Quantum numbers for diatomic molecules

The quantum state of an atom is defined by the quantum numbers L, M_L, S, M_S, and J, M_J, which define the magnitudes and z projections of the orbital, spin, and total angular momentum, respectively. In the case of an atom, the angular momenta are entirely electronic in origin. This is not true in a diatomic molecule, which may also have angular momentum associated with rotation of the nuclear framework. In addition, the potential energy term in the Hamiltonian for an atom is spherically symmetric, while this term in the Hamiltonian for a diatomic molecule has only cylindrical symmetry about the bond axis.

A consequence of the reduction in symmetry is that the Hamiltonian no longer commutes with the $\hat{L}^2$ operator, so that L is no longer a 'good' quantum number, i.e. $\hat{H}$ and $\hat{L}^2$ no longer share eigenstates, and the eigenvalues of $\hat{L}^2$ do not remain constant with time. Another way of thinking about this is to consider the two different types of angular momentum in a diatomic molecule. The molecule can rotate about a direction perpendicular to the bond axis, and this motion is quantised by the angular momentum quantum number N. The molecule also possesses electronic angular momentum $\boldsymbol{L}$, and these two angular momenta couple to give the total angular momentum $\boldsymbol{J}$. Only the total angular momentum has to be conserved, and it is the accompanying quantum number, J, that is generally referred to as the "rotational quantum number" for a diatomic molecule. In a closed-shell molecule, in which there are no unpaired electrons and $L=0$, the total angular momentum $\boldsymbol{J}$ is entirely rotational in character. However, in an open shell molecule there will also be an electronic contribution. In this case the coupling between $\boldsymbol{N}$ and $\boldsymbol{L}$ means that the two angular momenta are not conserved separately, even though their sum $\boldsymbol{J}$ is conserved. In addition, because $\boldsymbol{N}$ must lie perpendicular to the bond axis for a diatomic, only $\boldsymbol{L}$ can have a component along the bond axis. The z components of $\boldsymbol{J}$ and $\boldsymbol{L}$ are therefore the same, which means that L_z *is* conserved in time and M_L is therefore a good quantum number with which to describe the electronic contribution to the total angular momentum. Since the energy of the system is the same regardless of whether the projection is positive or negative, we usually use the quantum number $\Lambda = |M_L|$, i.e the absolute value of M_L. We can also define two further quantum numbers, $\Sigma = |M_S|$ and $\Omega = \Sigma + \Lambda$, which describe the projections of the spin angular momentum and total electronic angular momentum, respectively, onto the internuclear axis.

The precessional motion of $\boldsymbol{L}$, $\boldsymbol{S}$, and $\boldsymbol{N}$ about the total angular momentum $\boldsymbol{J}$ is treated in different ways for different molecules, depending on the relative strengths of the various couplings. The different cases are known as "Hund's cases". Further details of these coupling cases, together with vector diagrams of the precessional motion about $\boldsymbol{J}$ in each case, can be found in advanced textbooks on the spectroscopy of diatomic molecules. For example:

Gerhard Herzberg: *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules*
John M. Brown and Alan Carrington: *Rotational Spectroscopy of Diatomic Molecules*