24.4: The Separable-modes molecular Model

At this point in our development, we have a theory that gives the thermodynamic properties of a polyatomic ideal gas molecule. To proceed, however, we must know the energy of every quantum state that is available to the molecule. There is more than one way to obtain this information. We will examine one important method—one that involves a further idealization of molecular behavior.

We have made great progress by using the ideal gas model, and as we have noted repeatedly, the essential feature of the ideal gas model is that there are no attractive or repulsive forces between its molecules. Now we assume that the molecule's translational, rotational, vibrational, and electronic motions are independent of one another. We could say that this idealization defines super-ideal gas molecules; not only does one molecule not interact with another molecule, an internal motion of one of these molecules does not interact with the other internal motions of the same molecule!

The approximation that a molecule's translational motion is independent of its rotational, vibrational, and electronic motions is usually excellent. The approximation that its intramolecular rotational, vibrational and electronic motions are also independent proves to be surprisingly good. Moreover, the very simple quantum mechanical systems that we describe in Chapter 18 prove to be surprisingly good models for the individual kinds of intramolecular motion. The remainder of this chapter illustrates these points.

In Chapter 18, we note that a molecule's wavefunction can be approximated as a product of a wavefunction for rotations, a wavefunction for vibrations, and a wavefunction for electronic motions. (As always, we are simply quoting quantum mechanical results that we make no effort to derive; we begin with the knowledge that the quantum mechanical problems have been solved and that the appropriate energy levels are available for our use.) Our goal is to see how we can apply the statistical mechanical results we have obtained to calculate the thermodynamic properties of ideal gases. To illustrate the essential features, we consider diatomic molecules. The same considerations apply to polyatomic molecules; there are additional complications, but none that introduce new principles.

For diatomic molecules, we need to consider the energy levels for translational motion in three dimensions, the energy levels for rotation in three dimensions, the energy levels for vibration along the inter-nuclear axis, and the electronic energy states.