

## 2 | The Born-Oppenheimer Approximation and Potential Energy Surfaces

The previous chapter introduced the Schrödinger equation and the molecular Hamiltonian. At this point, we are going to examine an important approximation that allows us break down the complexity of the Schrödinger equation for molecules by separating the motion of electrons and nuclei. We will also formalize the concept of potential energy surface.

### 2.1 The Born-Oppenheimer or fixed nuclei approximation

One important simplification of the Schrödinger equation is to separate the motion of the electrons and the nuclei. This approach is justified by the fact that the mass of a nucleus is at least 1836 times larger than that of an electron. A good analogy is that of flies (electrons) that move around cows (nuclei). The motion of the flies does not perturb the cows, but if a cow moves then all the flies will rapidly readjust their motion to follow the cow.

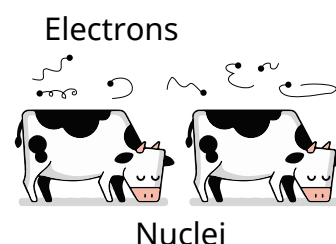
In the fixed nuclei approximation, also known as **Born-Oppenheimer (BO) approximation**, we separate the wave function of electron and nuclei in the following way

$$\Psi(\mathbf{r}, \mathbf{R}) \approx \Psi_{\mathbf{R}}^{\text{el}}(\mathbf{r}) \Psi^{\text{nuc}}(\mathbf{R}) \quad (2.1)$$

where to keep these expression compact we have indicated the coordinates of all electrons and nuclei with a single variable, that is,  $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots)$  and  $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots)$ .

This equation says that the total wave function can be written as a wave function for the electrons ( $\Psi^{\text{el}}$ ) times the wave function for the nuclei ( $\Psi^{\text{nuc}}$ ). Note that  $\Psi^{\text{nuc}}(\mathbf{R})$  only depends on the coordinate of the nuclei  $\mathbf{R}$  (nuclei are like the cows, they can almost completely ignore the exact position of the electrons). In contrast, the electron wave function  $\Psi_{\mathbf{R}}^{\text{el}}(\mathbf{r})$  depends both on the coordinates of the nuclei and the electrons. The way we should think of the electronic wave function is as providing information about all the electrons **for a given position** of the nuclei  $\mathbf{R}_1, \mathbf{R}_2, \dots$  (in our analogy, the electrons are like the flies, and their position depends significantly on the position of the cows). We say that in the BO approximation the electronic wave function depends **parametrically** on the nuclear coordinates.

When we assume the Born-Oppenheimer approximation, the Hamiltonian for



**Fig. 2.1:** The fly/cow analogy of the Born-Oppenheimer approximation.

the electrons takes a simpler form

$$\hat{H}^{\text{el}} = \hat{T}_{\text{e}} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} + V_{\text{nn}} \quad (2.2)$$

The first term in this expression is just the kinetic energy of the electrons. The second term accounts for the electron-electron repulsion energy. The third term is the electron-nuclear attraction (attractive force acting on the electron). In this approximation, the last term is just a constant, which accounts for the nuclear-nuclear repulsion energy.<sup>1</sup>

The wave functions for the electronic in the BO approximation satisfies the following Schrödinger equation

$$\hat{H}^{\text{el}} \Psi_{\mathbf{R}}^{\text{el}}(\mathbf{r}) = E(\mathbf{R}) \Psi_{\mathbf{R}}^{\text{el}}(\mathbf{r}) \quad (2.4)$$

which yields the potential energy  $E(\mathbf{R})$ , a quantity that depends on the position of the nuclei

$$E(\mathbf{R}) = E(\mathbf{R}_1, \mathbf{R}_2, \dots) \quad (2.5)$$

A useful way to think of this quantity is as describing a **potential energy surface**, that is, a high-dimensional surface that relates a molecular structure (described by nuclear coordinates  $\mathbf{R}_1, \mathbf{R}_2, \dots$ ) to its energy.

The potential energy  $E(\mathbf{R})$  **is the central quantity that computational chemists aim to obtain when doing a quantum chemistry computation**. This quantity should be understood as accounting for the energy of the electrons interacting with the nuclei at a given molecular geometry. The potential energy  $E(\mathbf{R})$  provides all the information we need to determine the structure of a molecule, the way it vibrates and rotates, and in most cases also the way it reacts. We will come back to some of these topics in later chapters.

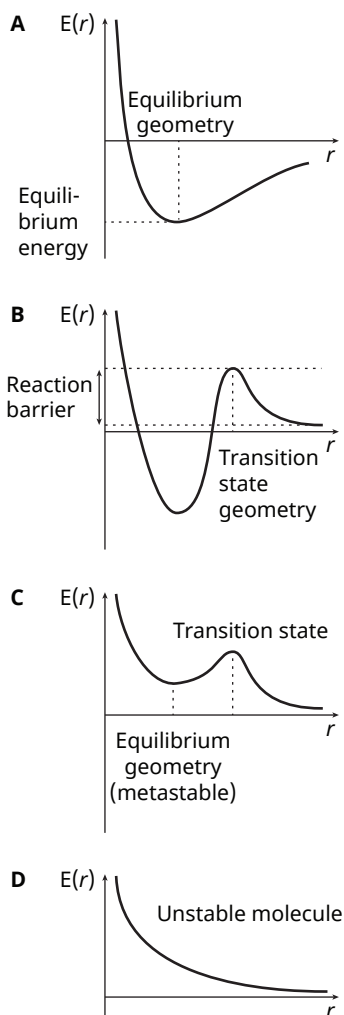
The Born-Oppenheimer approximation and the potential energy are fundamental concepts that are at the basis of how we understand and talk about molecules in chemistry. Even though you may not realize it, you are already very familiar with the BO approximation because it forms the basis of how we talk about the structure of molecules in introductory chemistry courses. When we say, for example, that a water molecule in the gas phase has a O-H bond length of 0.957 Å and a H-O-H angle of 104.5°, we are basically describing the geometric arrangements of the atoms H, H, and O with the minimum potential energy.

## 2.2 The potential energy surface of diatomic molecules

The potential energy surface for a diatomic molecule A–B is easy to visualize, because the energy depends only on the bond distance  $r = |\mathbf{R}_A - \mathbf{R}_B|$ , that is,  $E = E(r)$ , and we call it a **potential energy curve** (PEC). Fig. 2.2 shows four potential energy surfaces for a diatomic molecule. The top two plots show a stable AB molecule. In the first case (A), the reaction  $A + B \rightarrow AB$  is barrier-less and happens spontaneously. The bond distance  $r_e$  where the energy of AB is a minimum is the **equilibrium geometry** (often indicated with the symbol  $r_e$ ), and the corresponding energy is the **equilibrium energy**  $E(r_e)$ . In the second case (B), the reaction  $A + B \rightarrow AB$  proceeds via a **transition state**  $AB^*$  that has an energy higher than  $A + B$ . This reaction

<sup>1</sup> The nuclear-nuclear repulsion energy is given by

$$V_{\text{nn}} = \frac{1}{4\pi\epsilon_0} \sum_{i < j}^{\text{nuclei}} \frac{q_i q_j}{R_{ij}} \quad (2.3)$$



**Fig. 2.2:** The potential energy surface for a diatomic molecule. **A** and **B** show typical stable diatomic molecule. **C** and **D** show the case of a metastable molecule (stable only for a finite time) and an unstable molecule, respectively.

can happen only if A and B collide with enough energy to overcome the **reaction barrier**.

Mathematically, both equilibrium geometries and transition states correspond to **stationary points**  $r^*$  on the potential energy curve, which are characterized by a zero first derivative with respect to  $r$

$$\text{At a stationary point } r^* : \left. \frac{dE(r)}{dr} \right|_{r=r^*} = 0 \quad (2.6)$$

What distinguishes an equilibrium geometry and a transition state is the **curvature** of the potential energy curve at  $r^*$ . For equilibrium geometries, the energy is a minimum and the curvature is positive, that is, the second derivative of the potential is positive

$$\text{At a minimum } r_e : \left. \frac{d^2E(r)}{dr^2} \right|_{r=r_e} > 0 \quad (2.7)$$

A transition state instead corresponds to a negative curvature or negative second derivative

$$\text{At a transition state } r^* : \left. \frac{d^2E(r)}{dr^2} \right|_{r=r^*} < 0 \quad (2.8)$$

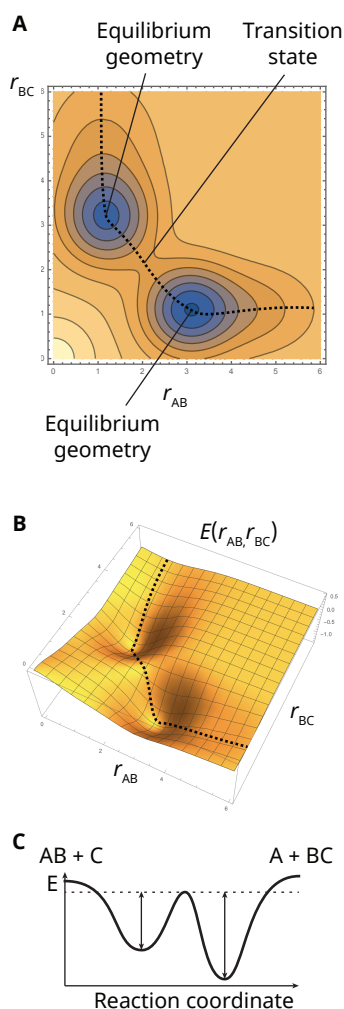
Plots **C** and **D** show two other scenarios in which the molecule AB is unstable. When there is transition state (**C**), then we call a molecule **metastable**, because it may be able to exist for a short amount of time before breaking down into A + B. If there is no transition state (**D**), then the molecule AB is unstable and the two atoms will seek to be as far as possible.

## 2.3 Potential energy surfaces of polyatomic molecules

More general potential energy surfaces are more difficult to visualize because the function  $E(\mathbf{R}_1, \mathbf{R}_2, \dots)$  corresponds to a high-dimensional hypersurface. For example, a molecule like  $\text{H}_3\text{CNO}$  has potential energy surface that is 14-dimensional (13 coordinates + energy). Thinking in 3D can already be challenging, and visualizing simple objects in 4D is already outside of the ability of most people, so think how complicated it would be to visualize a curve in 13 + 1 dimensions!

A much simpler case is that of a molecule with three atoms (ABC), which corresponds to a potential energy surface in four dimensions. This number comes from realizing that there are only three degrees of freedom that can change the molecular energy, the distances A-B and B-C, and the bond angle A-B-C. However, if we keep the angle A-B-C fixed at a given angle (for example,  $180^\circ$ ), then the resulting surface lives in only three dimensions and we can easily plot it. In this case, we can represent the potential energy surface with a contour map, in a way similar to topographic maps, which have two dimensions, and the third dimension is indicated by contour lines.

Fig. 2.3 shows the contour map for a hypothetical A-B-C system. From the PES, we can tell that there are two equilibrium structures that corresponds to energy minima. Of these two, the one with a short BC bond distance is more stable, and we would describe it as a BC molecule weakly interacting with A ( $\text{A}\cdots\text{B}-\text{C}$ ). The



**Fig. 2.3:** The potential energy surface for a linear triatomic molecule. **A** and **B** show the potential energy surface plotted using a contour plot and in 3D, respectively. A reaction path connecting  $A + BC$  to  $AB + C$  is shown, which goes through two local minima and one transition state. The energy profile for this reaction coordinate is shown in **C**.

second minimum (a local minimum) corresponds to the molecule  $AB$  weakly interacting with  $C$  ( $A-B \cdots C$ ). These two structures, are separated by a transition state  $A-B-C$ . These plots also show a the minimum energy reaction path that connects  $A + BC$  to  $AB + C$  and the corresponding energy potential. To go from  $A \cdots B-C$  to  $A-B \cdots C$ , the molecule has to overcome a reaction barrier. As you can see from the plot in **C**, the height of this barrier depends on the direction of the reaction.

## 2.4 Where are the bonds?

When we first encounter the concepts of BO approximation and potential energy surfaces, it is natural to try to embrace this new view with the help of concepts of bonding that we have acquired earlier. It is important to remember that bonds and atomic charges are interpretative concepts that are helpful to rationalize the behavior of molecules in chemistry, but do not correspond to well-defined quantum mechanical observables. By this we mean that there is no physical observable and a corresponding operator  $\hat{O}$  that we can directly link to the concepts of bonds and charges and use to extract these quantities from a quantum chemistry computation.

Therefore, it is important to be aware that when we solve the electronic Schrödinger equation of an hypothetical molecule like  $ABC$ , what we can control is only the position of the atoms  $A$ ,  $B$ , and  $C$ . This implies that we cannot computed the energy of a specific Lewis structure like  $A=B^+-C^-$  or  $A-B-C$ . However, once we specify a geometry and solve the electronic Schrödinger equation, we can then analyze the electronic wave function and try to attribute it to particular Lewis structure like  $A=B^+-C^-$  or  $A-B-C$ . This process is indicated schematically below

Specify geometry  $\rightarrow$  compute  $E(\mathbf{R})$  and  $\Psi_{\mathbf{R}}(\mathbf{r}) \rightarrow$  analyze  $\Psi_{\mathbf{R}}(\mathbf{r})$

## 2.5 Stationary points in polyatomic molecules

In the same way we characterized the stationary points of a diatomic molecule using the first and second derivatives of the potential energy curve, we can extend the same analysis to polyatomic molecules. A stationary point is similarly defined as a geometry  $\mathbf{R}^*$  at which **the partial derivatives with respect to all coordinates are zero**

$$\text{At a stationary point } \mathbf{R}^* : \left. \frac{\partial E(\mathbf{R}_1, \mathbf{R}_2, \dots)}{\partial \mathbf{R}_i} \right|_{\mathbf{R}=\mathbf{R}^*} = 0, \quad i = 1, \dots, N_{\text{atoms}} \quad (2.9)$$

To characterize the nature of a stationary point it is necessary to examine the curvature of the PES. In the case of a local or global minimum, the stationary point must have a positive curvature along any direction. Going back to the example in Fig. 2.3, you can see that both minima look like a 2D parabola (paraboloid), and moving away from the minimum always leads to an increase in energy.

Transition states are instead characterized by having at least one direction along which the curvature is negative (negative second derivative), while in any other orthogonal direction the curvature is positive. In the example in Fig. 2.3, at the transition state, the direction with negative curvature is a line along the dashed line.

We will come back to the question of how to characterize stationary points and give a more precise mathematical definition when we study vibrations in molecules.

## Summary

- ✎ The Born–Oppenheimer approximation separates the motion of electrons and nuclei to simplify the Schrödinger equation.
- ✎ The potential energy surface  $E(\mathbf{R})$  is the solution of the electronic Schrödinger equation at a fixed nuclear configuration  $\mathbf{R} \equiv (\mathbf{R}_1, \mathbf{R}_2, \dots)$ .
- ✎ The stationary points of the potential energy surface represent either stable molecular configurations (minima) or transition states (saddle points). These can be characterized by the curvature of the  $E(\mathbf{R})$  at a stationary point.