pseudopotential approaches where the latter use weak effective potentials for valence electrons in order to get rid of core oscillations which would require very large basis sets in plane-wave expansions. While newer codes allow for efficient full-potential calculations in a linear augmented plane wave (LAPW) basis [as, e.g., Blaha, Schwarz, and Luitz's (1999) package VIENNA], the problem can be avoided by using atomic-like basis sets at least near the ionic cores. In the muffin-tin orbital (MTO) approach, a minimal basis characterized by angular momentum quantum numbers is constructed where the external potential only acts inside a spherical "muffin tin". The energy dependence of the MTOs is linearized and an energy-independent set obtained in the LMTO method which is then reliable only for valence states (Andersen, 1975). Lifting the constraint of minimalism, more localized[8] "tight binding" basis functions were introduced in the TB-LMTO approach (Andersen, Pawlowska, and Jepsen, 1986) which is usually used in connection with the atomic sphere approximation (ASA) of a locally spherical resulting potential.

It should be stressed that DFT as a ground state method cannot directly be used for the determination of excitation spectra. In principle, apart from true ground state properties, only the sizes of energy gaps can be computed as differences of ground state energies for systems with N and $N+1$ electrons, respectively. In practice, however, the eigenvalues ϵ_i of the single particle problem (5.6) often compare favorably with experiment and are regularly regarded as band structures of the interacting system.

The various LDA methods have been used successfully for the computation of bulk properties of materials, in particular metals, as well as surface or impurity effects. While their superiority over preceding DFTs such as the Thomas-Fermi approximation can be explained from the vastly improved treatment of the kinetic energy, the accuracy of LDA, an effective single-particle theory without adjustable parameters ("ab initio") came as a surprise not only to its inventors. Still, LDA fails for important classes of materials with strong electronic correlations like $La_{1\text{-}x}Sr_xTiO_3$, which limits its general predictive power. In the next section we will discuss extensions of the LDA approach which address this problem.

5.3 LDA+DMFT

Since the LDA uses input from the jellium model, it is not surprising that the resulting errors are larger for localized than for extended states. One may suspect that both local correlations and the self-interaction contribute significantly to these errors for localized orbitals. In fact, self-interaction corrected (SIC-LDA) calculations yield a much better estimate for the total energy of isolated atoms than plain LDA which can be attributed to an improved treatment of core states.[9] Using a basis with localized

[8] Conventional MTOs fall off as $r^{-(l+1)}$ for angular momentum l.

[9] For the total energy of, e.g., Ne atoms, LDA is even inferior to the Hartree-Fock theory (HF). For ionization energies, however, the agreement with experiment is significantly better for LSDA than either for LDA or HF with no general improvement from inclusion of SIC (Gunnarsson and Jones, 1981).