

Ref: P. Fulde, "Electron Correlations in Molecules and Solids", Ch. 1

Heitler-London vs. Hartree-Fock

The H₂-Molecule

After the development of QM in 1925-26 (Heisenberg, Schrödinger, Born, Dirac), the Heitler-London treatment (1927) of the H₂ molecule "opened the way to a theoretical understanding of chemical bonding".

HL treat the H₂ electrons as "strongly-correlated" (exclude ionic configurations (-> "localized electrons"), in which the electrons "get in one another's way"):

$$\psi_{HL}(r_1, r_2) = [\phi_A(r_1)\phi_B(r_2) + \phi_B(r_1)\phi_A(r_2)](\alpha_1\beta_2 - \alpha_2\beta_1)$$

r_1 and r_2 give the positions of electrons 1 and 2, ϕ_A and ϕ_B are 1s-orbitals centered on atoms A and B, and the spinors α and β refer to spin up and down, respectively.

Hartree, Fock and Slater (1928-30) took a different approach to the many-body problem, treating the electrons as being independent of each other and introducing the "self-consistent field" (each electron experiences the average field produced by the other electrons). In this approximation, the ground-state H₂ wavefunction is:

$$\psi_{HF}(r_1, r_2) = [\phi_A(r_1)\phi_A(r_2) + \phi_A(r_1)\phi_B(r_2) + \phi_B(r_1)\phi_A(r_2) + \phi_B(r_1)\phi_B(r_2)](\alpha_1\beta_2 - \alpha_2\beta_1)$$

Note the ionic configurations $\phi_A\phi_A$ and $\phi_B\phi_B$. (-> "delocalized electrons")

ψ_{HL} gives the correct description when the atoms are moved apart, and ψ_{HF} gives the correct description when the atoms are moved together. The truth lies somewhere in between: electron correlations reduce the weight of the ionic configurations, but not to zero.

Quantum Chemistry

HL led Pauling (1960) to develop "resonant structures".

HF led Hund, Slater, Hückel (1928-32) to develop "molecular orbital theory". MO is good for (most) weakly correlated chemical bonds.

Solids

Sommerfeld and Bethe (1933) first described solids starting from free electrons. Landau (1957) explained this success in terms of the "quasiparticles" of Fermi-Liquid Theory. Anderson (1988) doesn't believe FLT applies to HiTc materials.

Transition Metals and TM-Oxides

d-electrons are delocalized, but highly correlated (e.g., Hund's rule holds). HL approach: Van Vleck (1953), HF approach: Slater (1936).

CoO should be a metal, but correlations make it a Mott-Hubbard insulator.

Self-Consistent Field led to Local-Density Approximation (Hohenberg, Kohn, Sham (1964-65) - originally based on independent electron approximation but later extended to include correlation effects. With new solution methods for the Schrödinger Equation (muffin-tin orbitals, augmented plane waves, ...), LDA "has penetrated all areas of solid-state theory". But it "provides no insight into the electron correlation problem", since it is based on independent electrons.