Decimating Covalency Gives Rise to Inverted Ionic Bonding in Non-metallic Heterodiatomic Molecules

Ishita Bhattacharjee, Debashree Ghosh, Ankan Paul*

School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata, India

The unexpected claim of the presence of a quadruple bond in C_2 from the Valence Bond community triggered a rather prolonged debate within the electronic structure community [1]. The standard tools for estimating bond orders based on MO techniques predict a lower number of bonds in C_2 [2]. We have formulated an approach for determining the number of bonds in the ground state of a diatomic molecule based on specific signatures of Potential Energy Curves(PECs) of a spin ladder of $^{2S+1}\sum_{u/g}$ states generated from electron excitation from the bonding to the corresponding anti-bonding orbitals [3]. We proposed that the presence of a purely dissociative PEC at the CASSCF/ MRCI levels of theory at the N^{th} spin state (i.e. the eigenvalue of the S^2 operator, 2S+1) is held as an indicator of (N-1)/2 number of bonds in the ground state of the diatomic. This approach predicted the presence of a quadruple bond in C_2. I will show that this approach can be used to determine the number of bonds in 2^{nd} and 3^{rd} period hetero/homo diatomic systems. Surprisingly, for hetero-diatomic systems we observe the universal presence of a bound $\sum$ state beyond the purely dissociative $\sum$ state, where the bound state exhibits the presence of an inverted pure ionic bond with the less electronegative element with a discrete negative charge and the more electronegative atom with a positive charge. The implications of the nature of the PECs along with the ionic bond in non-metallic diatomic molecules will also be discussed.

References:

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