$|\Psi|^2$ Analysis: Extracting Valence Bond Information from Arbitrary Wave Functions

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In the last decades, valence bond (VB) theory regained popularity due to the insight it offers into the nature of bonding in molecules. Since it describes resonance between Lewis structures, its results are often intuitively understandable for chemists. However, VB calculations are less computationally efficient than those of other methods and need theoretical preparation, which can add bias.

The $|\Psi|^2$ analysis is also connected to the Lewis picture of chemical bonding [1]. It can be applied to any wave function and gives information about the most probable electron arrangements, i.e. local maxima of $|\Psi|^2$ that partition $\mathbb{R}^{3N}$ into their basins of attraction. In many cases, these maxima resemble VB structures. A weight can be assigned to each maximum by Monte Carlo integration of its basin.

Ideally, both of these methods should give agreeing results. This is put to the proof in the present work: $|\Psi|^2$ weights of maxima are compared to Chirgwin-Coulson, Löwdin, and inverse weights of VB structures.
Furthermore, the transferability of this VB structure weight extraction to arbitrary wave functions is proven by application to complete active space (CAS), Jastrow-CAS, and Jastrow-VB wave functions.
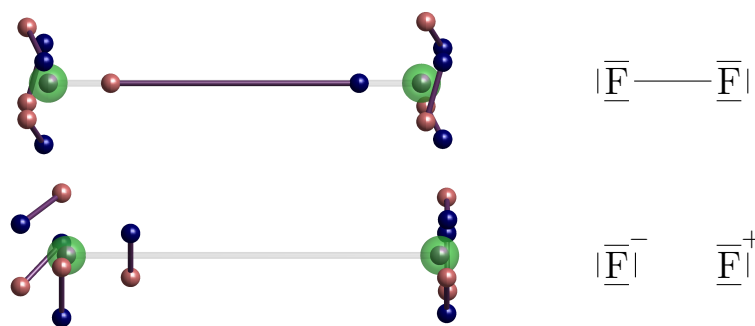

Figure 1: *covalent and ionic $|\Psi|^2$ maxima of a Jastrow-CAS wave function (left) resemble the respective VB structures (right) of fluorine.*

References

1. A. Lüchow, *J. Comput. Chem.* **35** (2014), 854.