

10.1: The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of

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acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, $a = f/m$, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 1000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-yard dash against someone whose acceleration is a 1000 times greater than yours. That person could literally run circles around you. So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei aren't moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

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where

[Math Processing Error]

and

[Math Processing Error]

In Equation *[Math Processing Error]*, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. Bold-face type is used to represent that *[Math Processing Error]* and *[Math Processing Error]* are vectors specifying the positions of all the electrons and all the nuclei, respectively.

Exercise *[Math Processing Error]*

Define all the symbols in Equations *[Math Processing Error]* through *[Math Processing Error]*.

Exercise *[Math Processing Error]*

Explain why the factor of 1/2 appears in the last term in Equation *[Math Processing Error]*.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation *[Math Processing Error]*, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction *[Math Processing Error]* is found as a solution to the electronic Schrödinger equation:

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Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, *[Math Processing Error]*.

As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product the Born-Oppenheimer Approximation

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This product wavefunction is called the Born-Oppenheimer wavefunction. The function [Math Processing Error] is the vibrational wavefunction, which is a function of the nuclear coordinates [Math Processing Error] and depends upon both the vibrational and electronic quantum numbers or states, [Math Processing Error] and [Math Processing Error], respectively. The electronic function, [Math Processing Error], is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, [Math Processing Error]. Translational and rotational motion is not included here. The translational and rotational wavefunctions simply multiply the vibrational and electronic functions in Equation [Math Processing Error] to give the complete molecular wavefunction when the translational and rotational motions are not coupled to the vibrational and electronic motion.

Crude Born-Oppenheimer Approximation

In the *Crude Born-Oppenheimer Approximation*, [Math Processing Error] is set equal to [Math Processing Error], the equilibrium separation of the nuclei, and the electronic wavefunctions are taken to be the same for all positions of the nuclei.

The electronic energy, [Math Processing Error], in Equation [Math Processing Error] combines with the repulsive Coulomb energy of the two nuclei, to form the potential energy function that controls the nuclear motion as shown in Figure [Math Processing Error].

[Math Processing Error]

Consequently the Schrödinger equation for the vibrational motion is

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In Chapter 6, the potential energy was approximated as a harmonic potential depending on the displacement, [Math Processing Error], of the nuclei from their equilibrium positions.

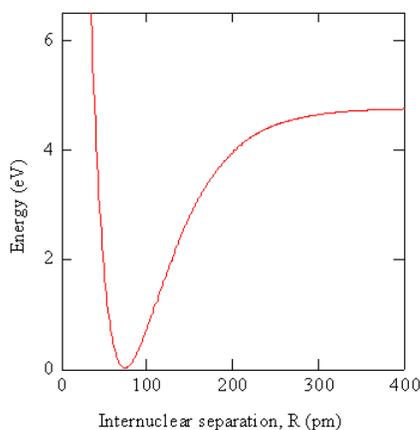


Figure [Math Processing Error]: The potential energy function for a diatomic molecule.

In practice the electronic Schrödinger equation is solved using approximations at particular values of [Math Processing Error] to obtain the wavefunctions [Math Processing Error] and potential energies [Math Processing Error]. The potential energies can be graphed as illustrated in Figure [Math Processing Error].

The graph in Figure [Math Processing Error] is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When [Math Processing Error] is very large there are two atoms that are weakly interacting. As [Math Processing Error] becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of [Math Processing Error], the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. Previously, we approximated this function by a harmonic potential to obtain the description of vibrational motion in terms of the harmonic oscillator model. Other approximate functional forms could be used as well, e.g. the Morse potential. The equilibrium position of the nuclei is where this function is a minimum, i.e. at [Math Processing Error]. If we obtain the wavefunction at [Math Processing Error]

Error], and use this function for all values of *[Math Processing Error]*, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise *[Math Processing Error]*

Relate Equation *[Math Processing Error]* to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Exercise *[Math Processing Error]*

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

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