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Theoretical and Computational Description of Equivalent Chemical Bonds

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Abstract: The chemical bond is a unifying concept that is widely employed in explaining and rationalizing many aspects related to the reactivity, selectivity and characterization of the different physical and chemical properties of molecules, substances and materials[1]. However, because it is not an observable it has been the source of debates and disputes, remaining a challenge to theoretical and computational chemistry[1]. One source of problems has been the approximations employed in the description of the chemical bond, particularly the orbital model or independent (quasi-)particle approximation. This leads to some apparent contradictions when applied to molecular spectroscopy of symmetric molecules such as angular AH_2 and tetrahedral AH_4. In these molecules, the A−H bonds are equivalent with the lengths, strengths and energies (degenerate), which lead to difficulties when describing the symmetric and antisymmetric stretches in their vibrational spectra as well as the presence of two peaks in the valence region of their photoelectron spectra. These have caused several erroneous conclusions and misconceptions regarding approximate theories and models used to describe the chemical bonds in these molecules. We propose to include the interactions between these equivalent bonds as a step towards solving these conceptual problems and allowing qualitative and quantitative interpretation of spectroscopic data. These interactions are treated as perturbations and the solution of the secular determinant within first-order perturbation theory for degenerate states provides the (partial) removal of degeneracy of the bond energies. In addition, this separation between the states is proportional to the strength of the perturbation, which can be related to chemical properties such as the bond pair-bond pair interaction. As result, the photoelectron and vibrational spectra of symmetric molecules can be explained within the scope of interacting equivalent and independent bonds.

In the vibrational spectra, the perturbation strength is proportional to the frequency difference between the symmetric and antisymmetric normal modes, which can be related to the coupling between the oscillators due to the removal of translational and rotational degrees of freedom. Thus, the perturbation represents the requirement for the center of mass of the molecule to remain unchanged during a vibration. Whereas, the peak separations in the valence region of photoelectron spectra represent the strengths of the interactions between the electron pairs in each chemical bond. Thus, this

approach may provide quantitative data for the valence shell electron pair repulsion (VSEPR) theory.

Quantum chemical methods (MP2 and DFT) were used to calculate the vibrational frequencies of symmetric molecules with different isotopes in order to correlate the reduced masses with the difference between the antisymmetric and symmetric wavenumbers Δ_{as}. For methane (CH_4) a linear relationship between Δ_{as} and the inverse of the square-root of the carbon isotope mass was found, where the slope depends upon the hydrogen isotope mass employed. This analysis is being extended to other symmetric angular, pyramidal and tetrahedral molecules and a theoretical foundation for this relationship is being developed.

The valence ionization energies (IEs) of molecules with equivalent bonds were calculated with electron propagator methods and provided the difference between the IEs, Δ_{IE}, which should be related to the bond-bond electron repulsion. The chemical bond overlap model (BOM) has been generalized and implemented with localized molecular orbitals, allowing the efficient treatment of polyatomic molecules[2]. BOM provides the overlap contributions for several properties of each chemical bond in a molecule such as charge density (ρ_{OP}) and polarizability (α_{OP}). In addition, numerical integration yields the Coulomb repulsion (J_{inter}) between the overlap charge densities of each pair of bonds. Some trends were observed between Δ_{IE} and overlap properties (ρ_{OP}, J_{inter}) and preliminary analyses show (semi-)quantitative correlations. However, the calculations of Δ_{IE} need to be improved, because the comparisons with available experimental Δ_{IE}´s indicate large non-systematic errors.

The proposed model based on perturbation theory for degenerate states is simple and can provide a unifying description of chemical bonds as well as yield quantitative results for important chemical properties or descriptors.

Key-words: chemical bond; perturbation theory; equivalent; interacting bonds.

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