For a diatomic species, the vibration-rotation \( \left( \dfrac{V}{R} \right) \) kinetic energy operator can be expressed as follows in terms of the bond length \( R \) and the angles \( \theta \) and \( \phi \) that describe the orientation of the bond axis relative to a laboratory-fixed coordinate system:

\[
\begin{align*}
T_{V/R} &= \dfrac{-\hbar^2}{2\mu} \left[ \dfrac{1}{R^2} \dfrac{\partial}{\partial R} \left( R^2 \dfrac{\partial}{\partial R} \right) - \dfrac{L(L+1)}{R^2\hbar^2} \right], \\
L^2 &= \hbar^2 \left[ \dfrac{1}{\sin \theta} \dfrac{\partial}{\partial \theta} \left( \sin \theta \dfrac{\partial}{\partial \theta} \right) + \dfrac{1}{\sin^2 \theta} \dfrac{\partial^2}{\partial \phi^2} \right].
\end{align*}
\]

where the square of the rotational angular momentum of the diatomic species is

\[
\begin{align*}
L^2 &= \hbar^2 \dfrac{1}{\sin \theta} \dfrac{\partial}{\partial \theta} \left( \sin \theta \dfrac{\partial}{\partial \theta} \right) + \dfrac{1}{\sin^2 \theta} \dfrac{\partial^2}{\partial \phi^2},
\end{align*}
\]

Because the potential \( E_j(R) \) depends on \( R \) but not on \( \theta \) or \( \phi \), the \( \dfrac{V}{R} \) function \( \chi^0_{j,m} \) can be written as a product of an angular part and an \( R \)-dependent part; moreover, because \( L^2 \) contains the full angle-dependence of \( T_{V/R} \), \( \chi^0_{j,m} \) can be written as

\[
\chi^0_{j,m} = Y_{J,M}(\theta,\phi)F_{j,J,v}(R).
\]

The general subscript \( n \), which had represented the state in the full set of 3M-3 \( R \)-space coordinates, is replaced by the three quantum numbers \( J,M, \) and \( v \) (i.e., once one focuses on the three specific coordinates \( R, \theta, \phi \), a total of three quantum numbers arise in place of the symbol \( n \)).

Substituting this product form for \( \chi^0_{j,m} \) into the \( \dfrac{V}{R} \) equation gives:

\[
\begin{align*}
\dfrac{-\hbar^2}{2\mu} \left[ \dfrac{1}{R^2} \dfrac{\partial}{\partial R} \left( R^2 \dfrac{\partial}{\partial R} \right) - \dfrac{J(J+1)}{R^2\hbar^2} \right] F_{j,J,v}(R) + E_j(R)F_{j,J,v}(R) &= E^0_{j,J,v}F_{j,J,v},
\end{align*}
\]

as the equation for the vibrational (i.e., \( R \)-dependent) wavefunction within electronic state \( j \) and with the species rotating with \( L(J+1) \) \( \hbar \) as the square of the total angular momentum and a projection along the laboratory-fixed \( Z \)-axis of \( M\hbar \). The fact that the \( \chi^0_{j,J,v} \) functions do not depend on the \( M \) quantum number derives from the fact that the \( T_{V/R} \) kinetic energy operator does not explicitly contain \( J_Z \); only \( J(J+1) \) appears in \( T_{V/R} \).

The solutions for which \( J=0 \) correspond to vibrational states in which the species has no rotational energy; they obey

\[
\begin{align*}
\dfrac{-\hbar^2}{2\mu} \dfrac{\partial}{\partial R} \dfrac{\partial}{\partial R} \chi_{j,0,v}(R) + E_j(R) \chi_{j,0,v}(R) &= E^0_{j,0,v}\chi_{j,0,v},
\end{align*}
\]

The differential-operator parts of this equation can be simplified somewhat by substituting \( F = \dfrac{\chi}{R} \) and thus obtaining the following equation for the new function \( \chi \):

\[
\begin{align*}
\chi_{j,0,v}(R) + E_j(R) \chi_{j,0,v}(R) &= E^0_{j,0,v}\chi_{j,0,v}.
\end{align*}
\]
Solutions for which $J \neq 0$ require the vibrational wavefunction and energy to respond to the presence of the 'centrifugal potential' given by $\frac{\hbar^2 J(J+1)}{2 \mu R^2}$; these solutions obey the full coupled V/R equations given above.

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