

## A Study of Charge-Shift Bonding using Valence Bond Theory

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Charge shift (CS) bonds have been defined as bonds that are neither ionic nor covalent. The majority of the bonding energy in CS bonds comes from ionic-covalent resonance mixing. Hetero- and homonuclear combinations of -H, -CH<sub>3</sub>, -NH<sub>2</sub>, -OH, and -F were studied to analyze CS character of the bonds. Substituent effects were studied by observing changes in CS character after the addition of -H, -CH<sub>3</sub>, -NH<sub>2</sub>, -OH, and -F in non-bonding regions. The geometries of all 75 molecules were optimized at the B3LYP/6-31G(d,p) level using Gaussian 03. Breathing Orbital Valence Bond (BOVB) calculations were then carried out at the B3LYP/6-31G(d,p) optimized geometries in order to determine CS character. It was observed that the resonance energy of each bond could be split into two parts. The first part is due to electrostatics and can be related to the difference in electronegativities. The second part is due to CS and can be related to the sum of electronegativities.

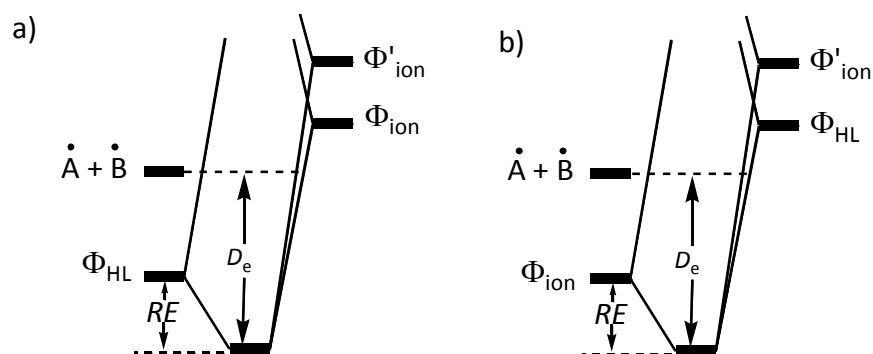


Figure 1. VB mixing diagrams for (a) purely covalent and (b) purely ionic bonds.