3.3: Vibration/Rotation States for Each Electronic Surface

The BO picture is what gives rise to the concept of a manifold of potential energy surfaces on which vibrational/rotational motions occur.

Even within the BO approximation, motion of the nuclei on the various electronic energy surfaces is different because the nature of the chemical bonding differs from surface to surface. That is, the vibrational/rotational motion on the ground-state surface is certainly not the same as on one of the excited-state surfaces. However, there are a complete set of wavefunctions $Xi^0_{j,m}(R)$ and energy levels $E^0_{j,m}$ for **each** surface $E_j(R)T + E_j(R)$ is a Hermitian operator in R-space for each surface (labelled j):

$$[T + E_j(R)]\Xi^0_{j,m}(R) = E^0_{j,m}\Xi^0_{j,m}.$$

The eigenvalues $E^0_{j,m}$ must be labelled by the electronic surface (j) on which the motion occurs as well as to denote the particular state (m) on that surface.