17.2: Electron Correlation Requires Moving Beyond a Mean-Field Model

To improve upon the mean-field picture of electronic structure, one must move beyond the single-configuration approximation. It is essential to do so to achieve higher accuracy, but it is also important to do so to achieve a **conceptually** correct view of chemical electronic structure. However, it is very disconcerting to be told that the familiar $1s^2 2s^2 2p^2$ configuration description of the carbon atom is inadequate and that instead one must think of the ^3P ground state of this atom as a 'mixture' of multiple (often considered "excited-state") configurations:

- $1s^2 2s^2 2p^2$
- $1s^2 2s^2 3p^2$
- $1s^2 2s^2 3d^2$
- $2s^2 3s^2 2p^2$

and any other configurations whose angular momenta can be coupled to produce $L = 1$ and $S = 1$.

Although the picture of configurations in which N electrons occupy N spin-orbitals may be very familiar and useful for systematizing electronic states of atoms and molecules, these constructs are approximations to the true states of the system. They were introduced when the mean-field approximation was made, and neither orbitals nor configurations describe the proper eigenstates $\{\Psi_k, E_k\}$.

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The inclusion of instantaneous spatial correlations among electrons is necessary to achieve a more accurate description of atomic and molecular electronic structure. **No** single spin-orbital product wavefunction is capable of treating electron correlation to **any** extent; its product nature renders it incapable of doing so.