Physics 555 Fall 2007
Mean field theory and Hartree-Fock theory

Perhaps the first mean-field theory was the alteration of the Curie law $\chi \propto 1/T$ for a paramagnet, to the Curie-Weiss law $\chi \propto 1/(T - T_c)$ for a ferromagnet at T above the Curie temperature T_c. The derivation says that roughly speaking, a microscopic spin sees, not the separate spins on its neighbors, but the number of neighbors times the average spin. This becomes more accurate, the more neighbors there are, and therefore less accurate the fewer, or the lower the spatial dimensionality.

There is a corresponding microscopic mean field theory. The simplest version is the Ising case where we pretend spins only orient along z. The notion σ_i denotes the z-component of the i^{th} spin. The Ising Hamiltonian is

$$H_{ISING} = -\frac{J}{2}\sum_{i\neq j}^{n.n.}\sigma_i\sigma_j = \frac{J}{2}\sum_{i\neq j}^{n.n.}\left[\sigma_i\langle\sigma_j\rangle + \langle\sigma_i\rangle\sigma_j - \langle\sigma_i\rangle\langle\sigma_j\rangle + (\sigma_i - \langle\sigma_i\rangle)(\sigma_j - \langle\sigma_j\rangle)\right] \quad (1)$$

The **mean-field approximation** consists of neglecting the last term, which is quadratic in fluctuations around mean values $\langle\sigma_j\rangle = \langle\sigma\rangle$. Then, neglecting a constant term, we have $H_{ISING,MF} = -\sum_i \sigma_i B_{eff}$, where the effective magnetic field is $B_{eff} = zJ\langle\sigma\rangle$, and z is the number of neighbors. This is the "Weiss molecular field," and generates the Curie-Weiss law, by solving self-consistently for $\langle\sigma\rangle$. It also gives a theory for the low-T broken-symmetry ferromagnetic phase.

Now consider the Hamiltonian for a system of electrons. It can be written as the sum of a single-particle part and the Coulomb term, namely

$$\hat{H}_1 + \hat{H}_{\rm int} = \sum_{n,m}\langle m|\hat{h}_1|n\rangle c_m^+ c_n + \frac{1}{2}\sum_{m,n,m',n'}\langle m'm|\hat{V}_{Coulomb}|n'n\rangle c_{m'}^+ c_m^+ c_n c_{n'}, \quad (2)$$

where $\hat{h}_1 = p^2/2m + V(\vec{r})$, and $\hat{V}_{Coulomb} = e^2/|\vec{r} - \vec{r}'|$. A mean-field version of this Hamiltonian is constructed analogously to the mean-field version of the Ising Hamiltonian, and is called the Hartree-Fock Hamiltonian,

$$\hat{H}_{HF} = \sum_{n,m}\langle m|\hat{h}_1|n\rangle c_m^+ c_n + \frac{1}{2}\sum_{m,n,m',n'}\langle m'm|\hat{V}_{Coulomb}|n'n\rangle\left[c_{m'}^+ c_m^+ c_n c_{n'}\right]_{pairwise-average}$$

The pairwise average is more complicated here than the partial spin average in the mean-field version of the Ising model. There are two different ways that the average of a pair of the c-operators can be non-zero, with opposite relative signs because of the anti-commuting property of the operators,

$$\left[c_{m'}^+ c_m^+ c_n c_{n'}\right]_{pairwise-average} = \hat{D} + \hat{E},$$
$$\hat{D} = \langle c_{m'}^+ c_{n'}\rangle c_m^+ c_n + c_{m'}^+ c_{n'}\langle c_m^+ c_n\rangle - \langle c_{m'}^+ c_{n'}\rangle\langle c_m^+ c_n\rangle \quad .$$
$$\hat{E} = -\langle c_{m'}^+ c_n\rangle c_m^+ c_{n'} - c_{m'}^+ c_n\langle c_m^+ c_{n'}\rangle + \langle c_{m'}^+ c_n\rangle\langle c_m^+ c_{n'}\rangle$$

Here $\hat{D}$ contains the "**direct**" terms, and $\hat{E}$ contains the "**exchange**" terms. The third part of both $\hat{D}$ and $\hat{E}$ is an average, not an operator, and doesn't affect dynamics, just total energy. It can be dropped for now. The first two terms of both $\hat{D}$ and $\hat{E}$ are identical, after re-labeling indices, and using $\langle c_a^+ c_b\rangle = \langle c_a^+ c_a\rangle\delta_{ab}$ (which is true when the states used in the average $\langle\ \rangle$ are single Slater determinants.) Then the Hartree-Fock Hamiltonian can be written

$$\hat{H}_{HF} = \sum_{m,n}\left\{\langle m|\hat{h}_1|n\rangle + \sum_s\langle c_s^+ c_s\rangle\left[\langle sm|\hat{V}_{Coulomb}|sn\rangle - \langle sm|\hat{V}_{Coulomb}|ns\rangle\right]\right\}c_m^+ c_n \,. \quad (3)$$

This equation, if diagonalized self-consistently, gives Hartree-Fock eigenvalues and orbitals.