Case where Reaction Hypersurface Depends on Rotational Constants of the Motion

In some reactions, the equation of the reaction hypersurface may depend on constants of the motion, in particular on the angular momentum. Several examples are some unimolecular dissociations, radical recombinations,[16] and ion-molecule reactions.[17] For example, the reactants in the two latter reactions have been treated as two particles which, in the activated complex, have their mutually attractive force balanced by their centrifugal force. The attraction was attributed to induced dipole-induced dipole forces in the recombination and to ion-induced dipole forces in the ion-molecule system. The centrifugal force was calculated by treating the pair of reactants as a "diatomic" activated complex.

The above treatments were based on the assumption that the reaction hypersurface is the set of coordinates for which the attractive force equals in magnitude the repulsive centrifugal force between the two particles. This set depends on the angular momentum. In these and other reactions this "diatomic" approximation is readily imposed on the treatment of the previous section, when an angular momentum dependence of the reaction hypersurface is to be considered: For a given angular momentum of the complex in any infinitesimal range the contribution to the overall reaction rate can be calculated. One may then integrate over all angular momenta. The result will emerge as a special case of the "symmetric top" approximation treated below, and its derivation will be omitted for that reason. (The derivation parallels the one below, but the angle ψ and the conjugate momentum p_ψ are omitted, and the "bar" subspace is one dimension larger.)