrees of freedom can be represented as a collection of harmonic oscillators
- The diagonalisation of the Hessian of the potential renders the molecular vibrations
- The vibrations constitute a new set of coordinates, the internal coordinates, more convenient to represent the molecule
- With the vibrations, the partition function is built and, hence, the thermodynamics of the molecule, and its reactions, can be calculated.

Optimising the Molecular Geometry (I)

Complexity of Potential Energy Surface

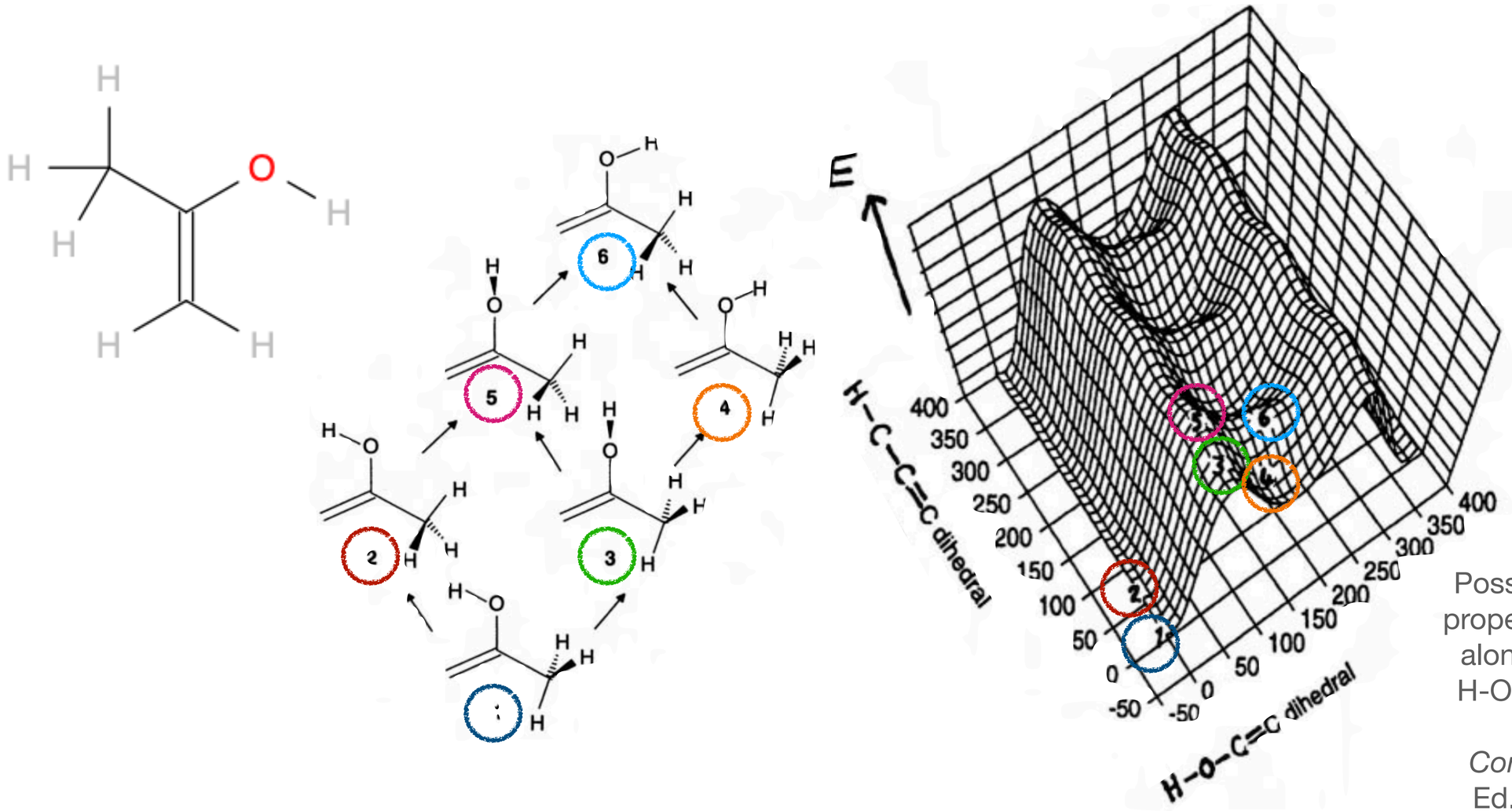
- So far, only molecules at the minimum of the PES considered
- How be sure that the molecule is at the minimun
- PES are indeed very complex
  - Minima
  - Saddle points
  - Maxima
- We need to make sure where the molecule as: OPTIMISE



Different Stationary Points in a multidimensional energy surface. Taken form F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed., p 380

Optimising the Molecular Geometry (II)

Complexity of Potential Energy Surface

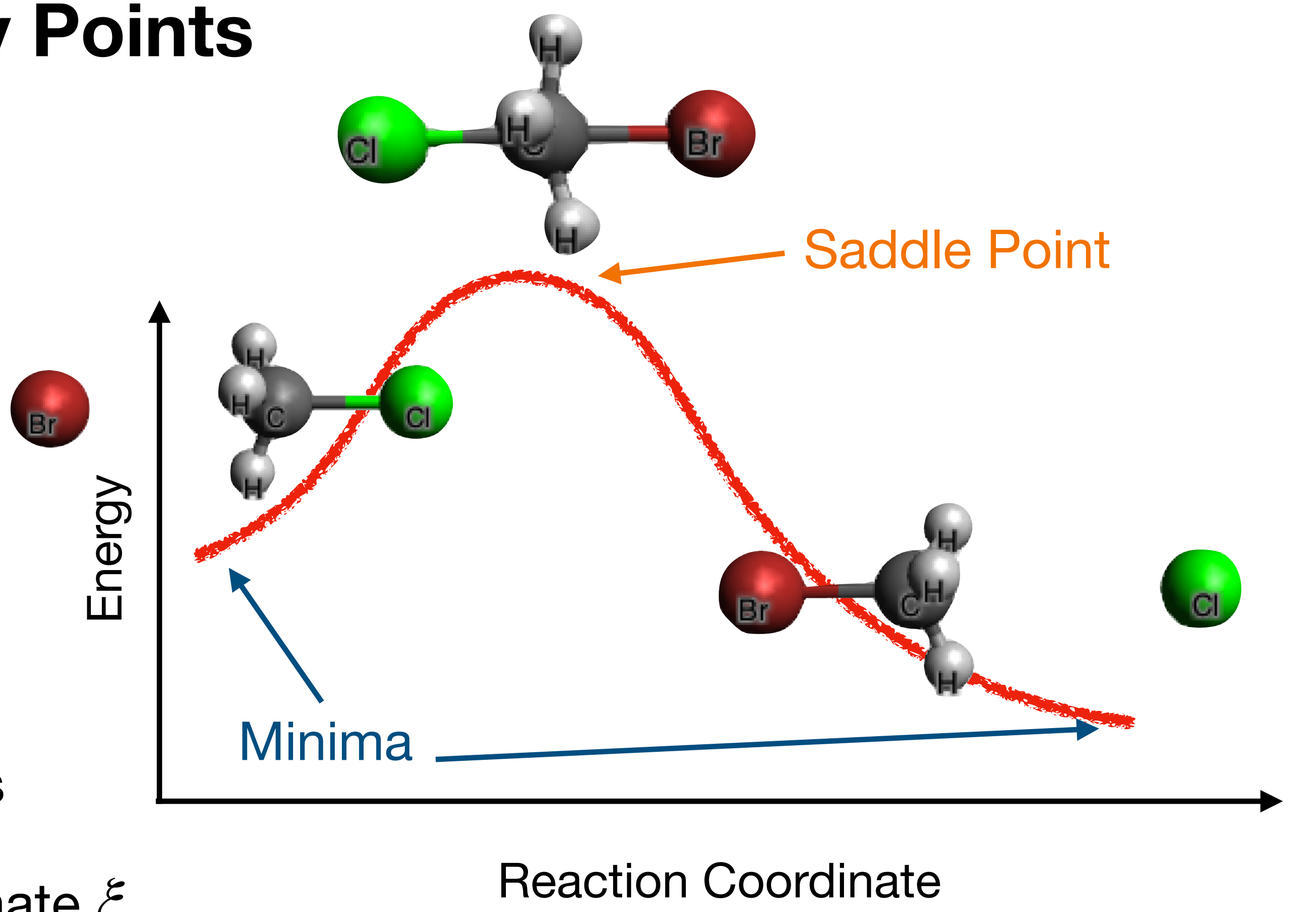


Possible stationary points for 1-propen-2-ol (left). Computed PES along the HCC=C dihedral and H-O-C=C dihedral coordinates. Taken from E. Lewars, *Computational Chemistry,* 1st Ed., Kuwler, New York, p. 24.

Optimising the Molecular Geometry (III)

Chemical Meaning of Stationary Points

- Stationary points fulfil that $\nabla V(\mathbf{x}) = 0$
- Not only minima are interesting in chemistry
- Minima are stable species:
  - Reactants and products
  - Reaction intermediates
- Saddle points: Transition States of reactions
  - Maxima in one direction: reaction coordinate ξ
  - Minimum in all others, minimum energy path (MEP)



Energy Profile along Reaction Coordinate

Optimising the Molecular Geometry (IV)

Chemical Meaning of Stationary Points

- Finding the stationary points we can determine the most important parameters of a chemical reaction
- Reaction Energy:

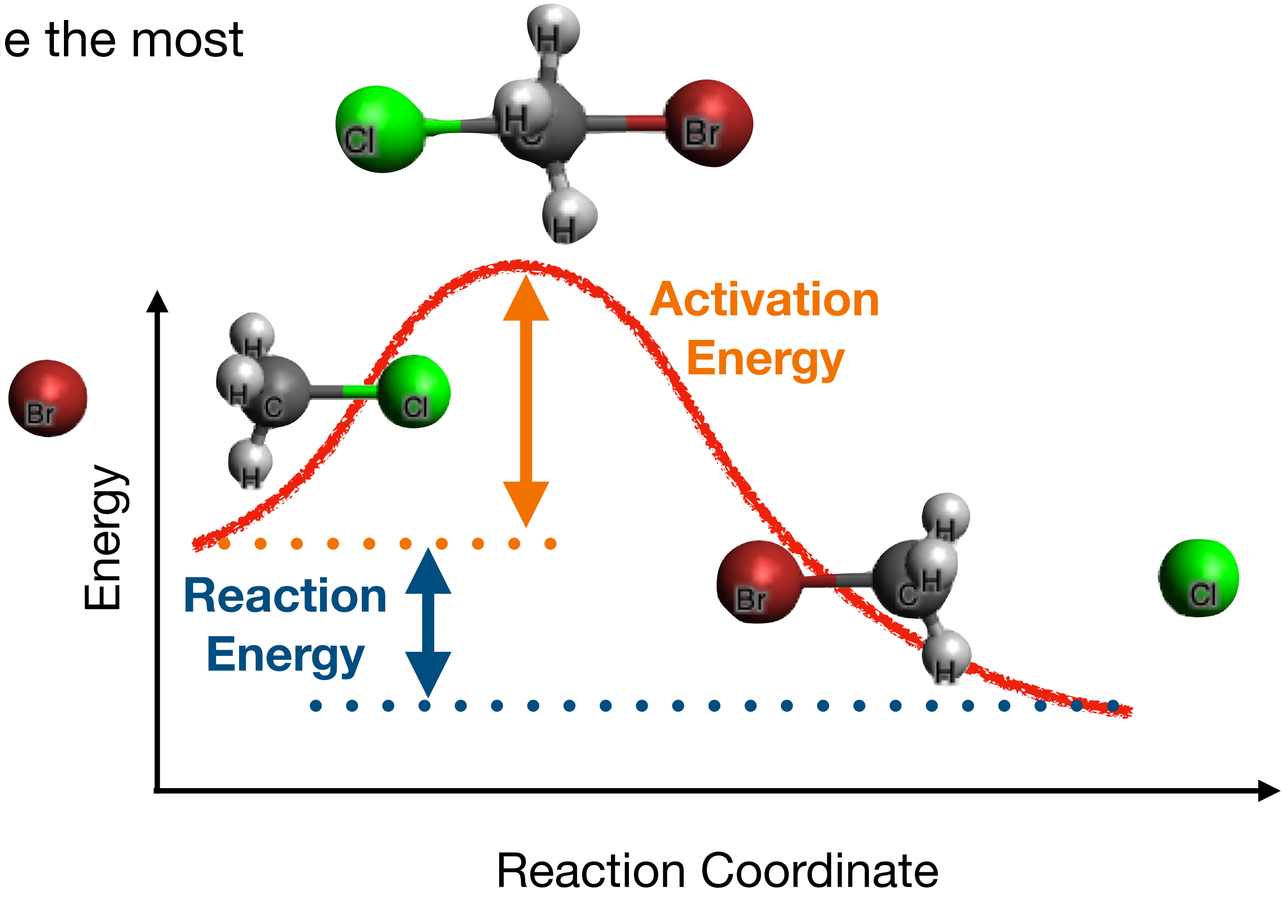
$$\Delta H_R = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

- Activation Energy

$$\Delta G^{\#} = G_{\text{TS}} - \sum G_{\text{reactants}}$$

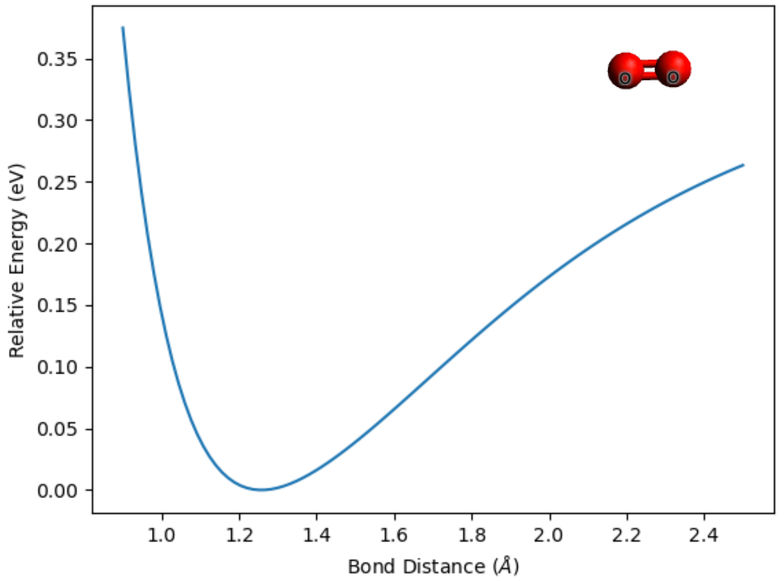
- Reaction rate / probability:

$$k = \frac{\kappa k_B T}{h} e^{-\frac{\Delta G^{\#}}{RT}}$$



Optimising a General Function

- Stationary points fulfil $\frac{\partial}{\partial \mathbf{x}} f(\mathbf{x}) = 0$
- Finding the minima of an analytical function is easy.
- $f(x) = a(x+b)^2; \frac{df}{dx} = 2a(x+b); x_{min} = -b$
- How calculate the minimum of a numerical function?
- $V(\mathbf{x})$ depends on $3N_{atoms} - 6$ variables!!
- Taylor expansion of the function, $V(\mathbf{x})$

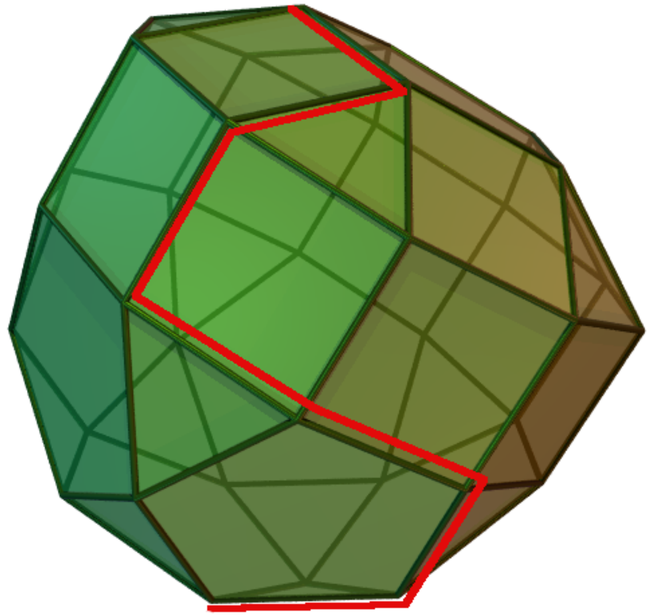



```
0.9,-149.83256851294857
0.916,-149.88230098440067
0.932,-149.92652818848006
0.9480000000000001,-149.96578509149447
0.964,-150.00055606052774
0.98,-150.0312802996513
0.996,-150.05835595863977
1.012,-150.0821435033207
1.028,-150.10296931406825
1.044,-150.1211288942191
1.06,-150.13688972421446
1.076,-150.15049369493423
1.092,-150.16215939406862
```

Simplex Method

0th-order Method

- The easiest way it so asume a 0th-order expansion, $V(\mathbf{x})\big|_{x_0} \approx V(\mathbf{x_0})$
- Constructs an irregular polyhedron with just the value of the function.
- Allows contractions and expansions to reach the minimum.
- 🙂 Only the value of $V(\mathbf{x_0})$ needed
- ☹️ Not so efficient with many variables, as is the case for molecular PES.

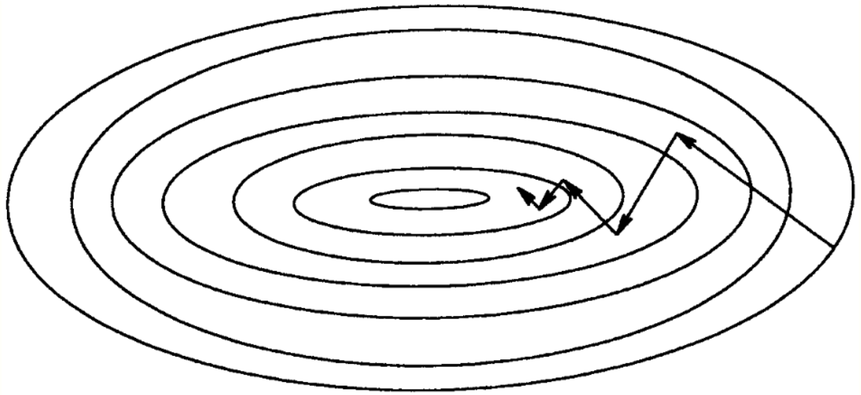


Taken from Wikipedia: https://en.wikipedia.org/wiki/Simplex_algorithm

Steepest Descent (I)

1st-Order Method

- 1st-order approximation, $V(\mathbf{x})\,|_{x_0} \approx V(\mathbf{x_0}) + \mathbf{g_0}^T(\mathbf{x} - \mathbf{x_0})$
- Gradient shows the direction of steepest ascent.
- Following opposite direction will lead to minimum
- $\mathbf{x_k} = \mathbf{x_{k-1}} - \alpha \cdot \nabla_{k-1}$
- Line search to find the optimum value for α
- Zig-zag search: next step moves orthogonal to previous one



Steepest descent minimisation. Taken form F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed., p 384

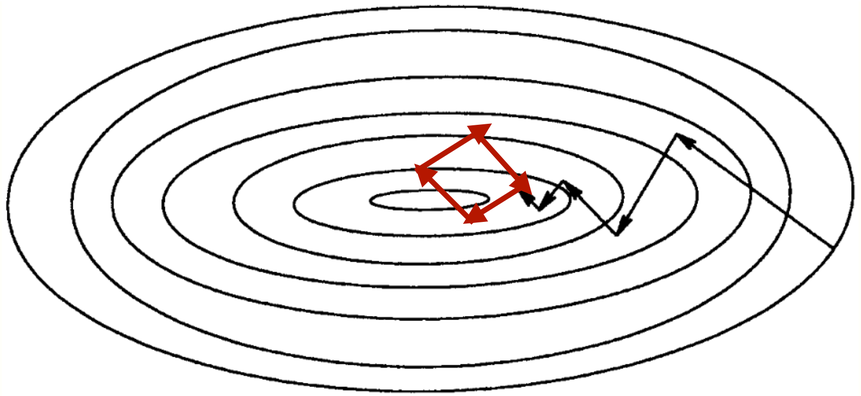
Steepest Descent (II)

1st-Order Method

- Accurate line search is needed to guarantee convergence to minimum
- An option is the Armijo rule (from Wolfe conditions):

$$f(\mathbf{x}_k + \alpha_k \mathbf{p}_k) \leq f(\mathbf{x}_k) + c_1 \alpha_k \mathbf{p}_k^T \nabla f(\mathbf{x}_k)$$

- α is the parameter to optimise, c_1 is a constant between 0 and 1 and $\mathbf{p}$ is the search direction
- Usually line search methods are approximate, and the algorithm ends up oscillating around the minimum
- 🙂 Bring system close to the minimum
- ☹️ Can oscillate around minimum
- ☹️ Can only locate minima

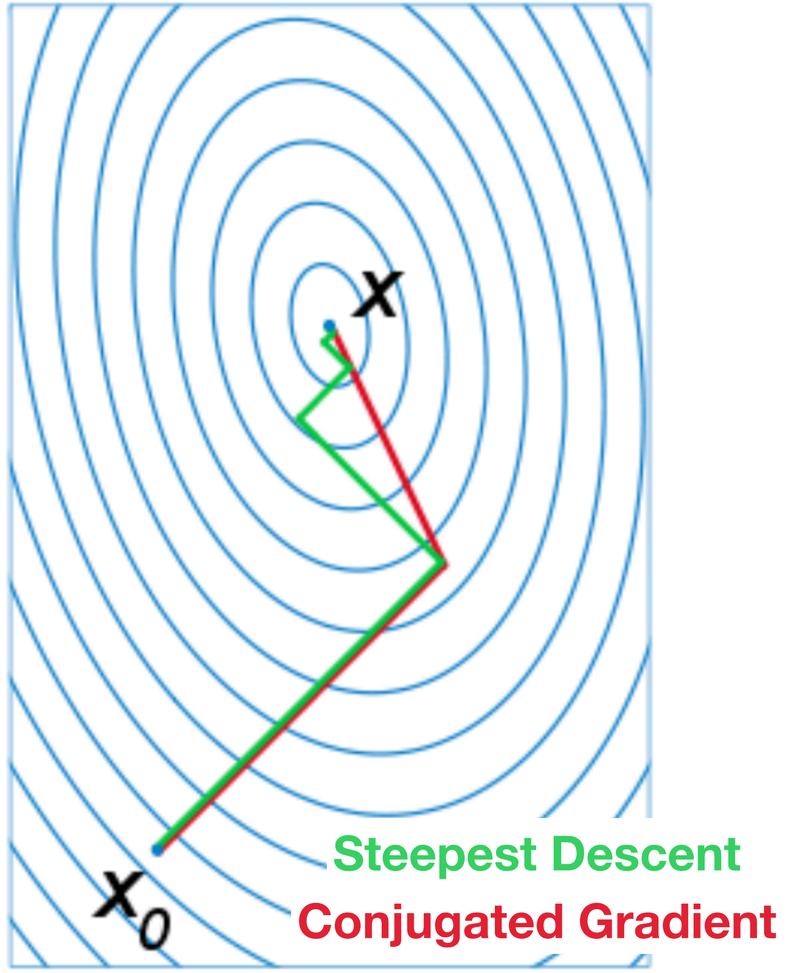


Conjugated Gradients (I)

1st-Order Method

- Overcomes deficiencies of steepest descent: “undoing” of previous step as going in is perpendicular direction.
- The step is a combination of gradient of current and previous step:
- $\mathbf{x_k} = \mathbf{x_{k-1}} - \alpha \left(\nabla_k + \beta \nabla_{k-1} \right)$
- If surface is quadratic, convergence assured in N_{var} steps
- α can be estimated as before
- A popular way to estimate β is the Polak-Ribiere relation:

$$\beta_i^{\mathrm{PR}} = \frac{\mathbf{g}_i^T \cdot (\mathbf{g}_i - \mathbf{g}_{i-1})}{\mathbf{g}_{i-1}^T \cdot \mathbf{g}_{i-1}}$$



Comparison between Steepest Descent and Conjugated Gradient algorithms. The latter converges in n=2 steep. Taken from: https://en.wikipedia.org/wiki/Conjugate_gradient_method

Conjugated Gradients (II)

1st-Order Method

- CG works best for near quadratic surface:
  - 🙂 The PES is near quadratic around minima
- 🙂 Better performance than Steepest Descent
- ☹️ In real applications, β needs to be reset to 0 after several steps
- ☹️ Can only locate minima

Newton-Raphson Methods (I)

2nd-Order Methods

- Newton-Raphson methods go beyond by approximation the function to a 2nd order Taylor expansion:

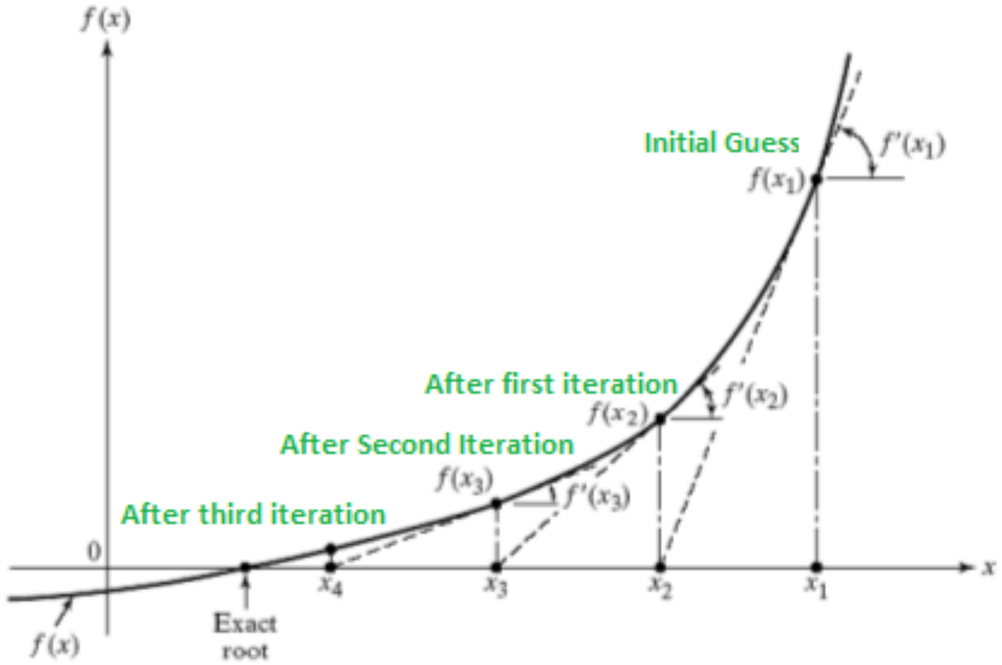
$$V(\mathbf{x})\,|_{\mathbf{x}_0} = V(\mathbf{x}_0) + \mathbf{g}_0^T(\mathbf{x}-\mathbf{x}_0) + \frac{1}{2}(\mathbf{x}-\mathbf{x}_0)^T\mathbf{H}_0(\mathbf{x}-\mathbf{x}_0)$$

- The step can be derived by requiring $\mathbf{g} = 0 \Rightarrow$

$$(\mathbf{x}-\mathbf{x}_0) = -\,\mathbf{H}^{-1}\mathbf{g}$$

- NR finds the solution of a quadratic function in a single step

- The real PES $V(\mathbf{x})$ contains terms beyond second order, NR leads to an iterative approach to stationary point

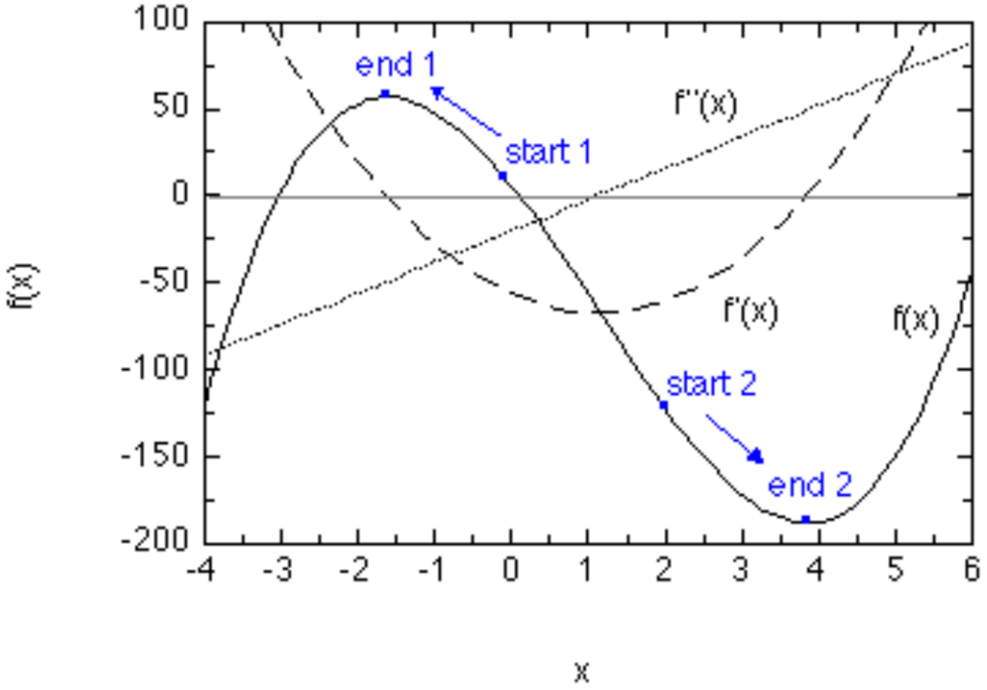


Iterative optimisation of $f(x)$ with the NR algorithm. Taken from https://www.geeksforgeeks.org/program-for-newton-raphson-method/

Newton-Raphson Methods (II)

2nd-Order Methods

- The NR method optimises to the nearest stationary point <u>whatever</u> that is: minimum, saddle point of maximum
  - 😃 Locate Transition States!
- The size of the step should be limited, otherwise the algorithm can shoot the step far away from the solution (*trust radius*):
  - The closer to the stationary point, the smaller the step.
- 😢 Computing $\mathbf{H}$ can take A LOT of time



Converged of NR algorithm with different starting points. Taken from <u>https://www.cup.uni-muenchen.de/ch/compchem/geom/nr.html</u>

Pseudo Newton-Raphson Methods (I)

1st or 2nd-Order Methods

- Main drawback of NR Algorithm: calculation of $\mathbf{H}$ in each optimisation step.
- What if it could be just updated?: $\mathbf{H}_{k+1} = \mathbf{H}_k + \Delta\mathbf{H}$
- Only the initial $\mathbf{H}_0$ needs be calculated
- For minimisation, the BFGS (Broyden–Fletcher–Goldfarb–Shanno) algorithm is preferred:

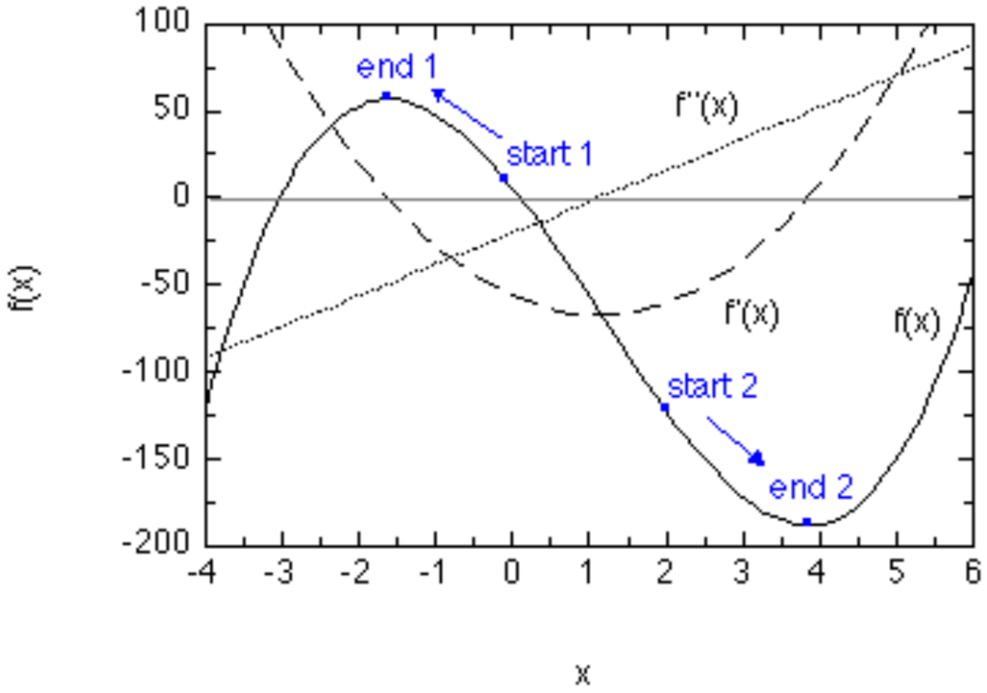
$$\Delta\mathbf{H}_{\mathrm{BGFS}} = \frac{\Delta\mathbf{g}^T\Delta\mathbf{g}}{\Delta\mathbf{g}^T\Delta\mathbf{x}} - \frac{\mathbf{H}\Delta\mathbf{x}\Delta\mathbf{x}^T\mathbf{H}}{\Delta\mathbf{x}^T\mathbf{H}\Delta\mathbf{x}}$$

- BFGS only allows for positive eigenvalues of $\mathbf{H}$ ⇒ not possible to optimise Transitions States:
- For that, the Powell update is used: $\Delta\mathbf{H}_{\mathrm{Powell}} = \frac{\Delta\mathbf{x}^T\Delta\mathbf{x}}{\Delta\mathbf{x}^T\Delta\mathbf{g}} - \frac{\mathbf{H}\Delta\mathbf{g}\Delta\mathbf{x}^T\mathbf{H}}{\Delta\mathbf{g}^T H\Delta\mathbf{g}}$

Pseudo Newton-Raphson Methods (I)

1st or 2nd-Order Methods

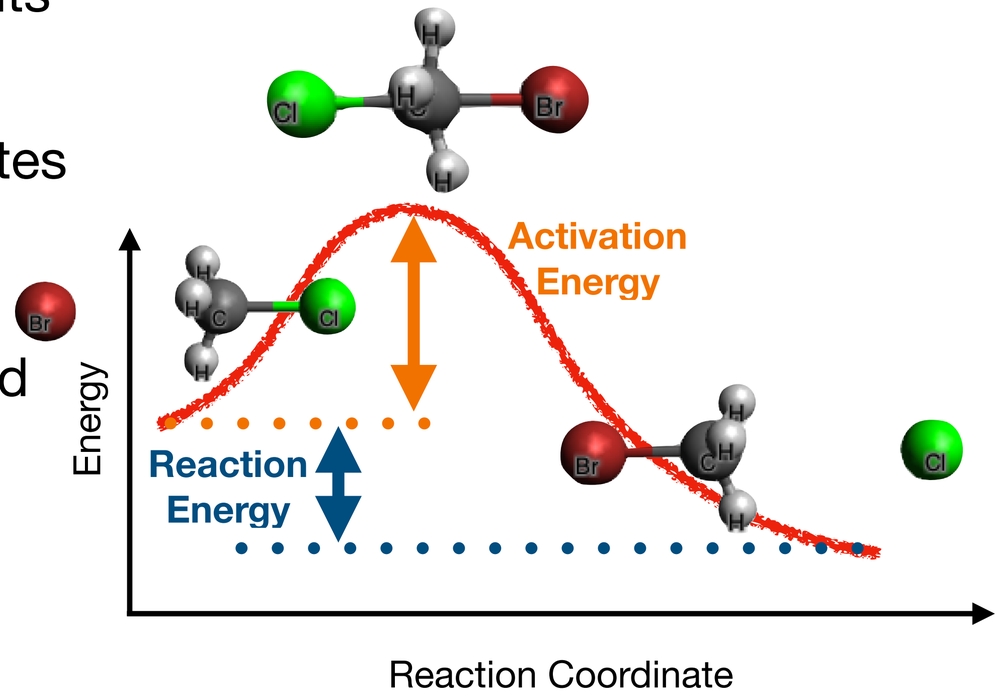
- The success of the optimisation depends on the initial $\mathbf{H}_0$
  - For minima: almost anything works, even $\mathbf{H}_0 = \mathbf{1}$
  - For Transition States and accurate Hessian is needed.
  - ☹ Pseudo NR need more iterations than true NR
  - 😀 Pseudo NR find the stationary point usually much faster than true NR ⇒ **preferred method**



Recapping (I)

Finding Chemical Structures and Reaction Parameters

- The PES has a complex shape and their stationary points correspond to chemical structures:
  - Minima: reactants, products and reaction intermediates
  - Saddle points: transition states
- Reaction energy and activation barrier can be calculated through the difference in energy of:
  - $\Delta H_R = \sum H_{\text{products}} - \sum H_{\text{reactants}}$
  - $\Delta G^{\#} = G_{\text{TS}} - \sum G_{\text{reactants}}; k = \frac{\kappa k_B T}{h} e^{-\frac{\Delta G^{\#}}{RT}}$



Recapping (II)

Finding Chemical Structures and Reaction Parameters

- Finding stationary points in the PES is key to understand its chemistry:
  - Pseudo Newton Raphsom algorithms are the method of choice
  - A good guess of the geometry helps to find the stationary point, specially for Transition States
  - For Transitions States the initial Hessian $\mathbf{H}_0$ needs to be calculated accurately.

Computational Chemistry at Work

Illustrating the Concepts (I)

Prediction of Molecular Geometries

- Start with H_2O, exp: $R_{OH} = 0.9578$ Å; $\theta_{HOH} = 104.49°$

Hartree-Fock (HF)

H_2O geometry as a function of basis set at the HF level of theory

Basis	R_{OH} (Å)	θ_{HOH} (°)	Basis	R_{OH} (Å)	θ_{HOH} (°)
			pc-0	0.9619	113.08
cc-pVDZ	0.9463	104.61	pc-1	0.9464	105.59
cc-pVTZ	0.9406	106.00	pc-2	0.9392	106.41
cc-pVQZ	0.9396	106.22	pc-3	0.9396	106.34
cc-pV5Z	0.9396	106.33	pc-4	0.9396	106.34
cc-pV6Z	0.9396	106.33			

Taken form F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed., p 351-353

Density Functional Theory (DFT)

Table 11.5 H_2O bond distances (Å) as a function of basis set with various DFT functionals

Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	0.9878	0.9962	0.9936	0.9854	0.9841	0.9806
pc-1	0.9764	0.9791	0.9763	0.9656	0.9683	0.9645
pc-2	0.9696	0.9706	0.9689	0.9589	0.9604	0.9574
pc-3	0.9700	0.9704	0.9689	0.9589	0.9604	0.9576
pc-4	0.9700	0.9704	0.9689	0.9590	0.9604	0.9576

Table 11.6 H_2O bond angles (°) as a function of basis set with various DFT functionals

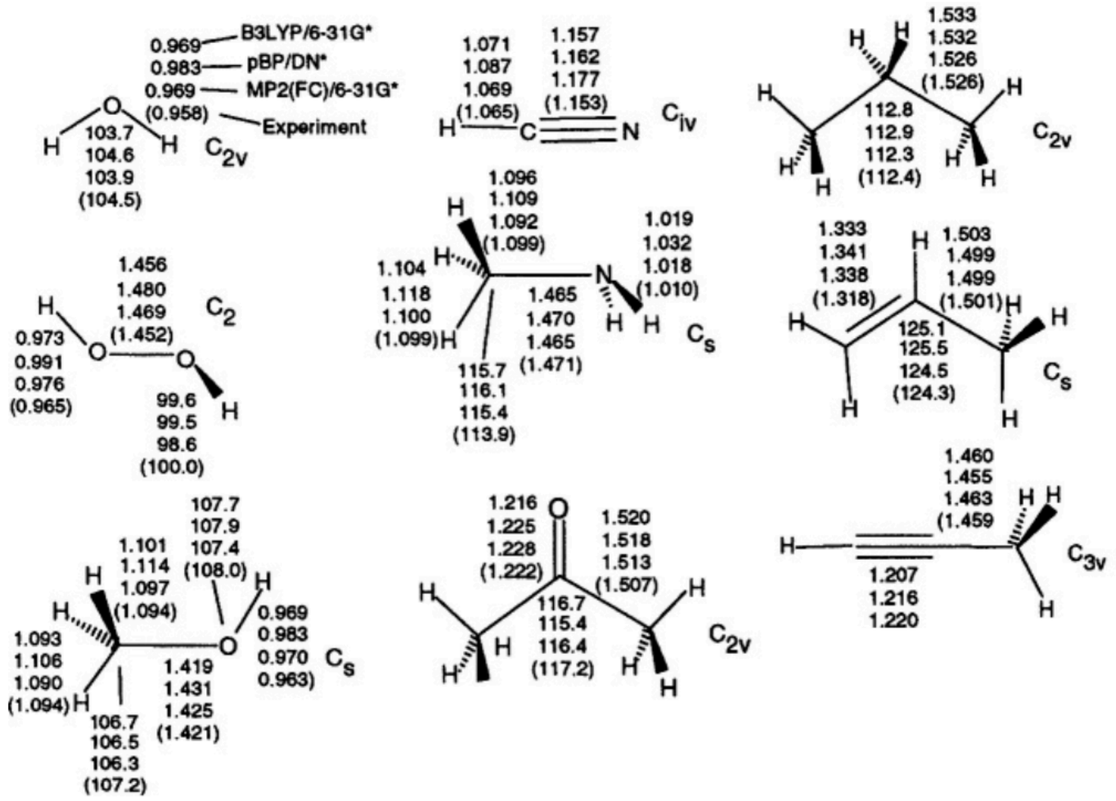
Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	111.82	109.27	109.40	109.43	110.72	110.93
pc-1	104.15	103.24	103.09	103.22	104.06	103.99
pc-2	105.10	104.56	104.27	104.52	105.19	104.98
pc-3	104.98	104.52	104.21	104.44	105.13	104.90
pc-4	104.98	104.52	104.21	104.42	105.13	104.90

Illustrating the Concepts (II)

Prediction of Molecular Geometries

Table 7.2. B3LYP/6-31G*, pBP/DN*, MP2(FC)/6-31G* and experimental dihedral angles (degrees). In each case the starting structure was an AM1 geometry

	Dihedral Angles				
Molecule	*B3LYP*	*pBP*	*MP2*	Exp.	Errors
HOOH	119.3	116.4	121.3	119.1[a]	0.3/−2.7/2.2
FOOF	87.2	89.2	85.8	87.5[b]	−0.3/1.7/−1.7
FCH_2CH_2F (FCCF)	70.0	69.2	69.0	73[b]	−3.0/−4/−4
FCH_2CH_2OH					
(FCCO)	63.3	64.0	60.1	64.0°	−0.7/0.0/−3.9
(HOCC)	62.7	62.6	54.1	54.6°	8.1/8.0/−0.5
$ClCH_2CH_2OH$					
(ClCCO)	61.2	63.1	65.0	63.2[b]	−2.0/−0.1/1.8
(HOCC)	60.0	62.5	64.3	58.4[b]	1.6/4.1/5.9
$ClCH_2CH_2F$ (ClCCF)	66.7	69.6	65.9	68[b]	−1.3/1.6/−2.1
HSSH	91.0	90.0	90.4	90.6[a]	0.4/−0.6/−0.2
FSSF	89.1	88.6	88.9	87.9[b]	1.2/0.7/1.0
					Deviations: 5+, 5−/5+, 4−, one 0/4+, 6− mean of 10: 1.9/2.4/2.3



Taken from E. Lewars, *Computational Chemistry,* 1st Ed., Kuwler, New York, p. 401-404

Illustrating the Concepts (III)

Dipole Moment

Table 11.12 H_2O dipole moment (debye) as a function of DFT functional and basis set; the experimental value is 1.847 debye

Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
aug-pc-0	2.721	2.602	2.618	2.605	2.655	2.675
aug-pc-1	1.823	1.762	1.760	1.758	1.821	1.826
aug-pc-2	1.837	1.781	1.779	1.782	1.837	1.842
aug-pc-3	1.834	1.778	1.774	1.779	1.833	1.837
aug-pc-4	1.833	1.778	1.774	1.777	1.833	1.836

Table 11.21 Dipole moment (debye) for CO; the experimental value is 0.122 debye

Method	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
HF	–0.259	–0.266	–0.265	–0.264
MP2	0.296	0.280	0.275	0.273
MP3	0.076	0.047	0.036	0.032
MP4	0.220	0.222	0.216	0.214
CCSD	0.097	0.070	0.059	0.055
CCSD(T)	0.141	0.127	0.118	0.115
CISD	0.050	0.023	0.011	0.008
LSDA	0.232	0.226	0.229	0.229
BLYP	0.187	0.184	0.185	0.185
PBE	0.229	0.224	0.224	0.224
HCTH	0.194	0.181	0.175	0.179
B3LYP	0.091	0.086	0.087	0.088
PBE0	0.107	0.101	0.102	0.102

Taken form F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed., p 358, p. 372

Illustrating the Concepts (IV)

Vibrational Frequencies

Table 11.13 H_2O HF harmonic frequencies (cm^{-1}) as a function of basis set

Basis	ν_1	ν_2	ν_3
pc-0	1690	3966	4145
pc-1	1751	4120	4233
pc-2	1744	4138	4239
pc-3	1748	4131	4232
pc-4	1748	4130	4231
Experimental	1649	3832	3943

Taken form F. Jensen, *Introduction to Computational Chemistry*, 2nd Ed., p 351-353

Table 11.17 H_2O lowest harmonic frequency (cm^{-1}) as a function of basis set with various DFT functionals; the experimental value is 1649 cm^{-1}

Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	1474	1535	1539	1567	1565	1578
pc-1	1548	1597	1596	1627	1628	1635
pc-2	1544	1595	1590	1617	1625	1630
pc-3	1549	1597	1594	1621	1629	1635
pc-4	1550	1598	1594	1621	1629	1635

Table 11.18 H_2O second lowest harmonic frequency (cm^{-1}) as a function of basis set with various DFT functionals; the experimental value is 3832 cm^{-1}

Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	3588	3453	3510	3574	3620	3691
pc-1	3690	3611	3664	3760	3767	3835
pc-2	3730	3669	3710	3796	3811	3870
pc-3	3718	3667	3707	3794	3807	3865
pc-4	3718	3666	3706	3794	3807	3865

Illustrating the Concepts (V)

Vibrational Frequencies - IR Spectrum

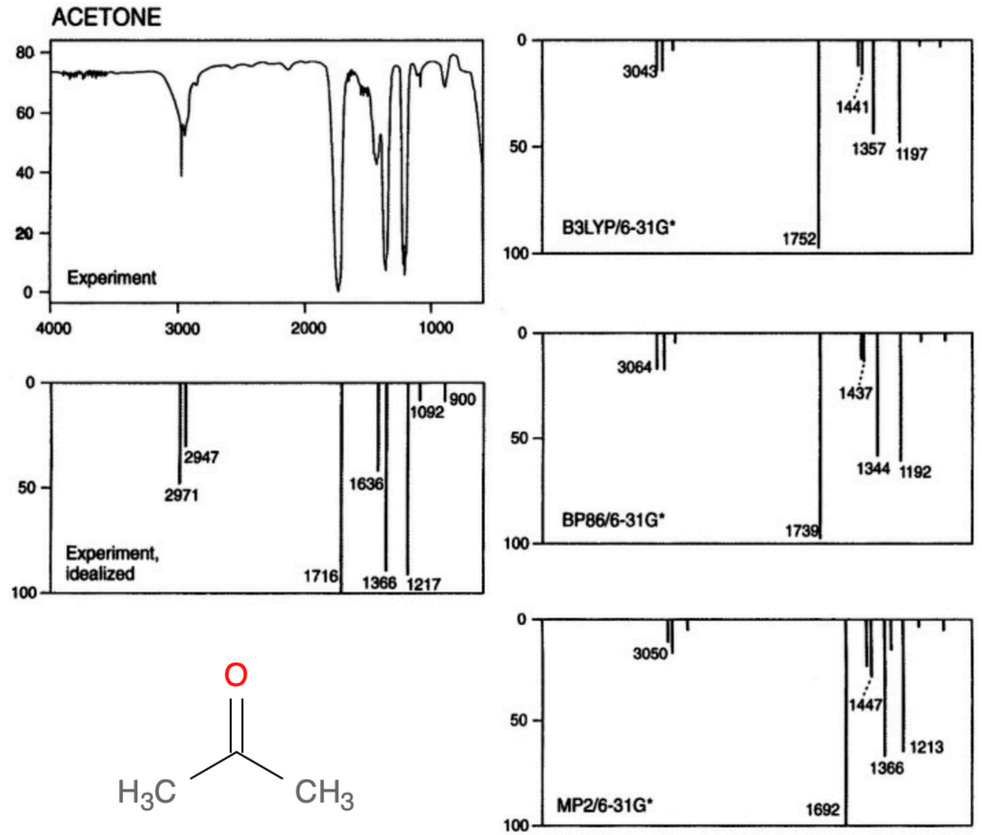


Figure 7.4. Experimental (gas phase) and DFT (B3LYP/6-31G* and BP86/6-31G*) and MP2(FC)/6-31G* calculated infrared spectra of acetone. The DFT spectra are based on the data in Table 7.6; the MP2 spectrum is that shown in Fig. 5.33.

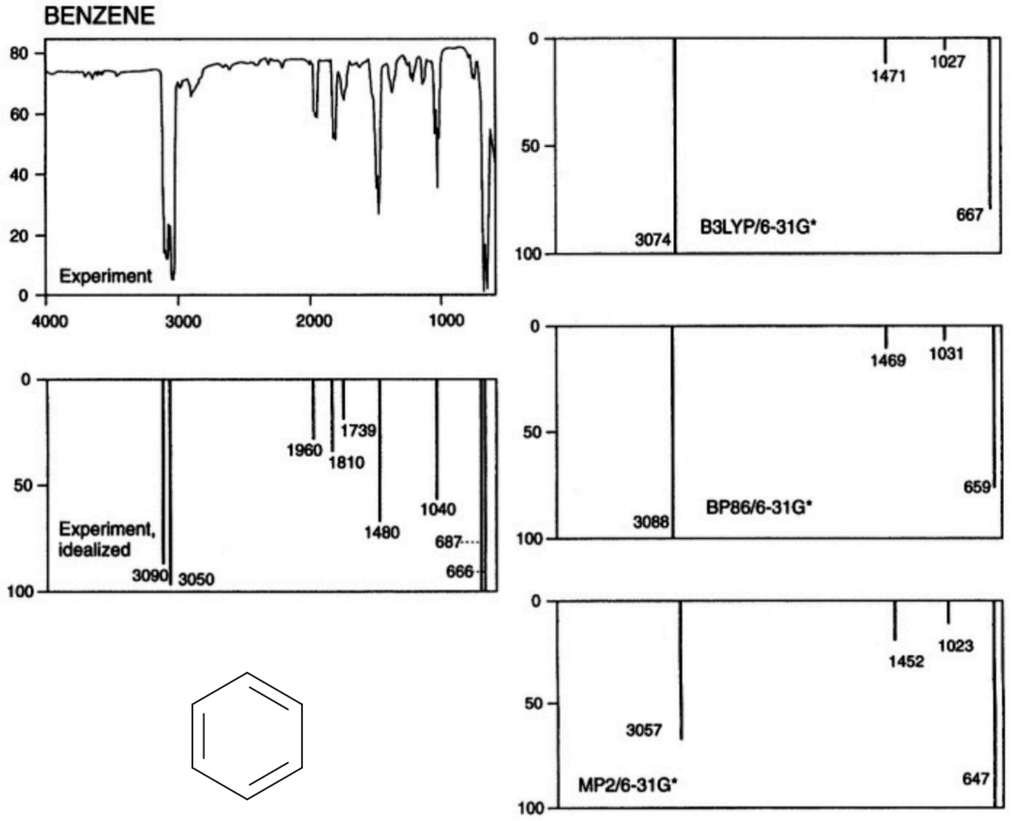


Figure 7.5. Experimental (gas phase) and DFT (B3LYP/6-31G* and BP86/6-31G*) and MP2(FC)/6-31G* calculated infrared spectra of benzene. The DFT spectra are based on the data in Table 7.6; the MP2 spectrum is that shown in Fig. 5.34.

Taken from E. Lewars, *Computational Chemistry,* 1st Ed., Kuwler, New York, p. 414

Illustrating the Concepts (V)

Reaction Energies

View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

PCCP

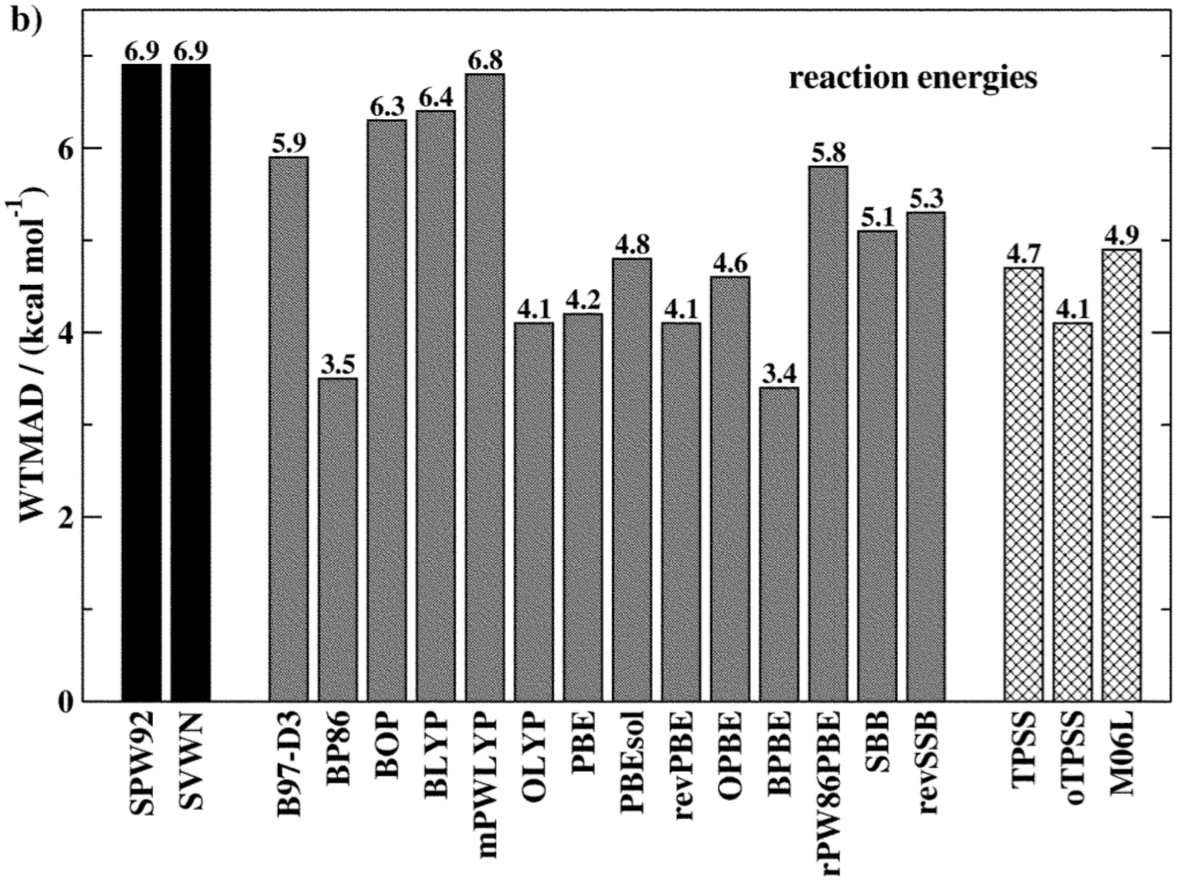
Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670–6688

www.rsc.org/pccp **PAPER**

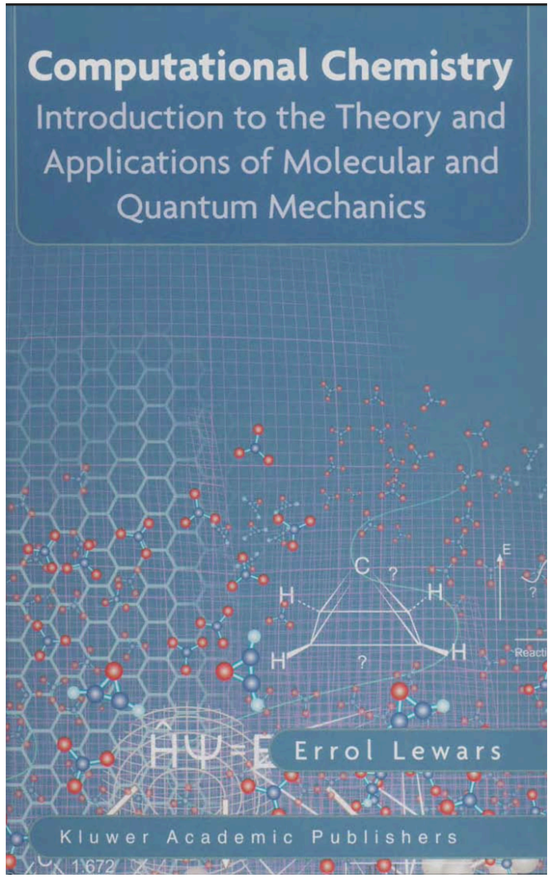
A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions†

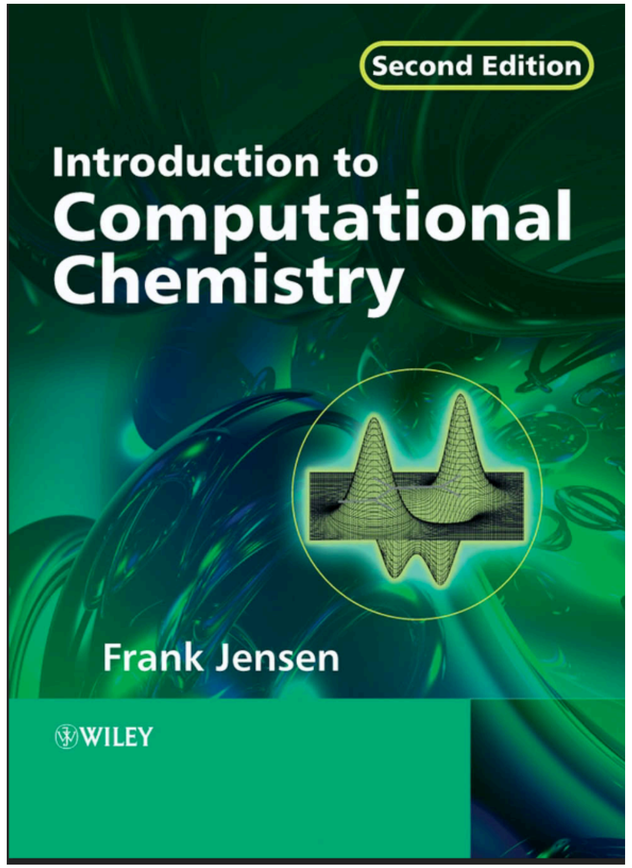
Lars Goerigk[ab] **and Stefan Grimme***[a]

Received 28th December 2010, Accepted 10th February 2011
DOI: 10.1039/c0cp02984j



Literature


Computational Chemistry
Introduction to the Theory and Applications of Molecular and Quantum Mechanics
Errol Lewars
Kluwer Academic Publishers


Second Edition
Introduction to
Computational
Chemistry
Frank Jensen
WILEY

Resources

To Perform Calculations:

	😀	😫
PySCF	Flexible, good for education Very performant, specially for GPUs Easy to customise	Requires a higher know-how Python skills required Not so well documented
Psi4	Flexible, good for education Very performant, specially for GPUs Easy to customise	Requires a higher know-how Python skills required Not so well documented
ORCA	Very intuitive and easy to use No programming skills required Many types of calculations work out of the box Very performant Good documentation	Out of the box, not possible to do what's not implemented

Resources

To Create Coordinates, Inputs and Visualize results

	😀	😫
NGLViwer	Run from a Jupiter Notebook Easy to install	Requires a higher know-how Python skills required Badly documented
Avogadro	Very intuitive and easy to use Supports most of more common formats	Can be a bit buggy Restricted with the type of graphics generated, postporcessing might be needed
JMol	Supports most of more common formats Well documented	Sometimes operation is not so straight forward Restricted with the type of graphics generated, postporcessing might be needed
Pymol	Supports most of more common formats Well documented Very flexible, you can do many visualisation types	Python skills required
VMD	High quality graphics Well documented and large community support Very flexible, you can do many visualisation types	Programming skills required, mainly TCL