EXCITATION OF COUPLED ELECTRONIC STATES

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Coupled molecular electronic states are responsible for many complex features in observed spectra. For example, Rydberg-valence interactions are well known to cause significant anomalies in the photoabsorption spectra of O_2, NO and N_2.[a] It is possible to explain such complexity using a coupled-channel Schrödinger equation (CSE) model based on the techniques of atomic scattering theory.[b] Such a model indicates that dramatic changes to the appearance of the optical spectrum occur when the relative magnitudes of the transition moments into the coupled states are altered.

We extend the CSE model to describe non-optical processes such as dissociative charge transfer (DCT) and electron energy loss (EEL) spectra merely by changing the transition moments to reflect the changed excitation mechanism. The dramatic changes in EEL spectra for allowed transitions into coupled states as the scattering conditions are changed can be easily explained by introducing the concept of a generalized transition moment.[c]

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[a] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).

[b] F. H. Mies, Mol. Phys. **14**, 953-972 (1980).

[c] M. Dillon, M. Kimura, R. J. Buenker, G. Hirsch, Y. Li, and L. Chantranupong, J. Chem. Phys. **102**, 1561-1568 (1995).