

18.4: The Schrödinger Equation for a Molecule

Molecules are composed of atoms, and atoms are composed of nuclei and electrons. When we consider the internal motions of molecules, we have to consider the motions of a large number of charged particles with respect to one another. In principle, we can write down the potential function (the V in the Schrödinger equation) that describes the Coulomb's law based potential energy of the system of charged particles. In principle, we can then solve the Schrödinger equation and obtain a series of wavefunctions, $\psi_n(x)$, and their corresponding energies, E_n , that completely characterize the motions of the molecule's constituent particles. Each of the E_n is an energy value that the molecule can have. Often we say that it is an energy level that the molecule can occupy.

Since every distance between two charged particles is a variable in the Schrödinger equation, the number of variables increases dramatically as the size of the molecule increases. The two-particle hydrogen-atom problem has been solved analytically. For any chemical species larger than the hydrogen atom, only approximate solutions are possible. Nevertheless, approximate results can be obtained to very high accuracy. Greater accuracy comes at the expense of more extensive calculations.

Let us look briefly at the more fundamental approximations that are made. One is called the **Born-Oppenheimer approximation**; it states that the motions of the nuclei in a molecule are too slow to affect the motions of the electrons. This occurs because nuclei are much more massive than electrons. The Born-Oppenheimer approximation assumes that the electronic motions can be calculated as if the nuclei are fixed at their equilibrium positions without introducing significant error into the result. That is, there is an approximate wavefunction describing the motions of the electrons that is independent of a second wavefunction that describes the motions of the nuclei.

The mathematical description of the nuclear motions can be further simplified using additional approximations; we can separate the nuclear motions into translational, rotational, and vibrational modes. Translational motion is the three-dimensional displacement of an entire molecule. It can be described by specifying the motion of the molecule's center of mass. The motions of the constituent nuclei with respect to one another can be further subdivided: rotational motions change the orientation of the whole molecule in space; vibrational motions change distances between constituent nuclei.

The result is that the wavefunction for the molecule as a whole can be approximated as a product of a wavefunction ($\psi_{\text{electronic}}$ or ψ_e) for the electronic motions, a wavefunction ($\psi_{\text{vibration}}$ or ψ_v) for the vibrational motions, a wavefunction (ψ_{rotation} or ψ_r) for the rotational motions, and a wavefunction ($\psi_{\text{translation}}$ or ψ_t) for the translational motion of the center of mass. We can write

$$\psi_{\text{molecule}} = \psi_e \psi_v \psi_r \psi_t$$

(None of this is supposed to be obvious. We are merely describing the essential results of a considerably more extensive development.)

When we write the Hamiltonian for a molecule under the approximation that the electronic, vibrational, rotational, and translational motions are independent of each other, we find that the Hamiltonian is a sum of terms. In some of these terms, the only independent variables are those that specify the locations of the electrons. We call these variables electronic coordinates. Some of the remaining terms involve only vibrational coordinates, some involve only rotational coordinates, and some involve only translational coordinates. That is, we find that the Hamiltonian for the molecule can be expressed as a sum of terms, each of which is the Hamiltonian for one of the kinds of motion:

$$H_{\text{molecule}} = H_e + H_v + H_r + H_t$$

where we have again abbreviated the subscripts denoting the various categories of motion.

Consequently, when we write the Schrödinger equation for the molecule in this approximation, we have

$$\begin{aligned} H_{\text{molecule}} \psi_{\text{molecule}} &= (H_e + H_v + H_r + H_t) \psi_e \psi_v \psi_r \psi_t \\ &= \psi_v \psi_r \psi_t H_e \psi_e + \psi_e \psi_r \psi_t H_v \psi_v + \psi_e \psi_v \psi_t H_r \psi_r + \psi_e \psi_v \psi_r H_t \psi_t \\ &= \psi_v \psi_r \psi_t E_e \psi_e + \psi_e \psi_r \psi_t E_v \psi_v + \psi_e \psi_v \psi_t E_r \psi_r + \psi_e \psi_v \psi_r E_t \psi_t \\ &= (E_e + E_v + E_r + E_t) \psi_e \psi_v \psi_r \psi_t \end{aligned}$$

We find that the energy of the molecule as a whole is simply the sum of the energies associated with the several kinds of motion

$$E_{\text{molecule}} = E_e + E_v + E_r + E_t$$

ψ_t , ψ_v , ψ_r , and ψ_e can be further approximated as products of wavefunctions involving still smaller numbers of coordinates. We can have a component wavefunction for every distinguishable coordinate that describes a possible motion of a portion of the molecule. The three translational modes are independent of one another. It is a good approximation to assume that they are also independent of the rotational and vibrational modes. Frequently, it is a good approximation to assume that the vibrational and rotational modes are independent of one another. We can deduce the number of one-dimensional wavefunctions that are required to give an approximate wavefunction that describes all of the molecular motions, because this will be the same as the number of coordinates required to describe the nuclear motions. If we have a collection of N atoms that are not bonded to one another, each atom is free to move in three dimensions. The number of coordinates required to describe their motion is $3N$. When the same atoms are bonded to one another in a molecule, the total number of motions remains the same, but it becomes convenient to reorganize the way we describe them.

First, we recognize that the atomic nuclei in a molecule occupy positions that are approximately fixed relative to one another. Therefore, to a good approximation, the motion of the center of mass is independent of the way that the atoms move relative to one another or relative to the center of mass. It takes three coordinates to describe the motion of the center of mass, so there are $3N - 3$ coordinates left over after this is done.

The number of rotational motions available to a molecule depends upon the number of independent axes about which it can rotate. We can imagine a rotation of a molecule about any axis we choose. In general, in three dimensions, we can choose any three non-parallel axes and imagine that the molecule rotates about each of them independently of its rotation about the others. If we consider a set of more than three non-parallel axes, we find that any of the axes can be expressed as a combination of any three of the others. This means that the maximum number of independent rotational motions for the molecule as a whole is three.

If the molecule is linear, we can take the molecular axis as one of the axes of rotation. Most conveniently, we can then choose the other two axes to be perpendicular to the molecular axis and perpendicular to each other. However, rotation about the molecular axis does not change anything about the molecule's orientation in space. If the molecule is linear, rotation about the molecular axis is not a rotation at all! So, if the molecule is linear, only two coordinates are required to describe all of the rotational motions, and there are $3N - 5$ coordinates left over after we allocate those needed to describe the translational and rotational motions.

The coordinates left over after we describe the translational and rotational motions must be used to describe the motion of the atoms with respect to one another. These motions are called vibrations, and hence the number of coordinates needed to describe the vibrations of a non-linear molecule is $3N - 6$. For a linear molecule, $3N - 5$ coordinates are needed to describe the vibrations.

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