CHEM3023: Spins, Atoms and Molecules

Lecture 3

The Born-Oppenheimer approximation

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Learning outcomes

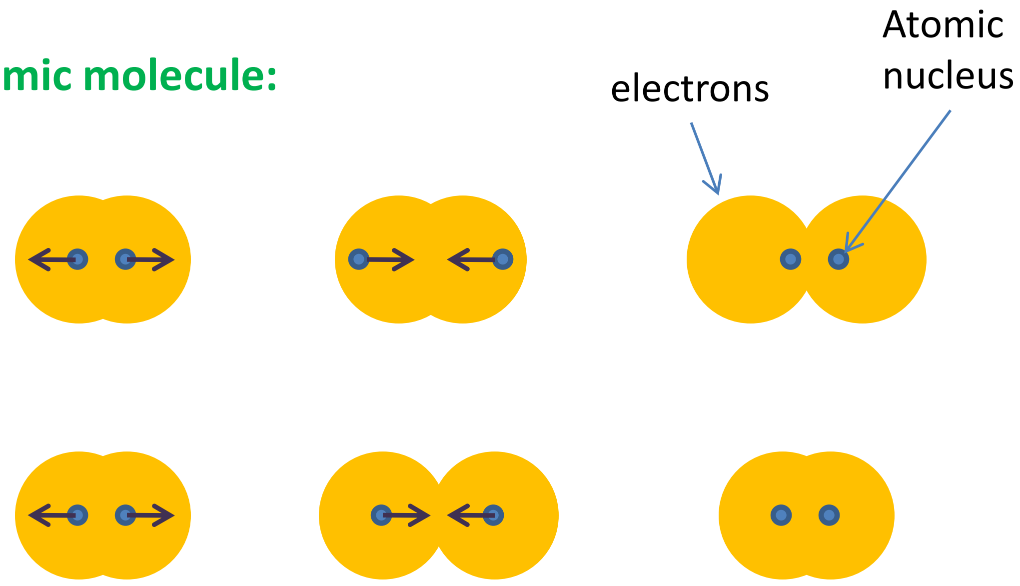
- Separate molecular Hamiltonians to electronic and nuclear parts according to the Born-Oppenheimer approximation
- Be able to manipulate expressions involving electronic wavefunctions, taking into account spin and space coordinates and antisymmetry

Separating electronic from nuclear coordinates

Nuclei are much heavier than electrons (e.g. Proton mass≈1800 times the mass of an electron => compare kinetic energy operators of proton and electron).

As a result nuclei move much slower than electrons. To a very good approximation, we can assume that the electronic motions are instantaneously “equilibrated” at each nuclear position.

Example: Vibration of diatomic molecule:



Wrong picture: “electron cloud” trails behind moving nuclei

Correct picture: “electron cloud” instantaneously re-arranges itself around moving nuclei

Hamiltonian operator for water molecule

Water contains 10 electrons and 3 nuclei. We will use the symbols “O” for the oxygen (atomic number Z_O=8) nucleus, “H1” and “H2” (atomic numbers Z_{H1}=1 and Z_{H2}=1) for the hydrogen nuclei.

$$\hat{H}_{\mathrm{H_2O}} = -\frac{1}{2M_{\mathrm{O}}}\nabla^2_{\mathbf{R}_{\mathrm{O}}} - \frac{1}{2M_{\mathrm{H1}}}\nabla^2_{\mathbf{R}_{\mathrm{H1}}} - \frac{1}{2M_{\mathrm{H2}}}\nabla^2_{\mathbf{R}_{\mathrm{H2}}} - \sum_{i=1}^{10}\frac{1}{2}\nabla^2_{\mathbf{r}_i}$$

Kinetic energy of O

Kinetic energy of H1

Kinetic energy of H2

Kinetic energy of electron i

$$-\sum_{i=1}^{10}\frac{8}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{O}}|} - \sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H1}}|} - \sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H2}}|}$$

Electron attraction to O

Electron attraction to H1

Electron attraction to H2

$$+\sum_{i=1}^{10}\sum_{j=i+1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \sum_{I=1}^{3}\sum_{J=I+1}^{3}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}$$

Electron-electron repulsion

nucleus-nucleus repulsion

E.g. Assume
$Z_1 = Z_O$
$Z_2 = Z_{H1}$
$Z_3 = Z_{H2}$

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$$\hat{H}_{\mathrm{H_2O}} = \overset{\text{B.O.}}{\cancel{-\frac{1}{2M_{\mathrm{O}}}\nabla^2_{\mathbf{R}_{\mathrm{O}}}}} \overset{\text{B.O.}}{\cancel{-\frac{1}{2M_{\mathrm{H1}}}\nabla^2_{\mathbf{R}_{\mathrm{H1}}}}} \overset{\text{B.O.}}{\cancel{-\frac{1}{2M_{\mathrm{H2}}}\nabla^2_{\mathbf{R}_{\mathrm{H2}}}}} - \sum_{i=1}^{10}\frac{1}{2}\nabla^2_{\mathbf{r}_i}$$

Kinetic energy of O

Kinetic energy of H1

Kinetic energy of H2

Kinetic energy of electron i

$$-\sum_{i=1}^{10}\frac{8}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{O}}|} - \sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H1}}|} - \sum_{i=1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{R}_{\mathrm{H2}}|}$$

Electron attraction to O

Electron attraction to H1

Electron attraction to H2

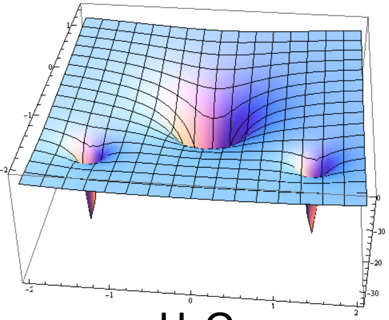
$$+\sum_{i=1}^{10}\sum_{j=i+1}^{10}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + \overset{\text{B.O.}}{\cancel{\sum_{I=1}^{3}\sum_{J=I+1}^{3}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}}}$$

Electron-electron repulsion

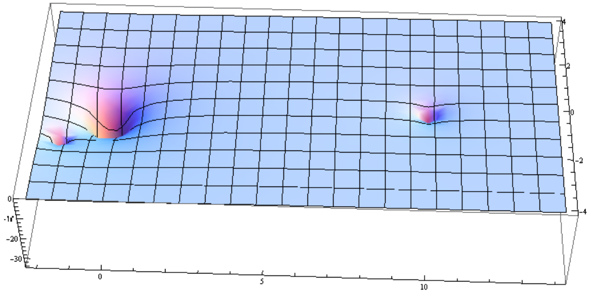
nucleus-nucleus repulsion

E.g. Assume
$Z_1 = Z_O$
$Z_2 = Z_{H1}$
$Z_3 = Z_{H2}$

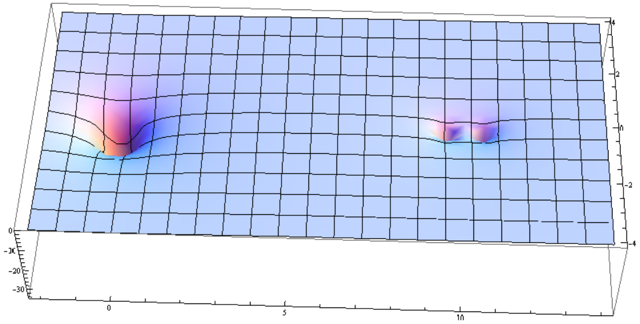
Example: Nuclear attraction potential for one O and two H



H_2O



$OH + H$



$O + H_2$

- How does the Hamiltonian operator differ between these examples?
- Can you suggest how you may model the reaction OH+H → H_2O

Born-Oppenheimer (or adiabatic) approximation

Solve Schrödinger's equation only in the electronic coordinates for each set of given (fixed) nuclear coordinates.

$$\hat{H} = -\sum_{I}\frac{1}{2M_I}\nabla_I^2+\sum_{I}\sum_{J>I}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\underbrace{-\sum_{i}\frac{1}{2}\nabla_i^2+\sum_{i}\sum_{j>i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\sum_{i}\sum_{I}-\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}}_{\hat{H}_{elec}}$$

$$\hat{H}_{elec}\Phi_{elec} = E_{elec}\Phi_{elec}$$

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\};\{\mathbf{R}_I\})$$

$$E_{elec} = E_{elec}(\{\mathbf{R}_I\})$$

The resulting wavefunctions and energies have a **parametric dependence** in the coordinates of the nuclei

- Central to Chemistry: allows to find reactants, products, transition states, reaction paths
- We will use the Born-Oppenheimer approximation throughout this course

Potential Energy Surface (PES)

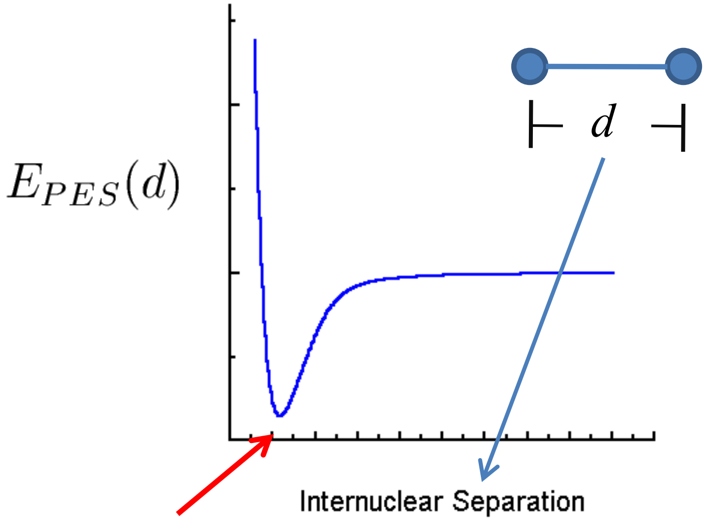
The electronic energy is a function of the nuclear positions. So is the internuclear repulsion energy. Their sum is the "total energy" of a molecule under the B.O. approximation. One can represent this as a surface, which is called the potential energy surface (PES).

$$E_{PES}(\{\mathbf{R}_I\}) = E_{elec}(\{\mathbf{R}_I\}) + \sum_{I} \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electronic energy

Repulsion energy between nuclei I and J

Example: PES of a diatomic



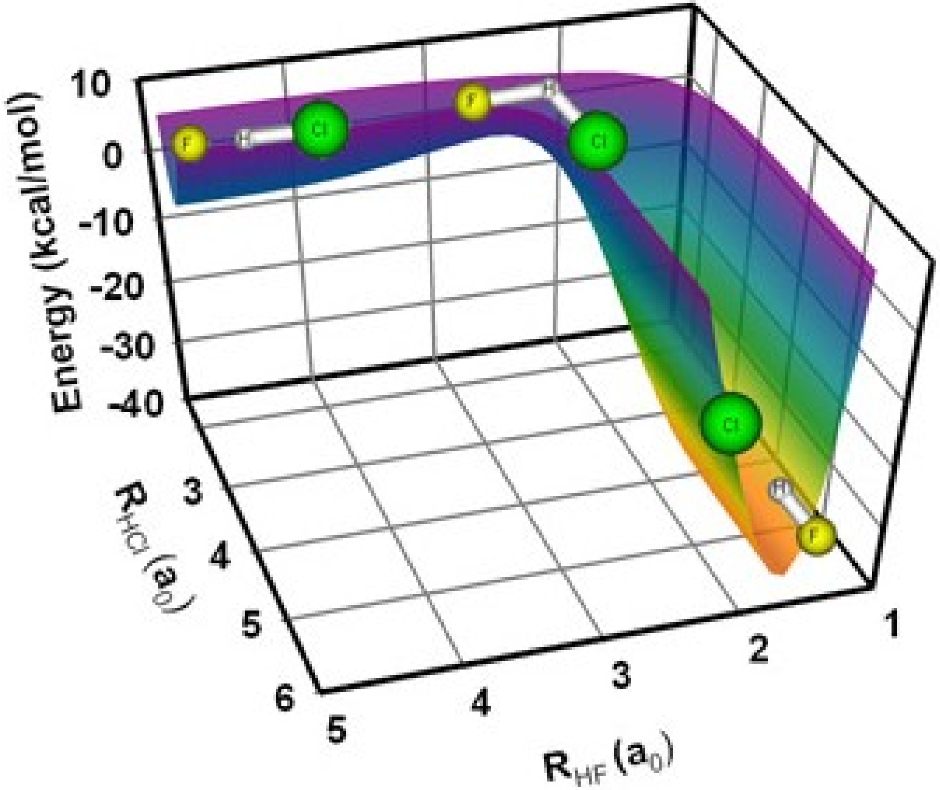
Equilibrium geometry d_e

Reactants, products, transition states, reaction paths

Chemical reactions can be represented as paths followed on a PES

- Reactants and products are minimum energy points on the PES

- Transition states are points on the PES where the energy is maximum along one direction and minimum along all other directions



- We can locate reactants, products and transition states by following paths on the PES until a minimum (or maximum in one direction for TS) is reached (zero partial derivative of energy with respect to each atomic coordinate)

Spin, antisymmetry and the Pauli principle

- Each electron has a "spin", an intrinsic property which has the characteristics of rotational motion, and is quantised
- Electronic spin is described by a spin angular momentum quantum number $s=½$, and its z-component $m_s = ½$ ("up" spin) or $-½$ ("down" spin)
- We represent the two spin states of the electron by two spin wavefunctions $\alpha(\omega)$ and $\beta(\omega)$ which are orthonormal:

$$\int \alpha^*(\omega)\alpha(\omega)d\omega = \int \beta^*(\omega)\beta(\omega)d\omega = 1$$

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$$

$$\int \alpha^*(\omega)\beta(\omega)d\omega = \int \beta^*(\omega)\alpha(\omega)d\omega = 0$$

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

Spatial and spin coordinates

- To describe the spin of an electron we therefore include an extra "spin-coordinate"
- Therefore, an electron is described not only by the three spatial coordinates *x,y,z* (=***r***) but also by its spin coordinate ω
- We will denote these four coordinates collectively by **x**

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

- Particles whose spin quantum number **s** is a half-integer (e.g. 1/2, 3/2, 5/2, etc) are called Fermions
- Electrons and protons are examples of Fermions
- Particles whose spin quantum number **s** is an integer (e.g. 1, 2, 3) are called Bosons. Photons are examples of Bosons

Antisymmetry of electronic wavefunctions

- Wavefunctions of Fermions change sign when the coordinates (space and spin) of any two particles are exchanged.
- This property is called antisymmetry:

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)$$

- Electrons are Fermions, therefore electronic wavefunctions **must be antisymmetric**
- We need to include antisymmetry in all approximate wavefunctions we construct

Summary / Reading assignment

- Born-Oppenheimer approximation (Cramer, page 110)
- Many-electron wavefunctions (Cramer, pages 119-122)
- Antisymmetry of electronic wavefunctions (Cramer, pages 122-126)