# 14.1: The Harmonic Bath Hamiltonian

In the theory of chemical reactions, it is often possible to isolate a small number or even a single degree of freedom in the system that can be used to characterize the reaction. This degree of freedom is coupled to other degrees of freedom (for example, reactions often take place in solution). Isomerization or dissociation of a diatomic molecule in solution is an excellent example of this type of system. The degree of freedom of paramount interest is the distance between the two atoms of the molecule - this is the degree of freedom whose detailed dynamics we would like to elucidate. The dynamics of the "bath" or environment to which is couples is less interesting, but still must be accounted for in some manner. A model that has maintained a certain level of both popularity and success is the so called "harmonic bath" model, in which the environment to which the special degree(s) of freedom couple is replaced by an effective set of harmonic oscillators. We will examine this model for the case of a single degree of freedom of interest, which we will designate $q$. For the case of the isomerizing or dissociating diatomic, $q$ could be the coordinate $r - \langle r \rangle$, where $r$ is the distance between the atoms. The particular definition of $q$ ensures that $\langle q \rangle = 0$. The degree of freedom $q$ is assumed to couple to the bath linearly, giving a Hamiltonian of the form

$$H = \frac{p^2}{2m} + \phi(q) + \sum_{\alpha} \left[ \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 \left( x_{\alpha} + \frac{g_{\alpha}}{m_{\alpha} \omega_{\alpha}^2} q \right)^2 \right]$$

where the index $\alpha$ runs over all the bath degrees of freedom, $\omega_{\alpha}$ are the harmonic bath frequencies, $m_{\alpha}$ are the harmonic bath masses, and $g_{\alpha}$ are the coupling constants between the bath and the coordinate $q$. $p$ is a momentum conjugate to $q$, and $m$ is the mass associated with this degree of freedom (e.g., the reduced mass $\mu$ in the case of a diatomic). The coordinate $q$ is assumed to be subject to a potential $\phi(q)$ as well (e.g., an internal bond potential). The form of the coupling between the system ( $q$ ) and the bath ($x_{\alpha}$) is known as *bilinear*.

Below, using a completely classical treatment of this Hamiltonian, we will derive an equation for the detailed dynamics of $q$ alone. This equation is known as the **generalized Langevin equation** (GLE).