DIABATIC VALENCE-HOLE STATES

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Diatomic molecules are fundamental in shaping our intuitive understanding of electronic structure theory. Despite their structural simplicity, chemical binding mechanisms (i.e., from R_e to dissociation) are well understood only for a few lowest energy electronic states, even for the C/N/O diatomic species. Pervasive configuration interactions and lumpy adiabatic potentials are prominent features of most electronically excited states. Interpretation of energy level structure and spectroscopic patterns becomes increasingly challenging for these higher energy states, because of the reduced utility of simple concepts such as bond order and correlation diagrams.

In this work, a global diabatization scheme, based on the valence-hole concept, is used to model the extensive web of avoided-crossing patterns in the electronically excited states of the CN ($^2\Sigma$), N_2 ($^1\Pi_u$, $^3\Pi_u$), Si_2 ($^3\Pi_g$), and SiC ($^3\Pi$) molecules. The validity of this diabatization scheme will be further demonstrated by its ability to reproduce the unusual energy level structure and predissociation dynamics of the extensively studied CN $^2\Sigma$ and N_2 $^3\Pi_u$ electronic states. As we have previously demonstrated with C_2 ($^1\Pi_g$, $^3\Pi_g$, $^1\Sigma_u^+$, $^3\Sigma_u^+$), the key concept of the model is the existence of valence-hole configurations that derive from an electron promotion from the nominally anti-bonding $2\sigma_u$ molecular orbital, i.e., $3\sigma_g(5\sigma) \leftarrow 2\sigma_u(4\sigma)$ for C_2, Si_2, CN, and SiC, and $1\pi_g \leftarrow 2\sigma_u$ for N_2. These valence-hole configurations have a nominal bond order of 3 or higher and correlate with separated-atom configurations with a 2p←2s promotion in one of the atomic constituents. The strongly-bound diabatic valence-hole state crosses multiple weakly-bound or repulsive states that are composed of electron configurations with a $2\sigma_g^2 2\sigma_u^2$ valence-core. These curve-crossings of diabatic potential curves result in an interconnected network of many avoided-crossings among multiple electronic states. Considering their systematic, disruptive impact on the global electronic structure and unimolecular dynamics, the valence-hole states should be treated as an integral part of our intuitive electronic structure model, along with familiar concepts such as Rydberg and ionic states.