The Extended Curl Equation

The extended Curl equation reads

$$F_{\alpha\beta jk} = \frac{\partial \tau_{\alpha jk}}{\partial q_\beta} - \frac{\partial \tau_{\beta jk}}{\partial q_\alpha} - \left[(\tau_\alpha \tau_\beta)_{jk} - (\tau_\beta \tau_\alpha)_{jk} \right], \tag{1}$$

where the $\tau_{\alpha jk}$ are the the derivative coupling terms,

$$\tau_{\alpha jk} = \left\langle \psi_j \left| \frac{\partial}{\partial q_\alpha} \right| \psi_k \right\rangle, \tag{2}$$

defined with respect to the (Cartesian) nuclear coordinates q_α and the adiabatic electronic states $|\psi_k\rangle$, and the $F_{\alpha\beta jk}$ are the components of the so-called gauge field tensor $\mathbf{F}$.

For a complete Hilbert space of electronic states, the gauge field tensor is identically zero. We, however, always work with a finite, N-dimensional Hilbert subspace of states $\{|\psi_k\rangle\}\,; k = 1, .., N$, the P-space, whose orthogonal complement is termed the Q-space. If we take the derivative coupling terms that couple the P-space and Q-space states to be of the order $O(\epsilon)$,

$$\tau_{\alpha jk} \simeq O(\epsilon) \quad ; j \leq N, k > N, \tag{3}$$

then the components of $\mathbf{F}$ will be of the order $O(\epsilon^2)$. Evaluation of the extended Curl equation may thus be used as a diagnostic of whether a set of electronic states constitutes a Hilbert subspace.