

2B3a

The field theoretical study of chemical interaction in terms of the Rigged QED: new reactivity indices.

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How the mode of bonding affects stability and reactivity of molecule on the frame of nonrelativistic limit of Rigged Quantum Electrodynamics using new indices for description of bond properties related to bond orders have been characterized here. These indices are in close relation with tensorial interpretation of bond that among others allows discriminating covalent bonds using spindle structure concept. The real three-dimensional space representation of new interaction energy density utilized in this study contribute to better understanding of interaction phenomena between atoms and molecules. The differences in reactivity and stabilities of molecules have their root in the redistribution of interaction energy density.

Lagrange point is the characteristic point of bond line that may represent bond properties using energy density data. The total energy density (calculated as the trace of stress tensor) is in close association with electronic and chemical properties of molecules. It is possible to characterize interactions and to evaluate their strengths and energy based bond orders using the energy density related indices. The correspondence of b_e , b_μ and $b_{\Delta e}$ indices describing reactivity with standard bond energies was found and only small basis set and immaterial method dependency of these indices have been inferred. However single point is not enough for full characterization of bonding interactions. The three-dimensional insight is much more informative. The differences in the redistribution of interaction energy densities are in close relation with activity of given molecule. The new indices, although reflect traditional bond orders, are carrying different information about interactions on the interfaces of quantum chemical subsystems. Our indices satisfy the earlier definition of bond order (by IUPAC) as “index of the degree of bonding between two atoms relative to that of a single bond”. The bond order is provided by energy density associated with localized electron density, as the combined effect of all occupied molecular orbitals (which in some part corresponds also to molecular-orbital bond order definition). Since electronic energy density includes the electronic spin angular momentum in the underling physics, so does the energy density based bond order. However depending on the specific information one may use either one or all new indices to characterize molecules and chemical interactions. Since energy density is in close association with electron density the b_e index express bonding in terms of electronic energy at chemical systems boundaries. The b_e index defines new energy-weighted bond order, sometimes different from commonly used one, however very useful for evaluation of interaction strength. The b_μ index is associated with local chemical potential of bonded atoms that is the potential of electrons to undergo physical or chemical change in the system. The competition between stabilization energy (reflected by $b_{\Delta e}$ index) and chemical potential explains reactivity and spontaneous tendency of atoms to disperse in hunt for maximum entropy.

The energy densities [au/bohr³] at Lagrange point for five highest occupied Molecular Orbitals of three “triple” bonded molecules. The core means sum of energy densities at Lagrange point of core MO's. The valance electron's orbitals: σ - is sigma bonding MO, σ^* - sigma antibonding MO, π - degenerated pi bonding MO.

MO	N ₂	C ₂ H ₂ ^(c-o)	P ₂	
π (HOMO)	-0.3174	-0.1440	-0.0320	□
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σ	-0.5567	-0.2632	-0.0955	□
σ^*	-0.0022	-0.0013	-0.0061	
σ	-0.8912	-0.3849	-0.0929	
core	-0.0050	-0.0038	-0.0017	

□ Comment: particular π bond is weaker (with higher energy) then σ (with lower energy), however in total effect the two degenerated π bonds taken together are stronger (have lower energy) then σ ; the P₂ molecule is an exception case.