Chapter 7

Conclusions and Outlook

In this thesis we presented solutions to two prominent problems in density-functional theory (DFT). Reduced-density-matrix-functional theory (RDMFT) was introduced to calculate the fundamental gap which is poorly described by currently employed DFT approximations. We showed that the fundamental gap in RDMFT is given as the discontinuity of the chemical potential at integer particle number. The numerical calculations using the Goedecker/Umrigar functional [16] yield remarkable results for both finite and periodic systems, the calculated gaps being in very good agreement with other theoretical calculations and experimental values. For the Li and Na atoms we obtained 0.177 Ha and 0.175 Ha, respectively, compared to the experimental values 0.175 Ha for Li and 0.169 Ha for Na. For solid Neon the RDMFT calculation yields a band gap of 0.76 Ha compared to the experimental value of 0.797 Ha. The chemical potential, however, is not discontinuous at integer particle number but at slightly larger values because of the approximate nature of the exchange-correlation energy functional. Future calculations with different functionals, especially those recently introduced in [31], will hopefully provide more insight.

In addition, we found the N-representability constraints for fractional particle number which turned out to be identical to the case of integer particle number. Extending the theory, and therefore the constraints, to fractional particle number was mandatory for putting the calculation of the gap on a sound theoretical basis.

While the numerical implementation of RDMFT for finite systems is rather straight-forward, applying the formalism to periodic systems can be based on either Bloch- or Wannier-states. Here, we chose the latter option and applied it to systems where the natural orbitals are expected to be localized. For future applications it is interesting to see if the use of Bloch-states changes the results significantly. If it does so an investigation of different systems using both methods can potentially give new insight into the electronic structure. This is of special interest for systems where the localization of the electronic orbitals is still under debate.

The temperature dependence of the band gap is also an interesting property especially for semiconductors where it should decrease with increasing temperature and the material should become metallic above a certain critical temperature. To

investigate such issues RDMFT needs to be extended to include temperature. First, one has to prove a Gilbert theorem and, second, an approximation for the free energy, the quantity to be minimized at $T \neq 0$, has to be found. For the total energy being part of the free energy one can use the available approximations. However, a completely new approximation for the entropy has to be introduced.

A different problem to be solved in the future is the calculation of the complete band structure within RDMFT. The introduction of an effective single-particle Hamiltonian having the natural orbitals as eigenfunctions does not yield a single-particle spectrum because the eigenvalues of this Hamiltonian turn out to be arbitrary [82]. Therefore, other ideas, like computing the energy change due to the removal of the occupation from a specific natural orbital, need to be analyzed.

In the second part of the thesis we investigated the treatment of systems in external magnetic fields in current-spin-density-functional theory (CSDFT). Here, the available LDA and GGA type approximations introduce both fundamental as well as numerical problems when external magnetic fields are applied. The poor man's solution to this problem had been an interpolation of two different LDA/GGA type approximations at high and low magnetic field. We showed that orbital functionals which do not rely on the HEG provide a viable solution to this problem. One and the same functional can be used for the whole range of applied external magnetic fields.

In order to use orbital functionals in CSDFT we extended the optimized effective potential (OEP) method to include the two additional potentials, the magnetic field and the vector potential, and the two corresponding densities, spin magnetization and paramagnetic current density. The formalism was applied in the collinear KLI approximation to quantum dots in an external magnetic field. For the exchange-correlation energy we used the exact-exchange approximation, the most commonly applied orbital functional. The results are in good agreement with other calculations where they are available. We observed the same numerical problems for the vector potential in the asymptotic region already found in [78]. As a first step we set the exchange vector potential to zero in that region. In order to increase the numerical accuracy the asymptotic form of $\mathbf{A}_x$ needs to be further investigated. Including the exchange vector potential has negligible influence on the total energy for the systems considered here. However, the corresponding spin-DFT calculations contain the coupling to the external vector potential but no exchange-correlation vector potential which makes the whole approach questionable. The filling of new levels with increasing magnetic field was observed but did not lead to any discontinuous changes in the energy or numerical difficulties, as expected for an orbital functional. For non-current carrying states the whole formalism reduces to its proper spin-DFT limit.

As the formalism was derived in full generality before specializing to the collinear and KLI approximations those can be easily dropped in future applications. For spin-DFT such a less approximative framework is currently investigated [74]. Also the application to systems where a larger exchange-correlation vector potential is ex-

pected should profit from the new approach. Of course, different orbital functionals, especially those including correlation effects, need to be implemented.

We conclude that the two extensions of DFT described in this thesis show the potential to solve both the problem of calculating the band gap in solids as well as the treatment of systems in external magnetic fields. Further tests are still necessary but are expected to confirm the positive results obtained so far.