

Chapter 1

Introduction

Many-particle physics is full of surprises. Although the interaction between all particles is known, and therefore the Hamiltonian given, predictions for experimentally interesting systems are generally difficult to obtain. Analytically, the Schrödinger equation can only be solved for a very limited number of systems, for example the hydrogen atom and the harmonic oscillator. Nevertheless, theoretical many-body physics aims at an ab-initio description of far more complicated systems. The necessary numerical treatment has made huge progress during the last decades due to the fast advances in computer technology. For small systems it is now even possible to expand the wave function in Slater determinants and to obtain an approximation of the true many-body ground-state wave function which is very close to being exact. However, with increasing number of particles the computational power and the available memory still pose severe restrictions. For example, the electron wave function of the nitrogen atom, having 7 electrons, depends on 21 spatial variables. If we create a rough table of the electronic wave function of this system at 10 different positions in each variable, this amounts to 10^{21} double precision entries. Storing it on DVDs the stack of discs would easily reach the moon.

From this little example, and nitrogen certainly passes as little, we see that computing and storing the wave function is highly unpractical and will be generally impossible even in the future. However, for most predictions, we are not even interested in the wave function at all. For the calculation of expectation values of local single-particle operators the knowledge of the density of the system is sufficient. In the case of non-locality only the complete one-body density matrix is required while for local two-particle operators one needs the diagonal of the two-particle density matrix. Of course, higher order operators require higher order density matrices for a *direct* calculation. However, it was shown by Hohenberg and Kohn [1] that the ground-state density alone is sufficient to completely determine systems which can be described by a Hamiltonian containing only a local external potential besides all the particle-particle interactions. This finding marks the birth of density functional theory (DFT), where all observables are given as functionals of the particle density. In practice, of course, the functional dependence of most observables on the ground-

state density is unknown and needs to be approximated. Computing the energy of a system one has to approximate the so-called exchange-correlation energy. The construction of high-quality approximations for the corresponding functional is one major subject within DFT. The most popular approximations, the local density approximation (LDA) [1] and generalized gradient approximations (GGA) [2, 3], are based on the exchange-correlation energy density of the homogeneous electron gas known from Monte-Carlo calculations [4].

The great success of DFT is largely due to the existence of the Kohn-Sham (KS) system [5], a system of non-interacting electrons with the same ground-state density as the interacting system of interest. It allows for an exact calculation of large parts of the kinetic energy such that the remaining exchange-correlation energy is only a relatively small contribution to the total energy. The KS system itself yields single-particle orbitals, the KS wave functions, which can also be used for the construction of approximate exchange-correlation energy functionals. This introduces a whole new class of functionals known as orbital functionals.

Since its invention in 1964, DFT has been successfully used to describe a wide range of systems from atoms and small molecules to quantum dots and solids, total or ionization energies and band gaps have been calculated. While the calculation of energies is successful the results for the fundamental gaps are usually poor. The fundamental gap is defined as the difference between the ionization potential and the electron affinity. For solids it is identical to what one usually calls the band gap. However, this more general definition is also valid for finite systems. Improving the predictions for the fundamental gap is the main topic of the first part of this work. The fundamental gap can be calculated if the energies of the N , $N + 1$ and $N - 1$ electron systems are known. The electron affinity is then given as the difference $E_{\text{total}}(N) - E_{\text{total}}(N + 1)$ and the ionization potential as $E_{\text{total}}(N - 1) - E_{\text{total}}(N)$. However, one frequently encounters the problem that the system does not bind an additional electron in a DFT calculation due to the approximation used for the exchange-correlation energy. As shown in Ref. [6, 7, 8], the fundamental gap within DFT is alternatively given by the sum of the KS gap and the derivative discontinuity of the exchange-correlation energy, i.e.

$$\Delta = \Delta_{KS} + \lim_{\eta \rightarrow 0} \left(\left. \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right|_{N+\eta} - \left. \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right|_{N-\eta} \right). \quad (1.1)$$

To evaluate this expression, DFT had to be extended to describe systems with fractional number of particles $N \pm \eta$ [9]. The evaluation of $\delta E_{xc}/\delta n(\mathbf{r})$ at $N \pm \eta$ ensures that the discontinuity at integer particle number N is captured. Depending on the approximation used for E_{xc} the results differ strongly. For LDA and all GGAs E_{xc} does not show a derivative discontinuity. Therefore, the fundamental gap is given solely by the KS gap. LDA typically underestimates the gap by 30–100%, including such extreme cases as Germanium which is predicted to be a metal instead of a semiconductor. If one uses the exact-exchange (EXX) approximation, the KS gap is

in quite good agreement with the total gap for some systems [10]. Further studies, however, show that the agreement is due to a fortuitous cancellation of errors in these systems and does not hold in general [11]. In addition, the derivative discontinuity is not zero for the exact-exchange functional. Adding it according to (1.1) leads to a total gap which is of the same order as the Hartree-Fock gap and, therefore, greatly overestimates the experimental values. There was some hope that the correlation energy shows a derivative discontinuity of the same absolute size as the exchange part such that the two discontinuities cancel. Recent calculations, however, show that including correlation, using an EXX plus random-phase approximation (RPA) functional [12, 13, 14], not only changes the derivative discontinuity but also affects the KS gap. The KS gap of an EXX+RPA calculation is of the same order as the LDA gap. Including the non-zero derivative discontinuity in EXX+RPA, finally, results in a good agreement with experiment, at least for the few systems calculated so far [15].

In other words, we need a very accurate approximation for the exchange-correlation energy in order to obtain reasonable results for the gap in DFT. But instead of improving the functionals one can also extend DFT itself and calculate the fundamental gap in the extended theory. Using improved functionals was recently investigated in [15]. Here, we consider reduced-density-matrix-functional theory (RDMFT) in the first part of this thesis. In RDMFT the basic variable is the one-body reduced density matrix (1-RDM), instead of the density in DFT. Due to the idempotency of a non-interacting 1-RDM, a property that is not shared by any interacting 1-RDM, there exists *no* KS system in RDMFT. The energy is therefore minimized directly with respect to the 1-RDM leading to the problem of N -representability. In the minimization one has to ensure that only 1-RDMs corresponding to properly anti-symmetrized N -particle wave functions are considered.

We derive a formula in analogy to Eq. (1.1) to calculate the fundamental gap in RDMFT. As in DFT, the original theory has to be extended to fractional number of particles. Consequently, the N -representability problem has to be addressed within the extended theory. We find a set of necessary and sufficient conditions to ensure N -representability for fractional particle number. The formula for the fundamental gap was applied to finite as well as periodic systems. The results are in excellent agreement with other theoretical calculations as well as experimental data. This is especially noteworthy since only a very limited number of approximations are available in RDMFT at present and the applications used a first generation functional [16].

First, we introduce RDMFT and its underlying theorems in Chapter 2. In Chapter 3 we present possible approximations and briefly comment on their quality. Chapter 4 contains our derivation of the formula for the fundamental gap calculated within RDMFT. In this context, the N -representability constraints, discussed in Chapter 2, are extended to fractional particle number. In Chapter 4 we also present our numerical results for several finite as well as periodic systems.

In the second part of this thesis, the treatment of systems in external magnetic

fields is discussed. The necessary formal extension of DFT to Current-Spin DFT (CSDF) was given by Vignale and Rasolt already in 1987 [17, 18]. Extending the approximations for E_{xc} from DFT to CSDF, however, turned out to be a non-trivial task. The LDA and GGAs all rely on calculations for the homogeneous electron gas (HEG). Applying an external magnetic field of variable strength to the HEG, the energy density changes discontinuously whenever a new Landau level is filled [19]. This is a physical effect but the consequences are quite severe if properties of the HEG are used as LDA-type approximations for other systems. The exchange-correlation potential suffers from divergencies at these points because it results from a functional derivative of the exchange-correlation energy. Hence, it is impossible to directly implement an LDA or GGA potential in a numerical calculation. In addition, the discontinuities and respective divergencies appear at the Landau levels of the HEG not at the ones of the inhomogeneous systems. Thus, they appear, in general, at the wrong magnetic field strengths. The only solution to this problem until very recently has been an interpolation between a functional at zero magnetic field and a different functional at high magnetic field such that the divergencies could be avoided completely. Since the filling of Landau levels is apparently an orbital effect, the idea of using orbital functionals seems appealing. To put this idea into practice, it is necessary to extend the orbital effective potential (OEP) formalism to CSDF which was done in my diploma thesis [20]. The OEP method needs to account for the two additional potentials in the Hamiltonian, the magnetic field and the corresponding vector potential treated as independent in this approach. As a consequence, one obtains three coupled OEP equations for the three corresponding exchange-correlation potentials. Their solution can be simplified by additional approximations such as collinear magnetism. In this PhD thesis, the OEP formalism is applied to describe quantum dots in an external magnetic field. The quantum dot itself is theoretically best described as a two-dimensional system with a parabolic potential. The constant external field is applied along the symmetry axis of the system.

Chapter 5 contains our extension of the optimized effective potential method to current-spin-density-functional theory. Also the resulting equations for several additional approximations, like collinear magnetism, are given in this chapter. We present the numerical implementation for quantum dots and the results of the calculation in Chapter 6. The whole thesis is concluded with a summary and outlook in Chapter 7.

Atomic units ($\hbar = e = m = 1$) are used throughout the whole thesis.