transitions within the DMFT and specify potentially useful observables. A first look at the history of the phase diagram is given in Sec. 3.3 where it will be seen that early QMC studies collaboratively performed in this work correctly captured some aspects of the phase diagram while failing in describing others. In Sec. 3.4, we explain the reasons for this failure and correct a fundamental problem of the QMC code previously used within our group. In addition, we quantify the remaining numerical errors and present further improvements of the QMC algorithm and code developed as part of this thesis.

Accurate phase boundaries are then determined in Sec. 3.5. Here, we show that the total internal energy (per site) is best suited for distinguishing metallic from insulating solutions, in particular in the extrapolation $\Delta\tau \to 0$. The resulting phase diagram is constructed and the controversy resolved in subsection 3.5.4. The observation of a coexistence region of metallic and insulating solutions generates the need to determine the true thermodynamic phase transition line using free energy information. Prior to this work, this task had seemed too complicated to be accomplished on the basis of numerically exact techniques; even in the context of iterative perturbation theory, results for this line had been contradictory. Using newly developed schemes, we demonstrate in Sec. 3.6 how the first order phase transition line can be located based on QMC simulations; using low-temperature thermodynamic information and well-established numerical zero-temperature results, the thermodynamic phase transition line is even extended down to zero temperature. The presentation of the full phase diagram in subsection 3.6.3 is supplemented by a discussion of possible scenarios for partially frustrated models in subsection 3.6.4.

Implications of the Landau theory of phase transitions for the convergence of the DMFT iteration process and the suitability of the fitting functions introduced in Sec. 3.5 are discussed in Sec. 3.7. In addition, we propose a new concept for computing free energy differences by solving impurity models which are (in general) not solutions of the DMFT equations. In the final section 3.8, local spectral functions are computed using the maximum entropy method. These results provide additional insight in the nature of the phase transition and will later be needed for the computation of the optical conductivity in chapter 4.

3.1 Motivation

3.1.1 Experiment

Experimentally, metal-insulator transitions may be observed upon variation of temperature and pressure for a given sample or as a function of doping within a class of materials. Since the induced variations of energy scales are relatively small, only few classes of materials, such as the oxides of vanadium, titanium, and chrome as well as $NiSe_{2-x}S_x$ display a correlation-induced MIT (Heine and Mattheiss, 1971; Mattheiss, 1972; Mott, 1990). The compound $La_{1\text{-}x}Sr_xTiO_3$, which will be treated within LDA+DMFT in chapter 5, falls into this group; among the most prominent and best characterized examples, however, is V_2O_3 (Rice and McWhan, 1970; McWhan, Remeika, Rice, Brinkman, Maita, and Menth, 1971; McWhan, Remeika,