Based entirely on symmetry arguments, it is shown that spatially equivalent atoms in a rigid molecule are totally equivalent only if they are related to one another by a center of inversion. This is a general condition that is independent of the level of approximation used in deriving the molecular Hamiltonian. Therefore, while a molecule can have a large number of spatially equivalent atoms, totally equivalent ones can only exist in pairs. The overall symmetries of molecules that cannot possess any totally equivalent atoms are identified. It is also shown that in the presence of an electric field a molecule cannot have any atoms that are totally equivalent.