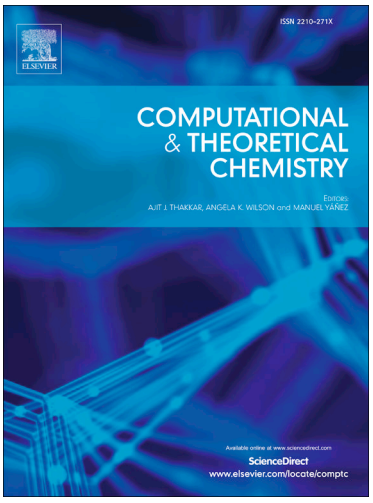

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The Axiomatic Approach to Chemical Concepts

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Many concepts that are central to chemical language and thought emerge from the wealth of chemists' historical experience and cannot be precisely defined mathematically from the underlying physics. In such cases, it is useful to take an axiomatic approach: list the chemical, mathematical and computational properties that one desires for a concept to possess, and then find the rigorous (and, if possible, elegant) mathematical formulation of the concept that satisfies those desiderata. This mathematical formulation is most useful if it relies on fundamental quantities—quantum-mechanical observables, reduced density matrices, or the *N*-electron wavefunction—rather than method-dependent quantities (e.g., orbitals) that are not defined for some computational approaches to the molecular electronic structure problem. This ensures that the pursuit of chemical intuition does not lead one too far from the underlying physics. It also ensures that one can interpret the results of any computational method, even methods (e.g., quantum Monte Carlo) that make no reference to any molecular-orbital or valence-bond model.

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