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## One-electron bonds from the quantum interference perspective

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**Abstract:** The valence bond-like picture of the chemical bond is deeply rooted into the qualitative general chemistry framework and electron-pair covalent bonds are often considered as the “standard” chemical bond. Conversely, odd-electron and multicenter bonds are seen as anomalous, unrepresentative, or just different types of bonds. In this work, the powerful Interference Energy Analysis (IEA) approach provided by the Generalized Product Function Energy Partitioning method (GPF-EP)[1] was extended to treat two-center one-electron bonds, by means of the Spin Coupled Valence Bond wave function for N electrons in M orbitals, SCVB(N,M) [2]. The bond in several sets of analogous molecules ( $H_2^+/H_2$ ), ( $Li_2^+/Li_2$ ), ( $Na_2^+/Na_2$ ), ( $LiNa^+/LiNa$ ), ( $K_2^+/K_2$ ), ( $LiH^+/LiH$ ), ( $Cu_2^+/Cu_2$ ), ( $H_3C\cdot CH_3^+/H_3CCH_3/H_3C\cdot BH_3$ ), ( $H_2C\cdot CH_2^+/H_2CCH_2/H_2CBH_2/H_2BBH_2^-$ ), as well as for  $[(H_3P)_3Cu\cdot BH_3]$ , were analyzed by the GPF-EP method. The components of the energy accounting for the formation of the bond were evaluated and the results for the analogous cases of the one-electron and the conventional two-electron bonds were compared.

The result of the GPF-EP analysis clearly shows that one-electron bonds have the same mechanism of formation as the regular covalent bonds. In other words, the same phenomenon, quantum interference, rules the stabilization of systems containing such bonds. In all cases studied, the chemical bond occurs because of the concentration of density in the bond region, and the drop in interference kinetic energy. By comparing the cases of one-electron bonds with two-electron bonds in correspondent molecules, calculations have shown that the largest differences in energy are due to quasi-classical factors, mostly the reference electron-electron potential. The case of the alkali metal dimers is different, because of the high polarizability of the atoms involved in bonding. Normally, one-electron bonds have lower bond dissociation energies (BDEs) than the correspondent two-electron bonds. This fact, however, has no relation with bond order – one-electron bonds are not “half-bonds”. Since the interference is the dominant factor for the formation of the bond and interference depends basically on the orbital overlaps, if the orbitals involved in bonding are similar in both cases, the difference has to come from the quasi-classical part. Even the case of the alkali metal dimers, whose cations have higher BDEs than the neutral molecules, can be explained by quasi-classical factors. In conclusion, there is no distinction between one- and two-electron bonds from the conceptual point of view, since they both result from the same phenomenon. This work opens perspectives for the study of other bonding systems, like three-electron two-center bonds and, in general, multicenter bonds.



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**References:**

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