LMFIT: Symmetry Considerations

We denote the components of the elements of the dipole matrix by

$$\mu_{ija}(\boldsymbol{Q}) = \left\langle \Phi_i \left| \frac{\partial \hat{H}_{el}}{\partial \epsilon_a} \right| \Phi_j \right\rangle ; \quad a = x, y, z, \tag{1}$$

where ϵ_a represents a component of the electric field vector. The parameters entering into the LMFIT models for these surfaces are the derivatives of these terms at the reference geometry $\boldsymbol{Q}_0$ with respect to the M nuclear coordinates, which we write as

$$\tau^{(i,j,a)}_{n_1,n_2,\ldots,n_M} = \left. \frac{\partial^N \mu_{ija}}{\partial^{n_1} Q_1 \partial^{n_2} Q_2 \cdots \partial^{n_M} Q_M} \right|_{\boldsymbol{Q}_0} ; \quad N = \sum_{\alpha=1}^{M} n_\alpha. \tag{2}$$

By simple group theoretical arguments, a given parameter can only be non-zero according to the following criterion:

$$\tau^{(i,j,a)}_{n_1,n_2,\ldots,n_M} \neq 0, \quad \left\{ \bigotimes_{\alpha=1}^{M} (\Gamma^\alpha)^{n_\alpha} \right\} \otimes \Gamma^i \otimes \Gamma^j \otimes \Gamma^a \ni \Gamma^1, \tag{3}$$

where Γ^1 is the totally symmetric irreducible representation of the point group of the molecule at $\boldsymbol{Q}_0$, and Γ^α, Γ^i and Γ^a are, respectively, the representations generated by the mode Q_α, the state $|\Phi_i\rangle$, and the unit vector pointing along the a-direction.

Similarly, for a parameter

$$\rho^{(i,j,a,b)}_{n_1,n_2,\ldots,n_M} = \left. \frac{\partial^N \alpha_{ijab}}{\partial^{n_1} Q_1 \partial^{n_2} Q_2 \cdots \partial^{n_M} Q_M} \right|_{\boldsymbol{Q}_0} ; \quad N = \sum_{\alpha=1}^{M} n_\alpha \tag{4}$$

entering into the expansion of the element

$$\alpha_{ijab} = \left\langle \Phi_i \left| \frac{\partial \hat{H}_{el}}{\partial \epsilon_a \partial \epsilon_b} \right| \Phi_j \right\rangle ; \quad a, b = x, y, z \tag{5}$$

of the polarisability tensor to be non-zero, the necessary, but not sufficient, condition reads

$$\rho^{(i,j,a,b)}_{n_1,n_2,\ldots,n_M} \neq 0, \qquad \left\{ \bigotimes_{\alpha=1}^{M} (\Gamma^{\alpha})^{n_\alpha} \right\} \otimes \Gamma^i \otimes \Gamma^j \otimes \Gamma^a \otimes \Gamma^b \ni \Gamma^1. \tag{6}$$

For the Abelian point groups, the decomposition of the direct products $\left\{ \bigotimes_{\alpha=1}^{M} (\Gamma^{\alpha})^{n_\alpha} \right\} \otimes \Gamma^i \otimes \Gamma^j \otimes \Gamma^a$ and $\left\{ \bigotimes_{\alpha=1}^{M} (\Gamma^{\alpha})^{n_\alpha} \right\} \otimes \Gamma^i \otimes \Gamma^j \otimes \Gamma^a \otimes \Gamma^b$ is carried out by the LMFIT program and requires only the specification by the user of the state symmetries and the symmetries of the unit vectors pointing along the $x-$, $y-$, and z-directions. If the point group of the molecule is non-Abelian, then the highest Abelian subgroup must be used.