8.2: Even N-Electron Configurations are Not Mother Nature's True Energy States

Moreover, even single-configuration descriptions of atomic and molecular structure (e.g., $1s^2 2s^2 2p^4$ for the Oxygen atom) do not provide fully correct or highly accurate representations of the respective electronic wavefunctions. As will be shown in this Section and in more detail in Section 6, the picture of N electrons occupying orbitals to form a configuration is based on a so-called "mean field" description of the coulomb interactions among electrons. In such models, an electron at **r** is viewed as interacting with an "averaged" charge density arising from the N-1 remaining electrons:

$$V_{\text{mean field}} = \int \rho_{N-1}(\mathbf{r'}) \frac{e^2}{|\mathbf{r}-\mathbf{r'}|} \mathbf{dr'}.$$

Here $\rho_{N-1}(\mathbf{r'})$ represents the probability density for finding electrons at $\mathbf{r'}$, and $\frac{e^2}{|\mathbf{r}-\mathbf{r'}|}$. is the mutual Coulomb repulsion between electron density at r and r'. Analogous mean-field models arise in many areas of chemistry and physics, including electrolyte theory (e.g., the Debye-Hückel theory), statistical mechanics of dense gases (e.g., where the **Mayer-Mayer cluster** expansion is used to improve the ideal-gas mean field model), and chemical dynamics (e.g., the vibrationally averaged potential of interaction).

In each case, the mean-field model forms only a starting point from which one attempts to build a fully correct theory by effecting systematic corrections (e.g., using perturbation theory) to the mean-field model. The ultimate value of any particular meanfield model is related to its accuracy in describing experimental phenomena. If predictions of the mean-field model are far from the experimental observations, then higher-order corrections (which are usually difficult to implement) must be employed to improve its predictions. In such a case, one is motivated to search for a better model to use as a starting point so that lower-order perturbative (or other) corrections can be used to achieve chemical accuracy (e.g., ± 1 kcal/mole).

In electronic structure theory, the single-configuration picture (e.g., the $1s^2 2s^2 2p^4$ description of the oxygen atom) forms the mean-field starting point; the configuration interaction (CI) or perturbation theory techniques are then used to systematically improve this level of description.

The single-configuration mean-field theories of electronic structure neglect correlations among the electrons. That is, in expressing the interaction of an electron at **r** with the N-1 other electrons, they use a probability density $\rho_{N-1}(\mathbf{r'})$ that is independent of the fact that another electron resides at r.

> *The single-configuration mean-field theories of electronic structure neglect correlations among the electrons.*

In fact, the so-called conditional probability density for finding one of N-1 electrons at **r'**, given that an electron is at r certainly depends on r. As a result, the mean-field coulomb potential felt by a $2p_x$ orbital's electron in the $1s^2 2s^2 2p_x 2p_y$ single-configuration description of the Carbon atom is:

$$V_{\text{mean field}} = 2\int |1s(\mathbf{r'})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r'}|}\mathbf{dr'} + 2\int |2s(\mathbf{r'})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r'}|}\mathbf{dr'} + \int |2p_y(\mathbf{r'})|^2 \frac{e^2}{|\mathbf{r}-\mathbf{r'}|}\mathbf{dr'}.$$

In this example, the density $\rho_{N-1}(\mathbf{r'})$ is the sum of the charge densities of the orbitals occupied by the five other electrons $2|1s(\mathbf{r'})|^2 + 2|2s(\mathbf{r'})|^2 + |2py(\mathbf{r'})|^2$, and is not dependent on the fact that an electron resides at **r**.