DIABATIC VALENCE-HOLE STATES IN THE C_2 MOLECULE: "PUTTING HUMPTY DUMPTY TOGETHER AGAIN"

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Each of the six C,N,O diatomic molecules has a unique role in shaping our intuitive understanding of electronic structure theory. In this work, the pathologically pervasive configuration interactions that occur in four electronic symmetry manifolds ($^1\Pi_g$, $^3\Pi_g$, $^1\Sigma_u^+$, and $^3\Sigma_u^+$) of the C_2 molecule are disentangled by a global multi-state diabatization scheme. The key concept of our model is the existence of two "valence-hole" configurations, $2\sigma_g^2 2\sigma_u^1 2\pi_u^3 3\sigma_g^2$ ($^{1,3}\Pi_g$) and $2\sigma_g^2 2\sigma_u^1 2\pi_u^4 3\sigma_g^1$ ($^{1,3}\Sigma_u^+$) that derive from a $3\sigma_g \leftarrow 2\sigma_u$ electron promotion. The lowest energy state from each of the four C_2 symmetry species is dominated by this type of valence-hole configuration at its equilibrium internuclear separation. These valence-hole configurations have a nominal bond order of 3 and correlate with the $2s^2 2p^2$+$2s2p^3$ separated-atom configurations. Facilitated by chemical intuition, the diabatic picture uncovers the disruptive impact of the valence-hole configurations on the global electronic structure and unimolecular dynamics of C_2. In each of the four symmetry manifolds studied in this work, the strongly-bound diabatic valence-hole state, the energy of which starts low and ends high, crosses multiple weakly-bound and repulsive states that are composed of electron configurations with a $2\sigma_g^2 2\sigma_u^2$ valence-core. These diabatic crossings result in an extensive, interconnected network of avoided-crossings among the low-lying electronic states of C_2. The C_2 molecule behaves "badly", yet its secrets are revealed by diabatic modeling of their lumpy adiabatic potentials and broken spectroscopic patterns. Based on our demonstration of the importance of valence-hole configurations in C_2, we propose a diabatic model re-analysis of similar interactions in the other second-row diatomic molecules, for which the valence-hole states are expected to have a similar impact on their global electronic structure.