22.5: Energy Levels for a Three-dimensional Harmonic Oscillator

One of the earliest applications of quantum mechanics was Einstein's demonstration that the union of statistical mechanics and quantum mechanics explains the temperature variation of the heat capacities of solid materials. In Section 7.14, we note that the heat capacities of solid materials approach zero as the temperature approaches absolute zero. We also review the law of Dulong and Petit, which describes the limiting heat capacity of many solid elements at high (ambient) temperatures. The Einstein model accounts for both of these observations.

The physical model underlying Einstein's development is that a monatomic solid consists of atoms vibrating about fixed points in a lattice. The particles of this solid are distinguishable from one another, because the location of each lattice point is uniquely specified. We suppose that the vibration of any one atom is independent of the vibrations of the other atoms in the lattice. We assume that the vibration results from a Hooke's Law restoring force

$$\overrightarrow{F} = -\lambda \overrightarrow{r} = -\lambda \left(x\, \overrightarrow{i} + y\, \overrightarrow{j} + z\, \overrightarrow{k} \right)$$

that is zero when the atom is at its lattice point, for which $\overrightarrow{r} = (0, 0, 0)$. The potential energy change when the atom, of mass m, is driven from its lattice point to the point $\overrightarrow{r} = (x, y, x)$ is

$$V = \int_{\overrightarrow{r} = \overrightarrow{0}}^{\overrightarrow{r}} -\overrightarrow{F} \bullet d\overrightarrow{r} = \lambda \int_{x=0}^{x} x dx + \lambda \int_{y=0}^{y} y dy + \lambda \int_{z=0}^{z} z dz = \lambda \frac{x^2}{2} + \lambda \frac{y^2}{2} + \lambda \frac{z^2}{2}$$

The Schrödinger equation for this motion is

$$-\frac{h^2}{8\pi^2 m} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] + \lambda \left[\frac{x^2}{2} + \frac{y^2}{2} + \frac{z^2}{2} \right] \psi = \epsilon \psi$$

where ψ is a function of the three displacement coordinates; that is $\psi = \psi(x, y, z)$. We assume that motions in the x-, y-, and z-directions are completely independent of one another. When we do so, it turns out that we can express the three-dimensional Schrödinger equation as the sum of three one-dimensional Schrödinger equations

$$\begin{aligned} &\left[-\frac{h^2}{8\pi^2 m} \frac{\partial^2 \psi_x}{\partial x^2} + \lambda \frac{x^2 \psi_x}{2} \right] \\ &+ \left[-\frac{h^2}{8\pi^2 m} \frac{\partial^2 \psi_y}{\partial y^2} + \lambda \frac{y^2 \psi_y}{2} \right] \\ &+ \left[-\frac{h^2}{8\pi^2 m} \frac{\partial^2 \psi_z}{\partial z^2} + \lambda \frac{z^2 \psi_z}{2} \right] \\ &= \epsilon\, \psi_x + \epsilon\, \psi_y + \epsilon\, \psi_z \end{aligned}$$

where any wavefunction $\psi_x^{(n)}$ is the same function as $\psi_y^{(n)}$ and $\psi_z^{(n)}$, and the corresponding energies $\epsilon_x^{(n)}$, $\epsilon_y^{(n)}$, and $\epsilon_z^{(n)}$ have the same values. The energy of the three-dimensional atomic motion is simply the sum of the energies for the three one-dimensional motions. That is,

$$\epsilon_{n,m,p} = \epsilon_x^{(n)} + \epsilon_y^{(m)} + \epsilon_z^{(p)},$$

which, for simplicity, we also write as

$$\epsilon_{n,m,p} = \epsilon_n + \epsilon_m + \epsilon_p.$$