Chapter 4

Relativistic Density Functional Theory

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4.1 Introduction

Over the last decade density functional theory (DFT) has left its traditional realm, condensed matter theory, and attracted widespread interest also in quantum chemistry, material science and biophysics (Becke 1992, Johnson et al. 1993, Moroni et al. 1997, Chetty et al. 1995, Krajci et al. 1997, Morgan et al. 1999, Barnett and Landman 1993, Eichinger et al. 1999, see, e.g.,). The question of a relativistic generalization (RDFT) thus emerges quite naturally. While the basic concepts of RDFT have been introduced quite some time ago (Rajagopal and Callaway 1973, Rajagopal 1978, MacDonald and Vosko 1979), their practical implementation has taken much more time. Both the advancement of the RDFT formalism and its implementation have been the subject of our contribution to the program *Relativistic Effects in Heavy-Element Chemistry and Physics* (REHE) of the Deutsche Forschungsgemeinschaft.

In this Chapter we summarize the various projects which have been pursued in this context. We place some emphasis on an overview of the various formulations of RDFT, which are found in the literature. Starting from quantum electrodynamics (QED) one is directly led to the covariant form of RDFT, in which the ground state four current $j^\nu = (cn, \boldsymbol{j})$ plays the role of the basic density variable. This RDFT variant is ideally suited for a discussion of the basic existence theorem, questions of gauge invariance and the field theoretical form of the effective single-particle equations (Engel et al. 1995b, Engel and Dreizler 1996, Engel et al. 1998a, Facco Bonetti et al. 1998). In practical calculations for magnetic systems, on the other hand, a RDFT version which depends on the magnetization density $\boldsymbol{m}$, rather than on $\boldsymbol{j}$, is utilized (MacDonald and Vosko 1979, Ramana and Rajagopal 1981a). Applications of this relativistic 'spin-density' functional approach is given in Chapter 5. As one of our projects within the REHE program, a stable algorithm for the investigation of open-shell atoms has been developed on this basis (Engel et al. 2001a).

Most frequently, however, a purely density-dependent version of RDFT is used. In this context we have examined the role of relativistic corrections to the exchange-correlation (xc) energy functional. In view of the limited accuracy of the relativistic local density approximation (RLDA) (Das et al. 1980, Ramana et al. 1982, Engel et al. 1995a) the generalized gradient approximation (GGA) has been extended into the relativistic domain (RGGA) (Engel et al. 1996, 1998b). Applications of the RGGA to Gold compounds as well as to the bulk showed, however, that, in spite of the obvious improvements obtained for atoms, the gradient terms overcorrect the errors of the RLDA for equilibrium distances and binding energies in molecules or solids with heavy constituents (Schmid et al. 1998, Varga et al. 1999). This deficiency of the RGGA indicates the need for truly nonlocal xc-functionals.

The prototype of such a functional is the exact exchange of RDFT, which not only includes the relativistic kinematics of the electrons but also the

(retarded) Breit interaction among them. As an explicit functional of the auxiliary single-particle spinors of RDFT, the exact exchange is an implicit density functional, for which the multiplicative Kohn-Sham (KS) potential must be evaluated indirectly via the relativistic version of the Optimized Potential Method (OPM) (Engel et al. 1995a, Kreibich et al. 1998, Engel et al. 1998a). Within the REHE program we have obtained a variety of exchange-only (x-only) ROPM results and put forward an accurate semi-analytical approximation to the full ROPM. A corresponding orbital-dependent correlation functional has been derived from perturbation theory on the basis of the KS Hamiltonian (Engel et al. 1998a) and studied for atoms and molecules (Engel et al. 2000a, Facco Bonetti et al. 2001).

In order to facilitate the application of the ROPM to more complex systems we have constructed relativistic pseudopotentials on the basis of the exact exchange (Höck and Engel 1998, Engel et al. 2001c), using a relativistic extension of the Troullier-Martins approach to normconserving pseudopotentials (Engel et al. 2001b). On this basis the antiferromagnetic (AFM) ground states of transition metal oxides have been studied (Schmid 2000).

As a fully relativistic density functional approach to the electronic and geometric structures of molecules containing heavy elements, the relativistic discrete variational method (RDVM) (Rosén and Ellis 1975) has been successively improved to a new quality within the REHE program. Individual projects addressed the efficient calculation of the Hartree potential (Bastug et al. 1995, Varga et al. 2000b), the interatomic forces (Varga et al. 2001) and the necessary multicenter integrals (Heitmann et al. 2001). As a result the RDVM now allows theoretical studies of rather complex systems, as clusters (Bastug et al. 1997b) and complexes or compounds containing superheavy and transactinide elements (Fricke et al. 1997, Varga et al. 2000a) (compare Chapter 6). It can also be applied to the investigation of problems in surface physics, e.g. adsorption processes of adatoms on surfaces (Geschke et al. 2000).

4.2 Foundations

4.2.1 Existence theorem

The appropriate starting point for the discussion of the foundations of RDFT is QED. Although relativistic quantum field theories like QED do not provide a Schrödinger-like wave equation for the relativistic many-body problem, there nevertheless exists a well-defined procedure for the derivation of the Hamiltonian of a stationary system. It emerges as one component of the energy-momentum tensor, which is most conveniently established within the framework of Noether's theorem. For the standard QED Lagrangian of interacting electrons coupled to some classical, stationary C-number potential V^μ

one obtains

$$\begin{aligned}
\hat{H} &= \hat{H}_e(x^0) + \hat{H}_\gamma(x^0) + \hat{H}_{int}(x^0) + \hat{H}_{ext}(x^0) \qquad (4.1)\\
\hat{H}_e(x^0) &= \frac{1}{2}\int d^3r\ \Big[\hat{\psi}^\dagger(x), \Big(-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta mc^2\Big)\hat{\psi}(x)\Big]\\
\hat{H}_\gamma(x^0) &= -\frac{1}{8\pi}\int d^3r\ \Big\{\partial^0\hat{A}_\nu(x)\partial^0\hat{A}^\nu(x) + \boldsymbol{\nabla}\hat{A}_\nu(x)\cdot\boldsymbol{\nabla}\hat{A}^\nu(x)\Big\}\\
\hat{H}_{int}(x^0) &= \frac{e}{c}\int d^3r\ \hat{j}^\mu(x)\ \hat{A}_\mu(x)\\
\hat{H}_{ext}(x^0) &= \frac{e}{c}\int d^3r\ \hat{j}^\mu(x)\ V_\mu(\boldsymbol{r})\ .
\end{aligned}$$

Here $\hat{\psi}(x)$ denotes the fermion field operator of the interacting, inhomogeneous system characterized by $\hat{H}$ (in the Heisenberg picture), $\hat{j}^\mu$ is the corresponding fermion four current operator,

$$\hat{j}^\mu(x) = \frac{c}{2}\Big[\hat{\psi}^\dagger(x), \alpha^\mu\hat{\psi}(x)\Big]\ ,$$

and $\hat{A}_\mu(x)$ represents the field operator of the photons, for which the covariant quantization scheme and Feynman gauge are used ($x^\mu = (ct, \boldsymbol{r})$, $\alpha^\mu = \gamma^0\gamma^\mu$). Both $\hat{H}$ and $\hat{j}^\mu$ have been formulated in the commutator form which ensures the correct behavior under charge conjugation (Källén 1958), although we will not dwell on this point in the following. The Hamiltonian commutes with the charge operator

$$\hat{Q} = \frac{e}{c}\int d^3r\ \hat{j}^0(x)\,.$$

This allows a classification of all many-electron states with respect to their total charge.

As is well known, the expectation values of $\hat{H}$ and $\hat{j}^\mu$ diverge if taken directly without some additional prescription. This is most easily seen for noninteracting electrons experiencing an external potential V^μ: The existence of the negative energy continuum states requires the redefinition of the energy scale, in order to take into account the nonvanishing energy of the vacuum. Furthermore, the fact that V^μ can create virtual electron-positron pairs makes a renormalization of the four current necessary. The situation is even more involved for interacting electrons. Within the standard perturbative approach the coupling between electrons and photons leads to large classes of divergent contributions which have to be first regularized and then renormalized by a suitable redefinition of the fundamental parameters of QED. For the ground state $|\Phi\rangle$ of the Fock space sector with charge Ne,

$$\hat{H}|\Phi\rangle = E|\Phi\rangle\ ,$$

the total binding energy E_R of the electrons is thus given by the energy difference between $|\Phi\rangle$ and the ground state of the zero-charge sector, i.e. the

interacting vacuum $|0\rangle$, augmented by the counterterm contributions (CTC) required to keep E_R finite,

$$E_R \equiv E_{tot} = \langle\Phi|\hat{H}|\Phi\rangle - \langle 0|\hat{H}|0\rangle + CTC\,. \tag{4.2}$$

An analogous renormalization is necessary for the ground state four current,

$$j_R^\mu(\boldsymbol{r}) = \langle\Phi|\hat{j}^\mu(x)|\Phi\rangle + CTC\,. \tag{4.3}$$

Of course, RDFT, whose central ingredients are the ground state energy and four current, must reflect this structure of the underlying quantum field theory. The need for renormalization thus shows up in the formulation of the basic existence theorem, in the single-particle equations and in the derivation of explicit functionals for the xc-energy. A detailed discussion of the various issues involved has been given in (Engel et al. 1995b, Engel and Dreizler 1996, Engel et al. 1998a) to which we refer the interested reader. In the following we always assume the quantities involved to be properly renormalized — all counterterms as well as the corresponding index R will, however, be suppressed for brevity.

On this basis, one can summarize the existence theorem of RDFT (Rajagopal and Callaway 1973, Rajagopal 1978, MacDonald and Vosko 1979, Engel et al. 1995b, Engel and Dreizler 1996) as follows: There exists a one-to-one correspondence between the class of ground states which result from external potentials just differing by gauge transformations and the ground state four current,

$$\left\{|\Phi\rangle \,\middle|\, |\Phi\rangle \text{ from } V_\nu + \partial_\nu\Lambda\right\} \Longleftrightarrow j^\nu(\boldsymbol{x}) \tag{4.4}$$

(here and in the following $|\Phi\rangle$ is always assumed to be nondegenerate). In other words, the class of physically equivalent realizations of the ground state is uniquely determined by j^ν. Choosing a suitable representative of each class, i.e. fixing the gauge for the complete set of V_ν, one can understand this representative $|\Phi\rangle$ as a unique functional of j^ν, $|\Phi[j^\nu]\rangle$. If one inserts a specific four current j_0^ν into this functional one obtains the ground state $|\Phi_0\rangle$ of the corresponding system, $|\Phi_0\rangle = |\Phi[j_0^\nu]\rangle$. No information beyond j_0^ν is needed, i.e. the same functional applies to atoms, molecules and solids ($|\Phi[j^\nu]\rangle$ is universal).

The existence of a unique relation between the ground state and j^ν immediately leads to the statement that all ground state observables are unique functionals of the four current, most notably the ground state energy,

$$E_{tot}[j^\nu] \quad = \quad \langle\Phi[j^\nu] \mid \hat{H} \mid \Phi[j^\nu]\rangle\,.$$

In view of its field theoretical basis, this energy functional not only accounts for the relativistic kinematics of both electrons and photons, but, in princi-

ple, also for all radiative corrections. With the Ritz principle[1], avoiding the question of interacting v-representability (Dreizler and Gross 1990), one may then formulate the basic variational equation of RDFT,

$$\frac{\delta}{\delta j^\nu(\boldsymbol{r})}\left\{E_{tot}[j^\nu] - \frac{\mu}{c}\int d^3x\, j^0(\boldsymbol{x})\right\}\Bigg|_{j=j_0} = 0\,, \tag{4.5}$$

where the subsidiary condition ensures charge conservation. Given the functional $E_{tot}[j^\nu]$, Eq.(4.5) allows the determination of the ground state four current j_0 corresponding to the external potential V^μ in the Hamiltonian (4.1) and, by subsequent insertion of j_0 into $E_{tot}[j^\nu]$, the ground state energy.

The proof for this existence theorem of RDFT (Engel et al. 1995b, Engel and Dreizler 1996) proceeds in a similar way as the original argument of Hohenberg and Kohn (1964) (HK), whose basic ingredients are the multiplicative nature of the external potential and the Ritz' variational principle. This proof involves inequalities between ground state expectation values of different Hamiltonians, so that one necessarily has to rely on their renormalized form (4.2). Fortunately, one can show that the HK-type proof is compatible with the QED renormalization scheme, if one utilizes the fact that the counterterms are unique functionals of the four current (Engel et al. 1995b).

One may nevertheless ask whether it is possible to base RDFT on an approximate relativistic many-body approach, as e.g. the Dirac-Coulomb (DC) Hamiltonian,

$$\begin{aligned}\hat{H}^{\mathrm{DC}} &= \hat{H}_e(0) + \hat{H}_{ext}(0) + \hat{H}_{e-e}\\ \hat{H}_{e-e} &= \frac{e^2}{2}\int d^3r d^3r'\,\frac{\hat{\psi}^\dagger(0,\boldsymbol{r})\hat{\psi}^\dagger(0,\boldsymbol{r}')\hat{\psi}(0,\boldsymbol{r}')\hat{\psi}(0,\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\,,\end{aligned}$$

or its Dirac-Coulomb-Breit (DCB) extension, so that one avoids the discussion of renormalization. In this case the no-pair approximation (np) plays the role of the renormalization scheme,

$$\hat{H}^{\mathrm{DC}}_{\mathrm{np}} = \hat{\Lambda}_+\hat{H}^{\mathrm{DC}}\hat{\Lambda}_+ \quad , \quad \hat{j}^\mu_{\mathrm{np}} = \hat{\Lambda}_+\hat{j}^\mu\hat{\Lambda}_+\,,$$

[1]We are not aware of any rigorous minimum principle for the renormalized ground state energies (4.2). There are, however, a number of arguments which can be given in favor of such a minimum principle. First of all, with increasing speed of light, i.e. in the nonrelativistic limit ($v/c \longrightarrow 0$), the energies (4.2) continuously approach values which do satisfy the Ritz principle. There seems to be no reason to assume that the minimum principle is restricted to the isolated value $c = \infty$. Secondly, one can explicitly verify that there exists a minimum principle for the renormalized ground state energy of noninteracting fermions in an arbitrary four potential V^μ (within the Furry picture (Rafelski et al. 1978, compare)). Finally, real atoms and molecules are stable (indicating that there exists a lower bound for energies) and QED has proven to be the most accurate theory available to date to describe these systems (note that, as a matter of principle, one does not have to rely on a perturbative treatment of QED-systems so that the asymptotic character of this perturbation expansion does not contradict this argument).

where $\hat{\Lambda}_+$ is a projection operator onto positive energy states. However, the no-pair approximation can be unambiguously specified only within some well-defined single-particle scheme. Even in this case $\hat{\Lambda}_+$ depends on the actual single-particle potential and thus on the external potential, $\hat{\Lambda}_+[V^\mu]$. As a consequence, $\hat{H}^{\rm DC}_{\rm np}$ is a nonlinear functional of V^μ, which does not allow the usual *reductio ad absurdum* of the HK-proof. In addition, the no-pair approximation introduces a gauge dependence into the ground state energy (Engel et al. 1998a), so that an unambiguous comparison of two ground state energies is only possible if one neglects the Breit interaction and restricts oneself to a purely electrostatic external potential. It thus seems that the existence theorem of RDFT can only be based on the field theoretical Hamiltonian (4.1) together with the standard QED renormalization scheme. The no-pair approximation, which is used in most applications, is much more easily introduced at a later stage, i.e. in the context of the single-particle equations of RDFT.

From this discussion it is obvious that the two central approximations of the DC or DCB approach, the no-pair approximation and the neglect of either the complete Breit interaction (DC) or the retardation corrections to it (DCB), play a different role in RDFT. In fact, while the no-pair approximation is a standard also in RDFT, there exists no fundamental conceptual problem with including the full electron-electron interaction. In order to understand this one has to recall that RDFT is not based on a Schrödinger-like single-time single-field wave equation, but only requires a suitable approximation for $E_{tot}[j^\nu]$. The building blocks for the evaluation of (4.2),(4.3) are the propagators of the noninteracting particles, as the free photon propagator,

$$D^{0,\mu\nu}(x-y) = -i\frac{e^2}{c}\langle 0_\gamma|T\hat{A}^\mu_0(x)\hat{A}^\nu_0(y)|0_\gamma\rangle\,,$$

where $\hat{A}^\nu_0$ denotes the noninteracting photon field operator and $|0_\gamma\rangle$ is the corresponding vacuum state. The derivation of explicit approximations to $E_{tot}[j^\nu]$ via the usual field theoretical methods thus automatically leads to the inclusion of the full transverse interaction. In fact, this is true not only in principle, but also in practice (Rajagopal 1978, MacDonald and Vosko 1979, Ramana and Rajagopal 1981b, Engel et al. 1998a, Engel and Facco Bonetti 2000).

On the other hand, there is also no fundamental problem with restricting RDFT to the Coulomb or Coulomb-Breit level. Choosing the Feynman gauge as used for the Hamiltonian (4.1), the full $D^0_{\mu\nu}$ is explicitly given by

$$D^{0,F}_{\mu\nu}(x-y) = \int \frac{d^4q}{(2\pi)^4}\, e^{-iq(x-y)}\, D^F_{\mu\nu}(q) \tag{4.6}$$

$$D^F_{\mu\nu}(q) = D(q^2)\, g_{\mu\nu} \tag{4.7}$$

$$D(q^2) = \frac{-4\pi e^2}{q^2+i\eta}\,, \tag{4.8}$$

which is easily reduced to the weakly relativistic (Coulomb-Breit),

$$D^{F,CB}_{\mu\nu}(q) = D(-\boldsymbol{q}^2) \begin{pmatrix} 1 + \frac{(q_0)^2}{\boldsymbol{q}^2} & 0 \\ 0 & g_{ij} \end{pmatrix}, \tag{4.9}$$

or the nonrelativistic (Coulomb) level,

$$D^{F,C}_{\mu\nu}(q) = D(-\boldsymbol{q}^2) g_{\mu 0} g_{\nu 0} \,. \tag{4.10}$$

However, the propagators (4.7) and (4.9) are equivalent to their Coulomb gauge counterparts (usually applied in quantum chemistry),

$$D^{F}_{\mu\nu}(q) \longrightarrow D^{\mathrm{C}}_{\mu\nu}(q) \quad = \quad \begin{pmatrix} D(-\boldsymbol{q}^2) & 0 \\ 0 & D(q^2)\left(g_{ij} + \frac{q_i q_j}{\boldsymbol{q}^2}\right) \end{pmatrix} \tag{4.11}$$

$$D^{F,CB}_{\mu\nu}(q) \longrightarrow D^{C,CB}_{\mu\nu}(q) \quad = \quad D(-\boldsymbol{q}^2) \begin{pmatrix} 1 & 0 \\ 0 & g_{ij} + \frac{q_i q_j}{\boldsymbol{q}^2} \end{pmatrix}, \tag{4.12}$$

only in gauge invariant expressions. In general, gauge invariance can only be ensured by the inclusion of the negative continuum in all intermediate sums over states (Engel et al. 1998a) (with one important exception — see Section 4.3.1). As soon as the no-pair approximation is applied a gauge dependence is introduced, so that a consistent comparison of RDFT and DCB data should be based on the same gauge. The absolute size of this gauge dependence has been examined for the correlation energy of the relativistic homogeneous electron gas (RHEG) by comparison of the gauge invariant standard form with its no-pair counterpart, evaluated for different gauges (Facco Bonetti et al. 1998). It was found that for high densities the error resulting from the combination of the no-pair approximation with a specific gauge can be substantial. On the other hand, the effect of this gauge dependence on atomic correlation energies is rather limited: Utilization of the no-pair form within the LDA showed that the gauge error is small compared with the error introduced by use of the LDA, in particular for the Coulomb gauge. Thus, assuming this result to also be characteristic of the gauge dependence of DCB data, gauge questions do not seem to be relevant for comparisons of DCB or experimental data with RLDA or RGGA results (or of different xc-functionals).

In most applications the external magnetic field

$$\boldsymbol{B}_{ext}(\boldsymbol{r}) \quad = \quad \boldsymbol{\nabla} \times \boldsymbol{V}(\boldsymbol{r}) \,,$$

vanishes. In this case the external Hamiltonian reduces to

$$\hat{H}_{ext} \quad \longrightarrow \quad \hat{H}'_{ext} = \int d^3r \; \hat{n}(x) v_{ext}(\boldsymbol{r}) \quad ; \quad v_{ext}(\boldsymbol{r}) = eV^0(\boldsymbol{r}) \,, \tag{4.13}$$

where we have introduced the more familiar n for the density,

$$\hat{n}(x) = \frac{1}{2}\left[\hat{\psi}^\dagger(x), \hat{\psi}(x)\right] \quad \longleftrightarrow \quad j^\nu(\boldsymbol{r}) = (cn(\boldsymbol{r}), \boldsymbol{j}(\boldsymbol{r})) \,.$$

Following the standard HK scheme one can then prove that there exists a one-to-one mapping between the zeroth component of the external potential, the ground state and the ground state density (MacDonald and Vosko 1979),

$$\left\{ v_{ext} \middle| v_{ext} + \text{const.} \right\} \Longleftrightarrow \left\{ |\Phi\rangle \middle| \; |\Phi\rangle \text{ from } v_{ext} + \text{const.} \right\} \Longleftrightarrow n(\boldsymbol{r}) \,.$$

In this case one can thus understand the ground state as a functional of the density alone, $|\Phi[n]\rangle$. The same is then true for the ground state observables as the energy, $E_{tot}[n]$. As a consequence, there is only one single variational equation,

$$\frac{\delta}{\delta n(\boldsymbol{r})} \left\{ E_{tot}[n] - \mu \int d^3x \, n(\boldsymbol{x}) \right\} \bigg|_{n=n_0} = 0 \,. \tag{4.14}$$

It must be emphasized that the restriction to an external potential of the type $V^\mu = (V^0, \mathbf{0})$ does not imply that the system cannot have some magnetic moment. Rather the spatial components of the four current must be viewed as functionals of the density, $\boldsymbol{j}[n] = \langle \Phi[n] | \hat{\boldsymbol{j}} | \Phi[n] \rangle \neq 0$.

Thus, in principle, the density is sufficient for an exact RDFT treatment of magnetic systems, similar to the situation in nonrelativistic DFT. In practice, on the other hand, spin-density functional theory proved to be necessary for the description of spin-polarized ground states in the nonrelativistic context. Its spin-density dependent energy functional allows a distinction between the spin-up and spin-down channels, which is important also if $\boldsymbol{B}_{ext} = \mathbf{0}$. As a matter of principle, the explicit inclusion of magnetic effects is possible via the four current version of RDFT. However, the standard energy functionals of (R)DFT are based on the (relativistic) homogeneous electron gas (see Section 4.4.1), for which $\boldsymbol{j}$ vanishes. Consequently, explicitly $\boldsymbol{j}$-dependent approximations for the energy cannot be derived from the RHEG. Thus a direct relativistic extension of spin-density functional theory is desirable, whose basic variables are suitably generalized spin-densities.

The starting point for this generalization is the Gordon decomposition, in which the total current is split into the paramagnetic (orbital) component $\boldsymbol{j}_p$, a gauge term proportional to the scalar density ρ_s and the curl of the magnetization density $\boldsymbol{m}$,

$$\begin{aligned}
\boldsymbol{j}(\boldsymbol{r}) &= \boldsymbol{j}_p(\boldsymbol{r}) - \frac{e}{mc} \boldsymbol{V}(\boldsymbol{r}) \rho_s(\boldsymbol{r}) - \frac{c}{e} \boldsymbol{\nabla} \times \boldsymbol{m}(\boldsymbol{r}) \\
\boldsymbol{j}_p(\boldsymbol{r}) &= -\frac{i\hbar}{2m} \langle \Phi | \hat{\psi}^\dagger(x) \beta \big[\boldsymbol{\nabla} \hat{\psi}(x) \big] - \big[\boldsymbol{\nabla} \hat{\psi}^\dagger(x) \big] \beta \hat{\psi}(x) | \Phi \rangle \\
\rho_s(\boldsymbol{r}) &= \langle \Phi | \hat{\psi}^\dagger(x) \beta \hat{\psi}(x) | \Phi \rangle \\
\boldsymbol{m}(\boldsymbol{r}) &= -\mu_B \langle \Phi | \hat{\psi}^\dagger(x) \beta \boldsymbol{\Sigma} \hat{\psi}(x) | \Phi \rangle
\end{aligned}$$

with

$$\mu_B = \frac{e\hbar}{2mc} \qquad ; \qquad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} .$$

Neglect, for the sake of argument, the coupling of $\boldsymbol{V}$ to the orbital current,

$$\hat{H}_{ext} \quad \longrightarrow \quad \hat{H}''_{ext} = \int d^3r \left\{ \hat{n}(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + \hat{\boldsymbol{m}}(\boldsymbol{r}) \cdot \boldsymbol{B}_{ext}(\boldsymbol{r}) \right\} .$$

The resulting Hamiltonian

$$\hat{H}'' \quad = \quad \hat{H}_e + \hat{H}_\gamma + \hat{H}_{int} + \hat{H}''_{ext} \tag{4.15}$$

is completely legitimate if one aims at the description of systems <u>not</u> subject to magnetic fields. In this case, one formulates a density functional approach for a more general class of systems than physically required. In this more general class the systems of interest are included as a subset which is obtained in the limit $\boldsymbol{B}_{ext} \longrightarrow 0$: $\hat{H}''$ only serves to identify the fundamental variables of a RDFT scheme for $\boldsymbol{B}_{ext} = \boldsymbol{0}$. On the basis of $\hat{H}''$ one can establish an existence theorem, connecting the ground state with the ground state charge and magnetization densities (MacDonald and Vosko 1979),

$$|\Phi\rangle \Longleftrightarrow (n, \boldsymbol{m}) . \tag{4.16}$$

In other words: $|\Phi\rangle$ is a unique and universal functional of $(n, \boldsymbol{m})$, $|\Phi[n, \boldsymbol{m}]\rangle$. Again the minimum principle for the ground state energy provides a set of variational equations,

$$\frac{\delta}{\delta n(\boldsymbol{r})} \left\{ E_{tot}[n, \boldsymbol{m}] - \mu \int d^3x \, n(\boldsymbol{x}) \right\} = 0 \quad , \quad \frac{\delta}{\delta \boldsymbol{m}(\boldsymbol{r})} E_{tot}[n, \boldsymbol{m}] = 0 \ . \tag{4.17}$$

RDFT in the form (4.16),(4.17) can be considered exact for $\boldsymbol{B}_{ext} \longrightarrow \boldsymbol{0}$. Due to its universality $|\Phi[n, \boldsymbol{m}]\rangle$ remains unchanged in this limit. The same statement then holds for all components of $E_{tot}[n, \boldsymbol{m}]$ for which the associated part of the Hamiltonian does not depend on $\boldsymbol{B}_{ext}$. Thus, the only point at which the limit $\boldsymbol{B}_{ext} \longrightarrow \boldsymbol{0}$ actually shows up is the explicit coupling term $\int d^3r \, \boldsymbol{m} \cdot \boldsymbol{B}_{ext}$. However, these statements should be taken with a grain of salt: In view of the prominent role of Ward identities and gauge invariance for the success of the QED renormalization scheme it is obvious that the arguments leading to (4.16),(4.17) are build on somewhat less solid ground than those underlying the four current version of RDFT, Eqs.(4.4),(4.5). A detailed investigation of this issue is not yet available. It seems worthwhile to remark that for $\boldsymbol{B}_{ext} \neq \boldsymbol{0}$ the Hamiltonian (4.15) and thus the RDFT variant (4.16),(4.17) represent approximations whose usefulness depends on the absolute size of $\boldsymbol{B}_{ext}$.

In the form (4.16),(4.17) RDFT is perfectly suited to deal with systems in which the direction of $\boldsymbol{m}$ varies with $\boldsymbol{r}$. On the other hand, if the non-collinearity of $\boldsymbol{m}$ is not an important feature for the system, one may restrict the artificial coupling between the electrons and the magnetic field to its z-component,

$$\hat{H}'''_{ext} = \int d^3r \left\{ \hat{n}(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + \hat{m}_z(\boldsymbol{r}) B_{ext,z}(\boldsymbol{r}) \right\} ,$$

so that the one-to-one mapping reduces to

$$|\Phi\rangle \Longleftrightarrow (n, m_z)\,. \tag{4.18}$$

In this case the ground state is uniquely determined by n and m_z, $|\Phi[n, m_z]\rangle$, and the variational equations (4.17) reduce accordingly.

4.2.2 Single-particle equations

The next task is to derive an alternative form of the fundamental variational equations of Section 4.2.1 which is more useful in practice. The basic idea is to represent the elementary density variables of RDFT in terms of auxiliary single-particle four spinors ϕ_k, (assuming that this is possible for arbitrary external fields, i.e. assuming noninteracting v-representability). Such a representation in general also includes all vacuum corrections to the ground state four current and energy (Engel and Dreizler 1996, Engel et al. 1998a). For most RDFT applications, however, these field theoretical effects are irrelevant. In the following we thus restrict ourselves to summarizing the no-pair form for brevity.

In the four current version of RDFT the auxiliary spinors are chosen to reproduce the complete j^μ,

$$j^\mu(\boldsymbol{r}) = c \sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r}) \alpha^\mu \phi_k(\boldsymbol{r})\,, \tag{4.19}$$

where

$$\Theta_k = \begin{cases} 0 & \text{for} \quad \epsilon_k \leq -mc^2 \\ 1 & \text{for} \quad -mc^2 < \epsilon_k \leq \epsilon_F \\ 0 & \text{for} \quad \epsilon_F < \epsilon_k \end{cases} \tag{4.20}$$

in the no-pair approximation and ϵ_F is the Fermi energy. Eq.(4.19) then induces a decomposition of E_{tot}, in which the manageable single-particle components are separated from the more complicated many-body contributions,

$$E_{tot} = T_s + E_{ext} + E_H + E_{xc}\,. \tag{4.21}$$

Here T_s denotes the kinetic energy of the 'auxiliary particles',

$$T_s \quad = \quad \int d^3r \sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r}) \big[-ic\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\beta - 1)mc^2 \big] \phi_k(\boldsymbol{r})\,, \tag{4.22}$$

and E_{ext} represents the coupling between the electrons and the external fields,

$$E_{ext} = \frac{e}{c} \int d^3r \; j_\mu(\boldsymbol{r}) \; V^\mu(\boldsymbol{r})\,. \tag{4.23}$$

E_H is the 'covariant' form of the Hartree energy, which can be split into the Coulomb contribution E_H^{C} and a transverse part E_H^{T},

$$E_H = \frac{1}{2c^2}\int d^3x \int d^4y \; D^0_{\mu\nu}(\boldsymbol{x}-\boldsymbol{y}, y^0)\; j^\mu(\boldsymbol{x}) j^\nu(\boldsymbol{y}) = E_H^{\mathrm{C}} + E_H^{\mathrm{T}} \tag{4.24}$$

$$E_H^{\mathrm{C}} = \frac{e^2}{2}\int d^3r \int d^3r' \; \frac{n(\boldsymbol{r})\; n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{4.25}$$

$$E_H^{\mathrm{T}} = -\frac{e^2}{2c^2}\int d^3r \int d^3r' \; \frac{\boldsymbol{j}(\boldsymbol{r})\cdot\boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,. \tag{4.26}$$

Finally, the xc-energy E_{xc}, in which all many-body aspects beyond the Pauli principle are absorbed, is defined by (4.21) (the rest mass of the electrons has been subtracted from E_{tot}). As the existence theorem (4.4) is equally valid for noninteracting particles, not only E_{tot} but also T_s is a unique functional of j^μ. Consequently, also E_{xc} must be a unique functional of j^μ, $E_{xc}[j^\mu]$. Minimization of E_{tot} with respect to the ϕ_k rather than j^μ thus leads to effective single-particle equations (Rajagopal 1978, MacDonald and Vosko 1979),

$$\big\{ -ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 + \alpha_\mu v_s^\mu(\boldsymbol{x})\big\}\phi_k(\boldsymbol{x}) = \epsilon_k\,\phi_k(\boldsymbol{x})\,, \tag{4.27}$$

with the multiplicative KS potential v_s^μ consisting of the sum of V^μ, the Hartree potential v_H^μ and the xc-potential v_{xc}^μ,

$$v_s^\mu(\boldsymbol{r}) = eV^\mu(\boldsymbol{r}) + v_H^\mu(\boldsymbol{r}) + v_{xc}^\mu(\boldsymbol{r}) \tag{4.28}$$

$$v_H^\mu(\boldsymbol{r}) = \frac{e^2}{c}\int d^3r' \; \frac{j^\mu(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{4.29}$$

$$v_{xc}^\mu(\boldsymbol{r}) = c\frac{\delta E_{xc}[j]}{\delta j_\mu(\boldsymbol{r})}\,. \tag{4.30}$$

Eqs.(4.19,4.27-4.30) have to be solved selfconsistently. With the exact $E_{xc}[j^\mu]$ their solution leads to the exact ground state four current, which, upon insertion into (4.21), yields the exact ground state energy. On the other hand, no statement is made about the true many-body ground state $|\Phi\rangle$. Moreover, as a matter of principle, the eigenvalues ϵ_k have no physical meaning in the case of interacting particles. The only exception is the eigenvalue of the highest occupied KS state, which, in nonrelativistic DFT, can be shown to be identical with the ionization potential (Almbladh and von Barth 1985) (for finite systems — no rigorous proof of this statement is known in the field theoretical situation).

At this point it is convenient, though not required, to define the exchange component E_x of E_{xc}. As in the nonrelativistic context (Sahni et al. 1982, Langreth and Mehl 1983, Sham 1985) one identifies E_x with the first order contribution to E_{xc} resulting from perturbation theory on the basis of the KS

auxiliary Hamiltonian (Engel et al. 1998a). Within the no-pair approximation this leads to

$$E_x = -\frac{e^2}{2}\sum_{k,l}\Theta_k\Theta_l\int d^3r\int d^3r'\,\frac{\cos(\omega_{kl}|\boldsymbol{r}-\boldsymbol{r}'|)}{|\boldsymbol{r}-\boldsymbol{r}'|} \times \phi_k^\dagger(\boldsymbol{r})\alpha_\mu\phi_l(\boldsymbol{r})\;\phi_l^\dagger(\boldsymbol{r}')\alpha^\mu\phi_k(\boldsymbol{r}')\,, \tag{4.31}$$

($\omega_{kl} = |\epsilon_k - \epsilon_l|/c$) which can be easily decomposed into a Coulomb part

$$E_x^{\mathrm{C}} = -\frac{e^2}{2}\sum_{k,l}\Theta_k\Theta_l\int d^3r\int d^3r'\,\frac{\phi_k^\dagger(\boldsymbol{r})\phi_l(\boldsymbol{r})\;\phi_l^\dagger(\boldsymbol{r}')\phi_k(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,, \tag{4.32}$$

and a transverse remainder $E_x^{\mathrm{T}} = E_x - E_x^{\mathrm{C}}$. It is worthwhile emphasizing that neither E_x nor E_x^{C} are identical with their Dirac-Fock (DF) counterparts: The KS spinors ϕ_k used for the evaluation of (4.31) or (4.32) are solutions of (4.27) with its *multiplicative* total potential, in contrast to the DF orbitals which experience the nonlocal DF exchange potential. In fact, the multiplicative nature of v_s^μ also ensures the gauge invariance of (4.31) (Engel et al. 1998a), which is lost as soon as the ϕ_k correspond to a nonlocal single-particle potential. So, while (4.31) is most easily derived in Feynman gauge, the Coulomb gauge propagator (4.11) finally leads to the same E_x. The correlation energy E_c of RDFT is then given by $E_c = E_{xc} - E_x$.

Variants of the single-particle equations (4.27) are obtained for the other versions of RDFT. Starting from the zeroth component of (4.19),

$$n(\boldsymbol{r}) = \sum_k \Theta_k\phi_k^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r})\,, \tag{4.33}$$

the selfconsistent equations of the purely n-dependent formalism (4.14) have the same form as the time-like component of Eq.(4.27),

$$\big\{-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 + v_s(\boldsymbol{r})\big\}\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r}) \tag{4.34}$$

$$v_s(\boldsymbol{r}) = v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + \frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})} + \frac{\delta E_H^{\mathrm{T}}[\boldsymbol{j}[n]]}{\delta n(\boldsymbol{r})}\,, \tag{4.35}$$

with $v_H \equiv v_H^0$ (MacDonald and Vosko 1979). In Eqs.(4.34),(4.35) one has used the fact that $\boldsymbol{j}$ can be understood as a functional of n, $\boldsymbol{j}[n] = \langle\Phi[n]|\hat{\boldsymbol{j}}|\Phi[n]\rangle$. This not only allows the exact inclusion of E_H^{T}, but also relates the j-dependent E_{xc} of Eq.(4.20) to the purely n-dependent E_{xc} of the present RDFT variant, $E_{xc}[n] \equiv E_{xc}[n,\boldsymbol{j}[n]]$. In practice, however, the functional $\boldsymbol{j}[n]$ is not at all known, so that one usually simply neglects E_H^{T} at this point. Note that for the large class of time-reversal invariant systems (closed shells) $\boldsymbol{j}$ vanishes, so that E_H^{T} does not contribute anyway.

For the Hamiltonian (4.15) one starts with a single-particle representation of the charge and the magnetization density rather than of the full j^μ,

$$n(\boldsymbol{r}) = \sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) \quad ; \quad \boldsymbol{m}(\boldsymbol{r}) = -\mu_B \sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r})\beta\boldsymbol{\Sigma}\phi_k(\boldsymbol{r}) \,. \tag{4.36}$$

The total energy can then be decomposed as in (4.20) with E_{ext} replaced by

$$E'_{ext} = \int d^3r \left\{ n(\boldsymbol{r})v_{ext}(\boldsymbol{r}) + \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}_{ext}(\boldsymbol{r}) \right\} . \tag{4.37}$$

In order to simplify the resulting single-particle equations, one next absorbs E_H^{T} into E_{xc} (MacDonald and Vosko 1979), relying on the fact that $\boldsymbol{j}$ is a unique functional of $n, \boldsymbol{m}$. However, as for Eqs.(4.34),(4.35) this usually implies the neglect of E_H^{T}. With this redefinition/approximation Eq.(4.17) leads to (Ramana and Rajagopal 1981a) (Eschrig et al. 1985, see also)

$$\{ -ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta - 1)mc^2 + v_s - \mu_B\beta\boldsymbol{\Sigma}\cdot\boldsymbol{B}_s\}\phi_k(\boldsymbol{r}) = \epsilon_k\phi_k(\boldsymbol{r}) \tag{4.38}$$

$$v_s(\boldsymbol{r}) = v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + \frac{\delta E_{xc}[n,\boldsymbol{m}]}{\delta n(\boldsymbol{r})} \tag{4.39}$$

$$\boldsymbol{B}_s(\boldsymbol{r}) = \boldsymbol{B}_{ext}(\boldsymbol{r}) + \frac{\delta E_{xc}[n,\boldsymbol{m}]}{\delta \boldsymbol{m}(\boldsymbol{r})} \,. \tag{4.40}$$

One can now easily take the limit $\boldsymbol{B}_{ext} = 0$. Eqs.(4.36)-(4.40) provide the appropriate starting point for density functional studies of magnetic systems. They have nevertheless not yet found widespread use due to their rather complex structure. Only recently the first calculations with truly non-collinear $\boldsymbol{m}$ have been performed (Nordström and Singh 1996, Eschrig and Servedio 1999). While ground states with non-collinear $\boldsymbol{m}$ were found for a number of solids (Sandratskii 1998, see, e.g.,), non-collinearity turned out to be only of limited importance for open-shell atoms (Eschrig and Servedio 1999). Moreover, presently only the exchange contribution to the RLDA for $E_{xc}[n,\boldsymbol{m}]$ is available (Ramana and Rajagopal 1979, 1981a, MacDonald 1983, Xu et al. 1984).

One is thus led to consider the RDFT formalism for collinear $\boldsymbol{m}$, Eq.(4.18), which serves as a standard tool for the discussion of magnetic systems. The corresponding single-particle equations follow from Eqs.(4.36)-(4.40) by restriction to the z-component of $\boldsymbol{m}$. A particularly useful form of the equations for collinear $\boldsymbol{m}$ is found in terms of the generalized spin-densities $n_\pm$,

$$n_\pm(\boldsymbol{r}) \quad = \quad \frac{1}{2}\left[n(\boldsymbol{r}) \mp \frac{1}{\mu_B} m_z(\boldsymbol{r})\right] = \sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r}) \frac{1 \pm \beta\Sigma_z}{2} \phi_k(\boldsymbol{r}) \,. \tag{4.41}$$

Setting $B_{ext,z} = 0$, one obtains

$$\left\{ -ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta-1)mc^2 + \frac{1+\beta\Sigma_z}{2}v_{s+} + \frac{1-\beta\Sigma_z}{2}v_{s-} \right\}\phi_k = \epsilon_k\phi_k \tag{4.42}$$

$$v_{s,\sigma}(\boldsymbol{r}) = v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + v_{xc,\sigma}(\boldsymbol{r}) \tag{4.43}$$

$$v_{xc,\sigma}(\boldsymbol{r}) = \frac{\delta E_{xc}[n_+,n_-]}{\delta n_\sigma(\boldsymbol{r})} = \frac{\delta E_{xc}[n,m_z]}{\delta n(\boldsymbol{r})} - sign(\sigma)\mu_B\frac{\delta E_{xc}[n,m_z]}{\delta m_z(\boldsymbol{r})}\,. \tag{4.44}$$

Given the explicit form of the projection matrices in Eqs.(4.41),(4.42),

$$\frac{1+\beta\Sigma_z}{2} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \frac{1-\beta\Sigma_z}{2} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

Eqs.(4.41)-(4.44) are immediately identified as the relativistic extension of the standard form of nonrelativistic spin-density functional theory.

Clearly, the choice of the appropriate variant of RDFT depends on the system under consideration. As already indicated, however, the availability of suitable approximations for E_{xc} is similarly important. Even within the purely n-dependent form of RDFT the relativistic $E_{xc}[n]$ is not identical with the nonrelativistic xc-functional. In $E_{xc}[n]$ relativity not only enters via the relativistic form of n, but also shows up in the functional dependence of E_{xc} on n. In applications, however, these corrections are often neglected, e.g. by use of nonrelativistic spin-density functionals with the relativistic $n_\pm$ in Eq.(4.44). Of course, the large variety of nonrelativistic forms for $E_{xc}[n_\uparrow, n_\downarrow]$ which have been suggested in the literature cannot be reviewed here — the interested reader is referred to Dreizler and Gross (1990). An overview of the few available relativistic forms for E_{xc} is given in the next two Sections.

4.3 Implicit Density Functionals

4.3.1 Optimized Potential Method

The exact exchange (4.31) immediately raises the question whether orbital-dependent xc-functionals can be utilized in practice. As in the case of T_s, Eq.(4.22), one can use the fact that, via the relativistic HK theorem for non-interacting particles, the KS orbitals are unique functionals of j^μ, $\phi_k[j^\mu]$. This allows the replacement of the functional derivative of E_{xc} with respect to j^μ required for the evaluation of v^μ_{xc} by functional derivatives to the ϕ_k and the corresponding KS eigenvalues ϵ_k. This leads to the ROPM integral equation of RDFT (Engel et al. 1998a) (in the no-pair approximation),

$$\int d^3r'\ \chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}')\ v_{xc,\nu}(\boldsymbol{r}') = \Lambda^\mu_{xc}(\boldsymbol{r})\,, \tag{4.45}$$

with χ_0 denoting the static response function of the KS system,

$$\chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}') = -\sum_k \Theta_k \phi_k^\dagger(\boldsymbol{r})\alpha^\mu G_k(\boldsymbol{r},\boldsymbol{r}')\alpha^\nu \phi_k(\boldsymbol{r}') + c.c. \tag{4.46}$$

$$\begin{aligned}\Lambda_{xc}^\mu(\boldsymbol{r}) &= -\sum_k \int d^3r' \left[\phi_k^\dagger(\boldsymbol{r})\alpha^\mu G_k(\boldsymbol{r},\boldsymbol{r}')\frac{\delta E_{xc}}{\delta\phi_k^\dagger(\boldsymbol{r}')} + c.c.\right] \\ &\quad + \sum_k j_k^\mu(\boldsymbol{r})\frac{\partial E_{xc}}{\partial \epsilon_k}\end{aligned} \tag{4.47}$$

$$G_k(\boldsymbol{r},\boldsymbol{r}') = \sum_{l\neq k}\frac{\phi_l(\boldsymbol{r})\ \phi_l^\dagger(\boldsymbol{r}')}{\epsilon_l - \epsilon_k} \quad ; \quad j_k^\mu(\boldsymbol{r}) = \phi_k^\dagger(\boldsymbol{r})\alpha^\mu\phi_k(\boldsymbol{r})\,. \tag{4.48}$$

Eqs.(4.45)-(4.48) are easily reduced to the purely density-dependent form of RDFT (Shadwick et al. 1989, Engel et al. 1995a). Recently, the ROPM equation for the $(n,\boldsymbol{m})$-version of RDFT has also been formulated (Auth 1999).

The numerical solution of Eqs.(4.45)-(4.48) is rather involved, due to the fact that the evaluation of G_k requires a summation over the complete KS spectrum. In the nonrelativistic case the semi-analytical Krieger-Li-Iafrate (KLI) approximation (Krieger et al. 1990) for (4.45)-(4.48) proved to be very accurate for atoms (Krieger et al. 1992), molecules (Engel et al. 2000b), and solids (Schmid 2000). The KLI approximation can be most easily extended into the relativistic domain by use of a closure approximation, $\epsilon_l - \epsilon_k \approx \Delta\overline{\epsilon}$, for G_k (Engel et al. 1998a),

$$\begin{aligned}v_{xc}^\mu(\boldsymbol{r}) &= \frac{1}{2n(\boldsymbol{r})}\left\{-g_\nu^\mu + g^{\mu 0}g_{\nu 0} + \frac{j^\mu(\boldsymbol{r})j_\nu(\boldsymbol{r})}{j^\rho(\boldsymbol{r})j_\rho(\boldsymbol{r})}\right\} \\ &\quad \times\left\{\sum_k\left[\phi_k^\dagger(\boldsymbol{r})\alpha^\nu\frac{\delta E_{xc}}{\delta\phi_k^\dagger(\boldsymbol{r})} - j_k^\nu(\boldsymbol{r})\overline{e}_k + c.c.\right] + 2\sum_k \Theta_k j_k^\nu(\boldsymbol{r})\overline{v}_k\right\}\end{aligned} \tag{4.49}$$

$$\overline{e}_k = \int d^3r\,\phi_k^\dagger(\boldsymbol{r})\frac{\delta E_{xc}}{\delta\phi_k^\dagger(\boldsymbol{r})} \quad ; \quad \overline{v}_k = \int d^3r\, j_{k,\lambda}(\boldsymbol{r})v_{xc}^\lambda(\boldsymbol{r})\,, \tag{4.50}$$

where, consistent with the closure approximation, the $\partial E_{xc}/\partial\epsilon_k$-contribution to (4.47) has been neglected. Alternatively, Eqs.(4.49),(4.50) may be derived from a rearranged form of (4.45)-(4.48) (Kreibich et al. 1998).

4.3.2 Results for the exact exchange

The x-only ground state energies of noble gas atoms obtained by solution of Eqs.(4.45)-(4.48) for different forms of the electron-electron interaction are listed in Table 4.1. In the Coulomb limit a direct comparison with fully numerical RHF calculations is possible. Due to the multiplicative nature of v_x^{OPM} the OPM energies are higher than the RHF data. The actual differences, however, are extremely small. As a consequence, basis set limitations easily dominate

Table 4.1: Exchange-only ground state energies from ROPM and RHF calculations for noble gas atoms: Coulomb(C)- and Coulomb-Breit(C+B)-limit in comparison with complete transverse exchange (C+T) (Engel et al. 1998a). For the RHF approximation the energy difference with respect to the ROPM is given, $\Delta E = E_{tot}(\mathrm{RHF}) - E_{tot}(\mathrm{ROPM})$, providing results from (a) finite differences calculations (Dyall et al. 1989) and (b) a basis set expansion (Ishikawa and Koc 1994) (all energies in mHartree — v_{ext} and c as in (Ishikawa and Koc 1994)).

Atom	$-E_{tot}^{\mathrm{C}}$ ROPM	ΔE^{C} RHF[a]	ΔE^{C} RHF[b]	$-E_{tot}^{\mathrm{C+B}}$ ROPM	$\Delta E^{\mathrm{C+B}}$ RHF[b]	$-E_{tot}^{\mathrm{C+T}}$ ROPM
He	2862	0	0	2862	0	2862
Ne	128690	−2	−2	128674	−2	128674
Ar	528678	−5	−5	528546	−5	528546
Kr	2788849	−13	−12	2787423	−12	2787431
Xe	7446882	−19	−6	7441115	−3	7441179
Rn	23601947	−35	−19	23572625	11	23573332

over these conceptual differences, as can be seen from the Coulomb-Breit energies in Table 4.1. Finally, the comparison of the Coulomb-Breit values with those found by inclusion of the complete E_x^{T}, demonstrates the size of the retardation corrections to the Breit interaction. It is obvious that these corrections are only relevant for truly heavy atoms.

The importance of a selfconsistent treatment of the transverse interaction is examined in Table 4.2. The fully selfconsistent handling is compared with a perturbative evaluation of only the beyond-Breit terms and a perturbative treatment of the complete E_x^{T}. Even for the heaviest atoms the perturbative evaluation of the retardation corrections to the Breit term seems to be sufficient. On the other hand, use of first order perturbation theory for the complete E_x^{T} leads to errors of the order of 1 eV for heavy atoms. An accurate description of inner shell transitions in these systems requires the inclusion of second order Breit corrections.

Table 4.2 also demonstrates the accuracy of the KLI approximation in the relativistic situation. In fact, for heavy elements the differences between the KLI and the full OPM energies are smaller than those resulting from a perturbative treatment of the transverse interaction.

4.3.3 Correlation

Given the possibility to use the exact exchange in actual applications, one needs a correlation functional which can be combined with the exact E_x. The

Table 4.2: Exchange-only ground state energies from ROPM, RHF, RKLI, RLDA and RGGA(PW91) calculations for noble gas atoms: In the case of the ROPM the selfconsistent (sc) treatment of the complete E_x^{T} (T) is compared with a selfconsistent inclusion of only its Breit (B) limit (together with a first order perturbative (pt) calculation of the beyond Breit contributions (T−B)) as well as a fully perturbative evaluation of E_x^{T}. The latter procedure has also been used for the RHF calculations (Dyall et al. 1989) (Engel et al. 1998a, all energies in mHartree).

	$-E_{tot}^{\mathrm{C+T}}$	$E_{tot}^{\mathrm{C+T}} - E_{tot}^{\mathrm{C+T}}$[ROPM: s(C+T)]						
	ROPM	ROPM		RHF	RKLI	RLDA	RGGA	GGA
sc:	C+T	C+B	C	C	C+T	C+T	C+T	C
pt:	—	T−B	T	T	—	—	—	—
He	2862	0	0	0	0	138	6	6
Ne	128674	0	0	−2	1	1080	−24	−43
Ar	528546	0	0	−5	2	2458	41	−111
Kr	2787429	0	2	−12	3	6543	−22	−1683
Xe	7441173	1	10	−11	6	13161	83	−6705
Rn	23573354	8	68	29	9	35207	−9	−35145

most appropriate form of such an E_c is an open question even in the nonrelativistic case (Görling and Levy 1994, Grabo and Gross 1995, Kotani 1998, Engel and Facco Bonetti 2000, Seidl et al. 2000, Facco Bonetti et al. 2001). In most applications the exact E_x has thus been augmented by the LDA or GGA for correlation (Kotani 1994, 1995, Kotani and Akai 1996, Bylander and Kleinman 1995a,b, 1996, 1997, Chen et al. 1996, Städele et al. 1997, Engel and Dreizler 1999, Kim et al. 1999). However, this strategy does not lead to a consistent improvement over x-only results (Engel and Dreizler 1999, Kim et al. 1999). Error cancellation between exchange and correlation plays an important role for the success of the LDA and is also relevant in the case of the GGA. Conceptually, a fully nonlocal, orbital-dependent approximation for E_c appears to be most adequate. Presently, the most promising scheme for the derivation of such a functional is perturbation theory on the basis of the auxiliary KS Hamiltonian (Sham 1985, Görling and Levy 1994). This approach can be directly extended into the relativistic domain (Engel et al. 1998a), including all transverse and vacuum corrections. In principle, not only low order perturbative E_c can be obtained in this way, but also resummed forms like the RPA (Engel and Facco Bonetti 2000). In practice, however, the resulting functionals are computationally much more demanding than the exact E_x, so that until now only the lowest order contribution has been applied.

Table 4.3: Coulomb correlation energies of the Helium isoelectronic series: $E_c^{(2)}$ (OPM) versus CS (Colle and Salvetti 1975), LDA (Vosko et al. 1980), GGA (Perdew et al. 1992), MP2 (Ishikawa and Koc 1994) and exact results (Davidson et al. 1991). Both the nonrelativistic values E_c^{NR} and the difference between the relativistic numbers and E_c^{NR} are given (all energies in mHartree).

Ion	$-E_c^{\mathrm{NR}}$						$E_c^{\mathrm{NR}} - E_c^{\mathrm{R}}$	
	LDA	GGA	CS	OPM	MP2	exact	ROPM	RMP2
He	112.8	45.9	41.6	48.21	37.14	42.04	0.00	0.00
Ne^{8+}	203.0	61.7	40.6	46.81	44.37	45.69	−0.07	−0.07
Zn^{28+}	267.2	71.3	33.2	46.67	45.71	46.34	−0.19	−0.19
Sn^{48+}	297.7	76.0	30.0	46.65	45.98	46.47	0.72	0.69
Yb^{68+}	318.0	79.3	28.2	46.63		46.53	3.71	
Th^{88+}	333.2	81.7	27.0	46.62		46.56	11.00	

Within the no-pair approximation and neglecting the transverse interaction this second order term reads

$$\begin{aligned} E_c^{(2)} &= E_c^{MP2} + E_c^{\Delta HF} \qquad (4.51) \\ E_c^{MP2} &= \frac{1}{2} \sum_{ijkl;\epsilon_F<\epsilon_k,\epsilon_l} \Theta_i \Theta_j \frac{(ij||kl)\,[(kl||ij)-(kl||ji)]}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l} \\ E_c^{\Delta HF} &= \sum_{il;\epsilon_F<\epsilon_l} \frac{\Theta_i}{\epsilon_i-\epsilon_l} \left| \langle i|\alpha_\mu v_x^\mu|l\rangle + e^2 \sum_j \Theta_j (ij||jl) \right|^2 \\ (ij||kl) &= \int d^3r_1 \int d^3r_2 \, \frac{\phi_i^\dagger(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_1)\phi_j^\dagger(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}, \end{aligned}$$

where $\langle i|\alpha_\mu v_x^\mu|l\rangle = \int d^3r\, \phi_i^\dagger(\boldsymbol{r})\alpha_\mu\phi_l(\boldsymbol{r})v_x^{\mathrm{C},\mu}(\boldsymbol{r})$.

Illustrative results obtained by a perturbative evaluation of this functional on the basis of a selfconsistent calculation with the exact E_x^{C} are given in Table 4.3 and Figs.4.1, 4.2. Table 4.3 lists the correlation energies of the Helium isoelectronic series, separating the nonrelativistic from the relativistic contribution. As is well known, the LDA overestimates the exact E_c of neutral atoms by roughly a factor of 2. This error increases to a factor of 5 or more for highly charged ions. Moreover, while the PW91-GGA is rather close to the exact E_c for neutral Helium, the error increases to a factor of 2 for Fm^{98+}. Obviously, these explicit density functionals do not scale properly with Z. The same is true for the orbital-dependent Colle-Salvetti (CS) functional, which, however, underestimates E_c by far. On the other hand, Eq.(4.51) leads to very

accurate E_c for the highly charged ions, reflecting its systematic origin. For neutral atoms $E_c^{(2)}$ and the conventional MP2 energies (also listed in Table 4.3) bracket the exact values. Also, the relativistic corrections in E_c obtained with $E_c^{(2)}$ are almost identical with their MP2 counterparts.

Table 4.3 shows that $E_c^{(2)}$ is less accurate for neutral atoms than for positive ions. As an example for a negative ion, the most critical case, we consider Cs^-. For Cs^- $E_c^{(2)}$ amounts to 3625 mHartree, which may be compared to the nonrelativistic value of 3593 mHartree. Lacking any information on the exact E_c, we resort to an analysis of the corresponding electron affinities (EA), for which one obtains 1.31 eV (rel.) and 1.17 eV (nonrel.). These values are much larger than the experimental EA of 0.47 eV, which indicates the importance of higher order correlation terms. In fact, the inclusion of the Epstein-Nesbet type diagrams in (4.51) reduces the EA to 0.46 eV. Nevertheless, even on the level of $E_c^{(2)}$ this example demonstrates (i) the mere existence of negative ions within the OPM (which is due to the complete elimination of the electronic selfinteraction by the exact E_x), and, (ii) the effect of relativity on the EA.

One can show that $E_c^{(2)}$ includes the leading component of the dispersion force between two atoms (Engel et al. 1998a). Thus, from a fundamental point of view, $E_c^{(2)}$ is the first xc-functional which allows a seamless description of van der Waals bond molecules. As an example we show the energy surface of He_2 in Fig.4.1 (Engel et al. 2000a). As is well known, the LDA is not able to reproduce the van der Waals interaction, due to its local density-dependence. Fig.4.1 reflects this fact: In the LDA the He dimer is contracted until the individual atomic densities overlap substantially. On the other hand, the x-only OPM predicts He_2 to be unbound, consistent with the HF result. As for the behavior of E_c for neutral atoms, the correlated OPM and the conventional MP2 results bracket the exact variational energy surface. Thus, while the need for higher order correlation is again obvious, Fig.4.1 verifies the basic ability of functionals of the type (4.51) to describe dispersion forces.

All $E_c^{(2)}$-results discussed so far have been obtained by a perturbative evaluation of $E_c^{(2)}$ on the basis of an x-only OPM calculation. One may thus ask to what extent e.g. the comparatively poor EA found for Cs^- is due to the lack of the correlation component in v_s. A straightforward selfconsistent application of $E_c^{(2)}$, however, is not only extremely involved, it also leads to a diverging v_c in the asymptotic regime (Facco Bonetti et al. 2001). This divergence originates from the dependence of (4.51) on unoccupied states, so that this problem can be avoided by use of a closure approximation in the OPM process (without affecting E_c) (Facco Bonetti et al. 2001). The resulting v_c for Ne is plotted in Fig.4.2. Fig.4.2 exhibits the complete failure of the LDA and PW91-GGA for atomic v_c. The CS potential has also little in common with the exact v_c. The closure approximated potential corresponding to (4.51) is the first DFT potential which at least qualitatively follows the exact v_c.

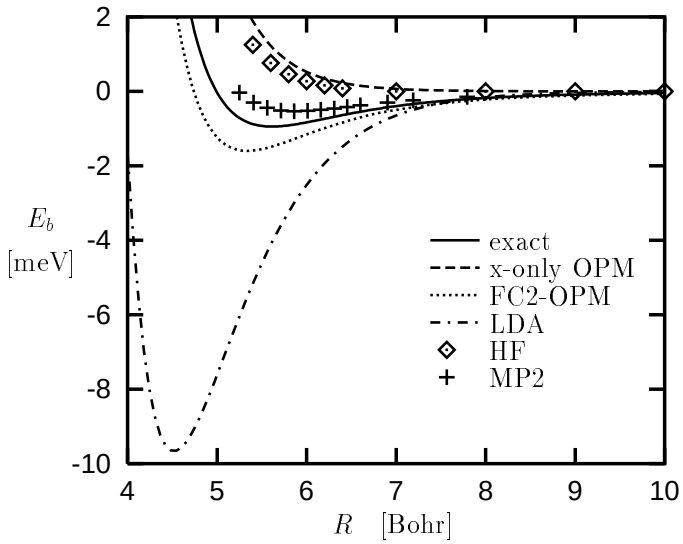

Figure 4.1: Energy surface of He_2: X-only and correlated OPM data (FC2$\equiv$ $E_x + E_c^{(2)}$) versus LDA, HF (Silver 1980), MP2 (Woon 1994) and exact (Aziz and Slaman 1991) results.

The need for the inclusion of higher order contributions is apparent from the overestimation of the 'shell structure' of v_c. In addition, the asymptotic $1/r^4$-behavior of the exact v_c is not reproduced. Clearly, perturbative correlation functionals like $E_c^{(2)}$ cannot be the final answer to the question which E_c should be combined with the exact E_x.

4.4 Explicit Density Functionals

4.4.1 Local density approximation

In view of the computational demands of OPM calculations and the open question for a suitable orbital-dependent E_c explicitly density-dependent xc-functionals, i.e. the LDA or GGA, will remain the standard in RDFT applications in the nearer future. The RLDA is obtained from the xc-energy density $e_{xc}^{RHEG}(n_0)$ of the relativistic homogeneous electron gas (Rajagopal 1978, MacDonald and Vosko 1979, Ramana and Rajagopal 1981b) by substitution of the gas density n_0 by the local $n(\boldsymbol{r})$. Decomposing e_{xc}^{RHEG} into exchange and correlation one has

$$E_{xc}^{RLDA}[n] = \int d^3r \left[e_x^{HEG}(n(\boldsymbol{r}))\Phi_{x,0}(\beta) + e_c^{HEG}(n(\boldsymbol{r}))\Phi_{c,0}(\beta) \right] \quad (4.52)$$

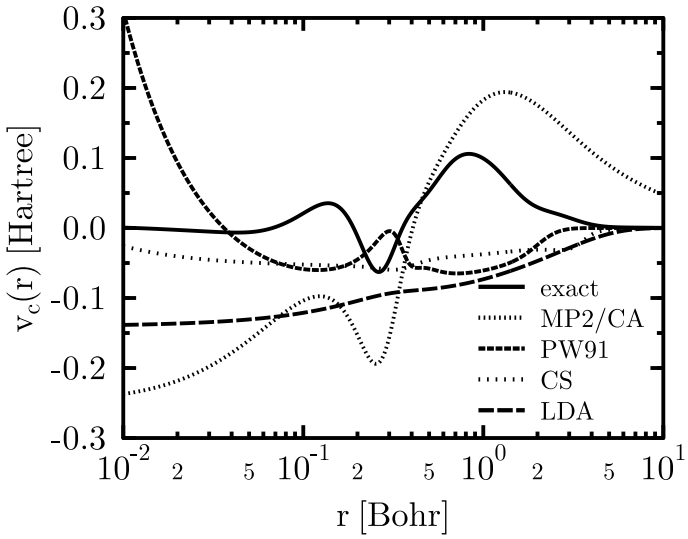

Figure 4.2: Correlation potential of Ne: Exact v_c (Umrigar and Gonze 1994) versus LDA, PW91-GGA (Perdew et al. 1992) and CS (Colle and Salvetti 1975) results as well as closure approximation for $v_c^{(2)}$ (MP2/CA).

where β is defined by

$$\beta = \frac{[3\pi^2 n(\boldsymbol{r})]^{1/3}}{mc}\,, \tag{4.53}$$

and both the exchange and correlation energy densities of the RHEG have been factorized into their respective nonrelativistic limits and relativistic corrections factors $\Phi_{x/c,0}(\beta)$. While $\Phi_{x,0}$ has been known for quite some time (Akhiezer and Peletminskii 1960),

$$\Phi_{x,0}(\beta) = 1 - \frac{3}{2}\left[\frac{\sqrt{1+\beta^2}}{\beta} - \frac{\mathrm{Arsh}(\beta)}{\beta^2}\right], \tag{4.54}$$

$\Phi_{c,0}$ has only been evaluated within the RPA (Ramana and Rajagopal 1981b, Engel et al. 1995a). The resulting correction factor can be accurately parameterized in the form (Schmid et al. 1998)

$$\Phi_{c,0}^{RPA}(\beta) = \frac{1 + a_1\beta^3\ln(\beta) + a_2\beta^4 + a_3(1+\beta^2)^2\beta^4}{1 + b_1\beta^3\ln(\beta) + b_2\beta^4 + b_3[A\ln(\beta) + B]\beta^7}\,, \tag{4.55}$$

which incorporates the analytically known high-density limits of both the relativistic RPA as well as its nonrelativistic limit. Both $\Phi_{x,0}$ and $\Phi_{c,0}^{RPA}$ include the full transverse interaction, and, to some extent, vacuum corrections beyond the no-pair approximation (Engel and Dreizler 1996). As the relativistic

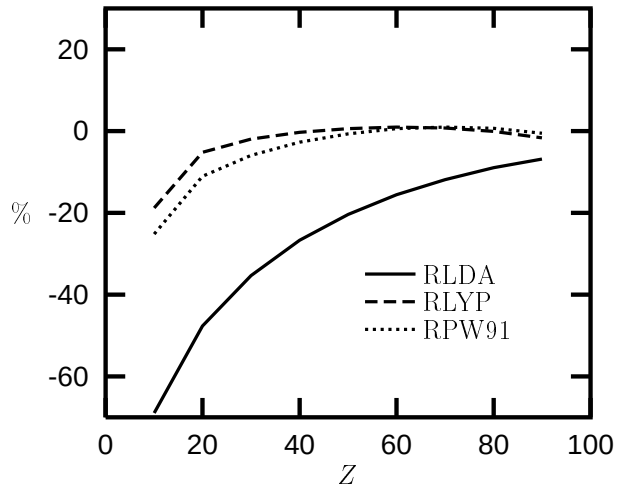

Figure 4.3: Relativistic contribution to E_c: Percentage deviation of RLDA- and RGGA-results from relativistic MP2-data for Ne isoelectronic series.

form of all non-RPA contributions to e_c^{RHEG} is not known, the corresponding relativistic corrections must either be neglected (Engel et al. 1995a), using $E_c^{RLDA} = E_c^{RRPA} - E_c^{RPA} + E_c^{LDA}$, or be taken into account in an empirical form, combining $\Phi_{c,0}^{RPA}$ with a parameterization for e_c^{HEG} which goes beyond the RPA (Schmid et al. 1998).

Applications of (4.52)-(4.55) to atoms, however, showed that the accuracy of the RLDA is not very satisfying (Das et al. 1980, Ramana et al. 1982, Engel et al. 1995a). This is illustrated in Table 4.2 and Fig.4.3. A rigorous reference standard for the analysis of the RLDA exchange is provided by x-only ROPM results. For heavy atoms the x-only RLDA ground state energies are off by more than 10 Hartree, which is mainly due to the incomplete elimination of the K-shell selfinteraction (see Table 4.2, (MacDonald et al. 1981, 1982, compare also); for a relativistic version of the Perdew-Zunger selfinteraction correction scheme (Perdew and Zunger 1981) see Rieger and Vogl (1995)). The picture is similar for the correlation energy. As discussed earlier the non-relativistic LDA overestimates atomic E_c by a factor of 2. At this point only the relativistic contribution to E_c, i.e. the performance of $\Phi_{c,0}^{RPA}$, is of interest. In Fig.4.3 we plot the deviation of the relativistic correction evaluated from Eqs.(4.52),(4.55) for the Ne isoelectronic series from the corresponding MP2 data (Ishikawa and Koc 1994) (which can serve as reference values for the present purpose, in spite of the fact that they have been evaluated with the Coulomb-Breit interaction in Coulomb gauge and the no-pair approximation (Facco Bonetti et al. 1998, compare)). As Fig.4.3 shows, the relativistic correction in E_c is overestimated by the RLDA, the error being as large as 70%

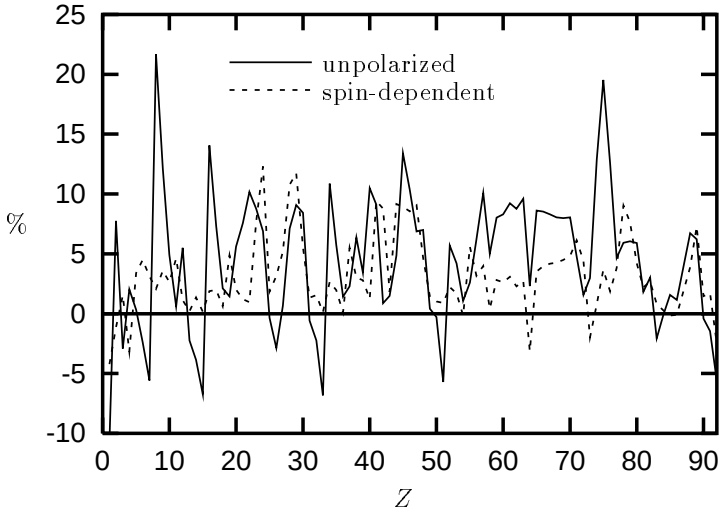

Figure 4.4: Ionization potentials of neutral atoms: Percentage deviation of spin-dependent and unpolarized LDA from experiment (Lide 1996).

for neutral atoms.

While Eqs.(4.52)-(4.55) correspond to a spin-saturated RHEG, the exchange energy has also been evaluated for a polarized RHEG (Ramana and Rajagopal 1979, 1981a, MacDonald 1983, Xu et al. 1984), which yields the input $E_x[n, \boldsymbol{m}]$ to Eqs.(4.39),(4.40) or (4.44). As its $\boldsymbol{m}$-dependence is only implicitly given, this functional has only rarely been used (Cortona et al. 1985, Cortona 1989, Eschrig and Servedio 1999). For magnetic systems usually the nonrelativistic LDA is utilized with (4.44) (Huhne et al. 1998, see, e.g.,). However, even for open-subshell atoms the solution of (4.42) under the assumption of spherical symmetry is nontrivial. Several variants for handling the resulting intricate set of four coupled radial differential equations have been suggested in the literature (Cortona et al. 1985, Cortona 1989, Ebert 1989, Yamagami et al. 1997, Forstreuter et al. 1997). Their solution is particularly difficult for neutral atoms, so that mostly results for ions are available. A new, more stable scheme has been developed recently (Engel et al. 2001a). This scheme relies on a careful analysis of the appropriate boundary conditions which allows the identification of a suitable criterion ('quantum number') to distinguish the 'spin-up' and 'spin-down' solutions. Its practical success is illustrated in Fig.4.4 in which the percentage deviation of the resulting ionization potentials (IPs) of neutral atoms from experiment is shown for the complete periodic table. The spin-dependent treatment via (4.42) is compared with the solution of (4.34) (on the basis of the LDA). The error of the spin-dependent IP in

general is considerably smaller than that of its unpolarized counterpart, most notably for the light atoms and the lanthanides. On the other hand, the error is still substantial for the $3d$ and $4d$ elements, so that the question of gradient corrections has to be raised.

4.4.2 Generalized gradient approximation

For a large variety of applications in quantum chemistry and condensed matter theory the inclusion of gradient corrections to the LDA in the form of the Generalized Gradient Approximation (GGA) (Becke 1988a, Perdew et al. 1992) turned out to be advantageous (Bagno et al. 1989, Becke 1992, Johnson et al. 1993). The direct use of nonrelativistic GGAs in RDFT calculations, however, leads to substantial errors in total energies as can be seen from Table 4.2. Consequently, a relativistic extension of the GGA (RGGA) is required. The most appropriate form of a RGGA for E_x is given by

$$E_x^{RGGA} = \int d^3r \; e_x^{HEG}(n) \; \left[\Phi_{x,0}(\beta) + g(\xi)\Phi_{x,2}(\beta)\right] \;, \tag{4.56}$$

with $\xi = [\boldsymbol{\nabla} n/(2(3\pi^2 n)^{1/3} n)]^2$ and $g(\xi)$ being the gradient part of a nonrelativistic GGA (Engel et al. 1996). The correction factor $\Phi_{x,2}$ can, in principle, be calculated from the first order response function of the RHEG. However, as this approach proved to be very involved already in the nonrelativistic limit (Antoniewicz and Kleinman 1985, Engel and Vosko 1990, Chevary and Vosko 1990) and as the gradient function $g(\xi)$ contains some semi-empirical information anyway, a semi-empirical approach to $\Phi_{x,2}$ should be sufficient. Following the strategy behind the Becke GGA (Becke 1988a), a reasonably accurate $\Phi_{x,2}$ may be obtained by making a sufficiently flexible ansatz (in the form of a Padé approximant) and fitting its coefficients to the exact relativistic E_x of a number of closed-subshell atoms (keeping the form of $g(\xi)$ fixed) (Engel et al. 1996, 1998b). Corresponding fits have been performed for the two most frequently used forms of GGAs (Becke 1988a, Perdew et al. 1992), the resulting $\Phi_{x,2}$ being very similar. As is demonstrated in Table 4.2 for the PW91-version, the RGGA leads to much more accurate atomic E_x (and v_x) than both the RLDA and the GGA.

The correlation functional requires a slightly different scheme, as, on the one hand, the RLDA is not known completely, and, on the other, some GGAs for E_c (Lee et al. 1988) are not based on the LDA. Therefore only one overall correction factor for the complete correlation part of the GGA has been used,

$$E_c^{RGGA}[n] = \int d^3r \; e_c^{GGA}(n, (\boldsymbol{\nabla} n)^2, ...) \; \Phi_c^{GGA}(\beta) \;,$$

keeping the nonrelativistic form $e_c^{GGA}(n, (\boldsymbol{\nabla} n)^2, ...)$ fixed (Engel et al. 1998b). In view of the fact that the relativistic corrections to atomic E_c are much

Table 4.4: Spectroscopic constants of noble metal dimers: PP (Engel et al. 2001b) versus AE results for both LDA and BP86-GGA (a: Mayer et al. (1996), b: Liu and van Wüllen (2000), c: Varga et al. (2000b) — the D_e in parentheses correspond to unpolarized atomic ground state energies).

mode	E_{xc}	Cu_2 R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]	Au_2 R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]
PP	LDA	4.04	2.83	304	4.61	3.02	198
AE	LDA^{a,b}	4.05	2.86	307	4.64	3.00	196
PP	GGA				4.72	2.38	179
AE	GGA^a	4.16	2.28	287	4.75	2.30	179
AE	RGGA^a	4.17	2.27	285	4.76	2.27	177
AE	GGA^c	4.20	3.27	283	4.78	(3.19)	188
AE	RGGA^c	4.21	3.27	282	4.79	(3.17)	187
expt.		4.20	2.05	265	4.67	2.30	191

smaller than those to atomic E_x this less sophisticated approach should be sufficient. Again a Padé approximant has been used as ansatz for Φ_c^{GGA}. Its coefficients have been fitted to the most systematic set of relativistic E_c available (MP2 results for the Ne isoelectronic series on the basis of the DCB Hamiltonian (Ishikawa and Koc 1994)), starting from two different e_c^{GGA} (Lee et al. 1988, Perdew et al. 1992). As Fig.4.3 shows, atomic E_c are clearly improved by this RGGA.

In contrast to the rather inaccurate RLDA, the RGGA allows an examination the importance of relativistic corrections to $E_{xc}[n]$ for the properties of molecules and solids. This question has been investigated both for noble metal compounds (Mayer et al. 1996, Varga et al. 1999) and for metallic Gold and Platinum (Schmid et al. 1998) within the framework of LAPW calculations (Blaha et al. 1995). Prototype results for Cu_2 and Au_2 are given in Table 4.4. It turns out that even for Au, which usually exhibits the effects of relativity most clearly (Pyykkö 1988), the impact of the correction factors $\Phi_{x/c}$ on the molecular binding properties is marginal, i.e. smaller than usual differences between two basis sets. It seems worthwhile to point out that in the case of the dissociation energy the similarity of GGA and RGGA results is due to the cancellation of the large relativistic corrections to the individual ground state energies of the molecule and its constituents. The same observation is made for solids, as can be gleaned from Table 4.5.

On the other hand, a comparison of the (R)GGA results in Tables 4.4, 4.5 with experiment reveals the limitations of GGAs for heavy elements: For

Table 4.5: Lattice constant a_0 and cohesive energy E_{coh} of Au and Pt obtained from LAPW calculations with various xc-functionals in comparison to experiment (Brewer 1977, Khein et al. 1995).

	Au		Pt	
	a_0 [Bohr]	$-E_{coh}$ [eV]	a_0 [Bohr]	$-E_{coh}$ [eV]
LDA	7.68	4.12	7.36	6.76
RLDA	7.68	4.09	7.37	6.73
GGA	7.87	2.91	7.51	5.34
RGGA	7.88	2.89	7.52	5.30
expt.	7.67	3.78	7.40	5.85

both Au_2 and the Au metal the gradient terms overcorrect the errors of the LDA. It seems worth to note that the particularly large deviations in the case of the metal are not due to the usual neglect of the spin-orbit coupling for the valence electrons within the LAPW approach. Table 4.6 provides a comparison of LAPW results with and without spin-orbit coupling for some $5d$ metals (on the basis of the LDA). While spin-orbit coupling contributes significantly to the cohesive energy, its effect is too small to explain the differences between GGA and experimental data in Table 4.5. Thus, on the one hand, the results in Table 4.4, 4.5 illustrate the role of error cancellation, in particular for the LDA. On the other hand, they indicate the need for fundamentally new concepts for $E_{xc}[n]$ (such as implicit functionals) in the relativistic regime.

4.5 Normconserving Pseudopotentials

A particularly efficient method for the inclusion of relativity in electronic structure calculations is the pseudopotential (PP) approach. In the framework of DFT usually normconserving PPs (Hamann et al. 1979, Bachelet et al. 1982, Troullier and Martins 1991) are applied for this purpose. The standard form of normconserving PPs is given by

$$\begin{aligned}\langle \boldsymbol{r}|\hat{v}_{\rm ps}|\boldsymbol{r}'\rangle &= v_{\rm loc}(r)\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}') + \frac{\delta(r-r')}{r^2} \\ &\times \sum_{l=0}^{L}\sum_{j=l\pm 1/2}\left[\frac{2j+1}{4l+2}v_{{\rm ps},lj}(r) - v_{\rm loc}(r)\right]\sum_{m=-l}^{l} Y_{lm}(\Omega)Y^*_{lm}(\Omega')\,,\end{aligned} \tag{4.57}$$

where the individual components $v_{{\rm ps},lj}$ correspond to the various relevant valence states of the atom (and, as usual, a local component v_{loc} has been ex-

Table 4.6: Cohesive properties of $5d$ metals from LDA-LAPW calculations with (+SO) and without (−SO) spin-orbit coupling of the valence electrons.

		a_0 [Bohr]	$-E_{coh}$ [eV]	B_0 [GPa]
W	−SO	5.93	10.47	335
	+SO	5.94	10.72	316
	expt.	5.98	8.90	310
Ir	−SO	7.22	9.45	419
	+SO	7.22	9.58	377
	expt.	7.26	6.93	355
Au	−SO	7.67	4.29	214
	+SO	7.65	4.23	217
	expt.	7.67	3.78	171

tracted from the $v_{\mathrm{ps},lj}$). In (4.57) a j-average is used to generate j-independent PPs as DFT PP calculations are typically based on nonrelativistic (spin-) density functional theory. However, the $v_{\mathrm{ps},lj}$ could equally well be utilized in relativistic PP calculations, similar to energy-adjusted PPs (Seth et al. 1996). The construction of the $v_{\mathrm{ps},lj}$ proceeds in three steps. First an all-electron (AE) calculation is performed for the atom of interest, utilizing the n-dependent version of RDFT. Next, a screened PP $v^{\mathrm{sc}}_{\mathrm{ps},lj}$ is generated from the results of the AE calculation, requiring the lowest eigenstate obtained from $v^{\mathrm{sc}}_{\mathrm{ps},lj}$, the pseudoorbital (PO), to be identical with the corresponding AE orbital for r larger than a suitably chosen cutoff radius $r_{c,l}$. Finally, the interaction among the valence electrons is eliminated from $v^{\mathrm{sc}}_{\mathrm{ps},lj}$. The most simple form for this unscreening reads

$$v_{\mathrm{ps},lj}(r) \quad = \quad v^{\mathrm{sc}}_{\mathrm{ps},lj}(r) - v_H([n_{\mathrm{v,ps}}]; r) - v_{xc}([n_{\mathrm{v,ps}}]; r)\,, \qquad (4.58)$$

where $n_{\mathrm{v,ps}}$ is the valence density obtained from the POs. In (4.58) the nonlinear contributions to the core-valence interaction, resulting from the nonlinearity of $E_{xc}[n]$, are neglected. While this is an acceptable approximation for first and second row atoms, the nonlinearity of the core-valence interaction cannot be ignored in LDA or GGA calculations for many others, most notably the transition metal elements. In this case the inclusion of nonlinear core corrections (nlccs) is necessary (Louie et al. 1982).

Among the various schemes for the construction of $v^{\mathrm{sc}}_{\mathrm{ps},lj}$ presently the Troullier-Martins (TM) form (Troullier and Martins 1991) seems to be most widely used. However, in contrast to the original approach (Hamann et al.

1979, Bachelet et al. 1982) the TM scheme has been formulated for nonrelativistic situations. A consistent relativistic extension (Engel et al. 2001b) is presented in the next Section.

4.5.1 Relativistic Troullier-Martins scheme

For atoms Eq.(4.34) reduces to two coupled radial equations for the large and small components of the orbitals,

$$c\left(\partial_r + \frac{\kappa}{r}\right) a_{nlj}(r) = \left(2mc^2 - v_s(r) + \epsilon_{nlj}\right) b_{nlj}(r) \tag{4.59}$$

$$c\left(\partial_r - \frac{\kappa}{r}\right) b_{nlj}(r) = \left(v_s(r) - \epsilon_{nlj}\right) a_{nlj}(r) \tag{4.60}$$

(Eqs.(4.59),(4.60) imply a spherical average in the case of open subshells, $\kappa = -2(j-l)(j+1/2)$). The corresponding components of the PO satisfy Eqs.(4.59),(4.60) with v_s replaced by $v^{\rm sc}_{{\rm ps},lj}$. Given the AE solutions of Eqs.(4.59),(4.60) the explicit construction of $v^{\rm sc}_{{\rm ps},lj}$ starts with an ansatz for the large component of the PO,

$$a_{{\rm ps},lj}(r) = \begin{cases} a_{nlj}(r) & \text{for } r > r_{c,l} \\ r^{l+1}\exp[p(r)] & \text{for } r \le r_{c,l} \end{cases} \quad ; \quad p(r) = \sum_{i=0}^{6} c_{2i} r^{2i} \, .$$

For valence states, for which the associated screened PP has a depth of no more than 100 Hartree, $v^{\rm sc}_{{\rm ps},lj}$ can then be extracted from (4.59),(4.60), using a weakly relativistic expansion,

$$\begin{aligned} v^{\rm sc}_{{\rm ps},lj} &= \begin{cases} v_s & \text{for } r > r_{c,l} \\ v^{\rm sc,nr}_{{\rm ps},lj} + \delta v_{lj} & \text{for } r \le r_{c,l} \end{cases} \\ v^{\rm sc,nr}_{{\rm ps},lj} &= \epsilon_{nlj} + \frac{l+1}{r}\frac{p'}{m} + \frac{p'' + (p')^2}{2m} \\ \delta v_{lj} &= \frac{(v^{\rm sc,nr}_{{\rm ps},lj} - \epsilon_{nlj})^2}{2mc^2} + \frac{(v^{\rm sc,nr}_{{\rm ps},lj})'}{4m^2c^2}\left(\frac{a'_{{\rm ps},lj}}{a_{{\rm ps},lj}} + \frac{\kappa}{r}\right), \end{aligned}$$

where the primes denote derivatives with respect to r. The corresponding small component $b_{{\rm ps},lj}$ of the PO then follows from (4.59). Finally, the coefficients c_{2i} are determined by requiring continuity of $a_{{\rm ps},lj}$ and its first four derivatives at $r_{c,l}$, proper normalization as well as a smooth PP at the origin, $(v^{\rm sc,nr}_{{\rm ps},lj})''(0) = 0$.

Prototype LDA and GGA results obtained with these PPs are given in Tables 4.4, 4.7. As Table 4.4 demonstrates, the PP calculations reproduce the AE results for both Cu_2 (Mayer et al. 1996) and Au_2 (Liu and van Wüllen 2000) very accurately, both on the LDA and on the GGA level. Similar agreement is found for the transition metal compounds listed in Table 4.7, for

Table 4.7: Spectroscopic constants of transition metal compounds: PP versus AE (Castro and Salahub 1994, Engel et al. 2001b) results and experimental data (Purdum et al. 1982, Moskovits et al. 1984, Moskovits and DiLella 1980, Murad 1980, Cheung et al. 1981). For $3d$ elements the valence space includes the complete M shell. nlccs have been used.

			nonrelativistic			relativistic		
	Mode	E_{xc}	R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]	R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]
Fe_2	AE	LDA	3.68	4.38	497			
$^7\Delta$	PP	LDA	3.68	4.31	440	3.66	3.95	451
	PP	GGA				3.77	2.67	414
	expt.					3.82	1.30	300
FeO	AE	LDA	3.01	7.06	957			
$^5\Delta$	PP	LDA	2.99	7.00	968	2.97	6.80	984
	PP	GGA				3.04	5.36	913
	expt.					3.06	4.06	881
FeO	AE	LDA	3.06	6.70	942			
$^5\Sigma$	PP	LDA	3.04	6.60	947	3.01	6.59	969

which, however, only nonrelativistic AE reference values (Castro and Salahub 1994, Engel et al. 2001b) are available. Nevertheless, the relativistic corrections are not negligible even for these $3d$ elements. In fact, in the case of FeO relativity reduces the excitation energy from the $^5\Delta$ ground state to the first excited state ($^5\Sigma$) from the nonrelativistic value of 0.4 eV to 0.2 eV. On the other hand, the comparison of the LDA results with experiment clearly shows the need for nonlocal corrections. The GGA results are consistently closer to the experimental data, in particular for R_e. The GGA values for D_e are nonetheless not completely satisfying, which underlines the importance of the truly nonlocal contributions to E_{xc}.

4.5.2 Results for the exact exchange

The use of PPs is particularly attractive in the case of implicit xc-functionals: Even an x-only calculation within the KLI approximation (4.49),(4.50) is computationally more demanding than corresponding LDA or GGA calculations as an evaluation of the Slater integrals in (4.31) or (4.32) is required. PPs for the exact E_x have been introduced both on the KLI level (Bylander and Kleinman 1995a) and for the full OPM (Höck and Engel 1998, Moukara et al. 2000). However, it has been noted very early that standard normconserving

Table 4.8: Equilibrium lattice constant a, cohesive energy E_{coh} and bulk modulus B of fcc Al: Exact exchange in comparison with LDA results.

E_{xc} x	c	mode	a [Bohr]	E_{coh} [eV/atom]	B [GPa]
exact	—	OPM-PP	7.10	3.98	135
exact	—	SC-OPM-PP	7.79	1.37	71
LDA	LDA	LDA-PP+nlcc	7.48	4.05	88
expt.			7.65	3.39	77

PPs for the exact E_x suffer from a spurious long-range exchange component in the ionic PP (Bylander and Kleinman 1995a). This xc-tail originates from the nonlocality of E_x which leads to a contribution of the core states to the exchange potential in the valence regime. This feature of the core-valence interaction cannot be eliminated by (4.58). In applications to molecules or solids the xc-tail leads to a spurious ionic force which prevents accurate structural optimizations, in particular for solids. As an example we show fcc Aluminum in Table 4.8. The original OPM-PP for the exact E_x yields a lattice constant which is much too small, although the bond length of Al_2 is overestimated by an AE-OPM calculation (Engel et al. 2001c).

In order to eliminate the spurious xc-tail a selfconsistent scheme for the generation of normconserving PP has been developed (Engel et al. 2001c). In this parameter-free scheme the screened PP is iterated until its asymptotic structure matches that of $v_{xc}([n_{\mathrm{v,ps}}]; r)$ in (4.58), so that the final unscreened PP $v_{\mathrm{ps},lj}$ has the correct ionic behavior. The resulting PPs (SC-OPM-PP) substantially improve OPM results for molecules and solids, as can be seen from Table 4.8. While the cohesive energy reflects the missing correlation energy, both the lattice constant and the bulk modulus are clearly closer to the experimental values than the original OPM-PP data.

It seems worthwhile to emphasize that, apart from the fact that they lead to the spurious xc-tail, the nonlinear contributions to the core-valence interaction seem to be less important for the exact E_x than for the LDA. This is illustrated in Table 4.9 which lists atomic excitation energies associated with the transfer of an electron from one spin channel into the other. While in the case of the LDA nlccs are required for the accurate reproduction of these transfer energies, linear unscreening is sufficient for the exact E_x.

As already noted in Section 4.4, the exact E_x provides a standard that can be used to analyze conventional density functionals. As an example we show in Fig.4.5 the v_x of bulk Aluminum obtained within the PP approach. The solution of (4.45) (in a plane-wave basis) is compared with the KLI

Table 4.9: $s-p$ and $p-p$ transfer energies of first row atoms: PP versus AE x-only OPM results versus LDA data (all energies in eV).

	$2s_\downarrow \longrightarrow 2p_\uparrow$				$2p_\uparrow \longrightarrow 2p_\downarrow$		
	mode	LDA	OPM		mode	LDA	OPM
Be	AE	2.47	1.67	C	AE	1.20	1.35
	PP	2.37	1.67		PP	1.34	1.35
	PP+nlcc	2.46			PP+nlcc	1.21	
B	AE	3.23	2.13	N	AE	2.70	3.24
	PP	3.00	2.16		PP	2.98	3.26
	PP+nlcc	3.21			PP+nlcc	2.73	
C	AE	4.05	2.46	O	AE	1.48	1.93
	PP	3.68	2.50		PP	1.62	1.95
	PP+nlcc	4.01			PP+nlcc	1.49	

approximation as well as the corresponding LDA and PW91-GGA potentials (Schmid 2000). While the LDA is reasonably close to the exact v_x (at least, if one excludes the vicinity of the atomic core), the GGA is much less accurate, in spite of the improved cohesive properties found with the GGA (Fuchs et al. 1998). Even in the interstitial regime the gradient contributions to the GGA potential have the wrong sign. This demonstrates once more that the performance of GGAs is to some extent based on the cancellation of local errors (Engel and Vosko 1993). The KLI approximation, on the other hand, just underestimates the shell structure in the exact v_x.

As a final example for the application of the exact E_x, the band structure of FeO in AFM-II structure is plotted in Fig.4.6. For this PP calculation the exact E_x has been combined with the LDA for E_c. In spite of the use of the exact exchange functional, FeO is predicted to be a metal, in contrast to experiment. At present, it is not clear whether this failure to reproduce the insulating ground state of FeO originates from the use of the LDA for E_c or from the technical limitations of the PP calculation (KLI-approximation for v_x, only 3 special k-points for the integration over the Brillouin zone, $3s$ electrons in core). It must be emphasized, however, that the band structure shown in Fig.4.6 is rather different from its LDA counterpart (Dufek et al. 1994), which emphasizes the importance of the exact v_x for this system.

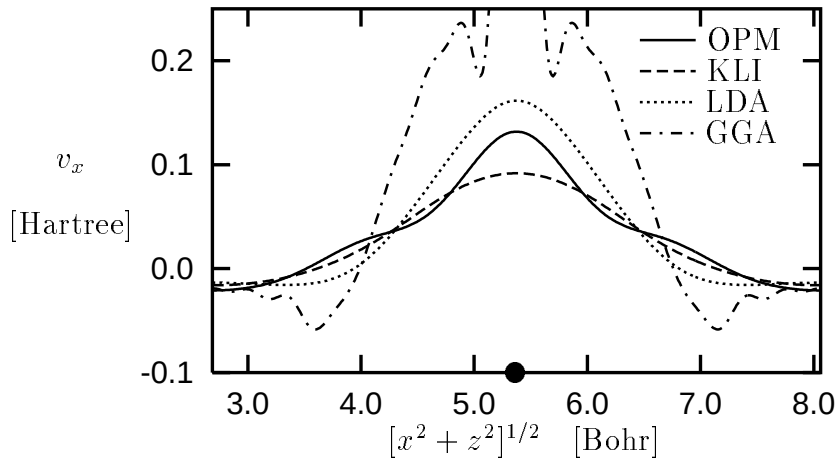

Figure 4.5: Exchange potential of fcc Al in [110] direction: Full OPM versus KLI approximation, LDA and PW91-GGA (E_{cut} =100Ryd, 44 special k-points, 750 states (per k-point) in G_k, $\bullet$ = the position of atom).

4.6 Applications of RDFT using the Relativistic Discrete Variational Method

In this Section a summary of four component molecular density functional calculations within the RDVM (Rosén and Ellis 1975) is given. In the RDVM one restricts oneself to the no-pair limit of RDFT, since QED effects are irrelevant for chemical bonding. On the other hand, all relevant relativistic effects are fully included *a priori*. The starting point for the molecular calculations is the purely n-dependent version of RDFT, Eqs.(4.33)-(4.35), with neglect of E_H^{T}. Accordingly, the total energy consists of the kinetic energy (4.22), the external energy (4.13) with inclusion of the associated ionic interaction energy,

$$\begin{aligned} E_{ext}[n] &= \int d^3r\, n(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + \frac{1}{2}\sum_{\alpha}\sum_{\beta\neq\alpha} \frac{Z_\alpha Z_\beta e^2}{\mid \boldsymbol{R}_\alpha - \boldsymbol{R}_\beta \mid} \qquad (4.61) \\ v_{ext}(\boldsymbol{r}) &= -\sum_{\alpha} \frac{Z_\alpha e^2}{\mid \boldsymbol{R}_\alpha - \boldsymbol{r} \mid}, \end{aligned}$$

the Coulomb contribution to the Hartree energy (4.25) and the xc-energy. The molecular wavefunctions ϕ_k in the RDVM are linear combinations of

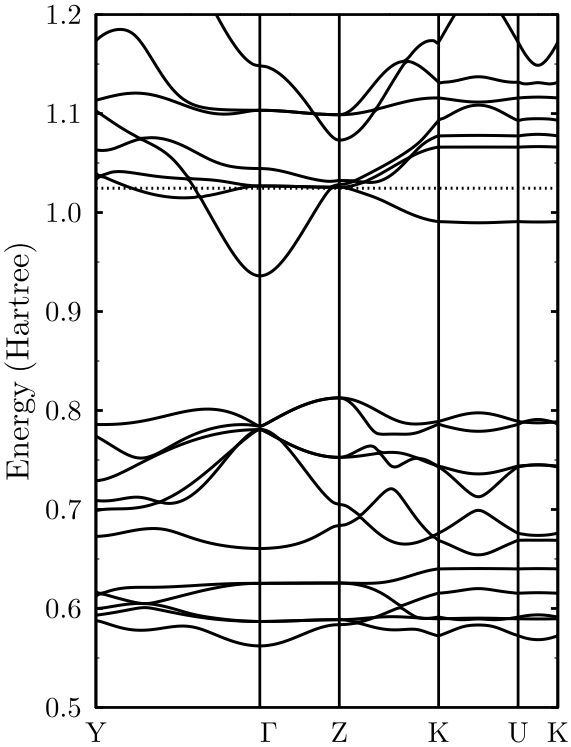

Figure 4.6: Band structure of FeO from OPM-PP calculation with exact E_x and LDA correlation. The dashed line represents ϵ_F (KLI-approximation, $3p$, $3d$, $4s$ states of Fe in valence space, E_{cut} =250 Ryd, 3 special k-points)

numerical atom-centered Dirac-spinors ξ_μ,

$$\phi_k(\boldsymbol{r}) = \sum_\mu c_{k\mu}\xi_\mu(\boldsymbol{r}) \quad ; \quad \xi_\mu(\boldsymbol{r}) = \frac{1}{r}\begin{pmatrix} f_i^{n\kappa}(r)\mathcal{Y}_\kappa^m(\Omega) \\ ig_i^{n\kappa}(r)\mathcal{Y}_{-\kappa}^m(\Omega) \end{pmatrix},$$

($\mu \equiv (in\kappa m)$). An important computational simplification is obtained by the decomposition of the molecular orbital basis into a symmetry adapted basis according to the irreducible representations of the molecular point (double) group (Meyer et al. 1996). Eq.(4.34) is thus recast as an algebraic eigenvalue problem. The corresponding matrix elements are evaluated with the highly accurate multicenter integration scheme of Boerrigter et al. (1988). It is based on a clever partitioning of the whole space into so-called Voronoi cells around each atom. These cells have the shape of Wigner-Seitz-type cells. The singularities caused by the cusps of relativistic wavefunctions at the nuclear sites are eliminated by suitable transformations of the sample points, which leads

to an improved numerical representation of the wavefunctions (Bastug et al. 1995). With this method, a total number of approximately 1400 sample points is needed to achieve a relative accuracy of 10^{-8} in calculations for diatomic molecules.

The most difficult step in this molecular approach is the evaluation of the Hartree potential $v_H = v_H^0$, Eq.(4.29), and the Hartree energy (4.25). In the present version of the RDVM v_H is obtained by utilizing an auxiliary charge density $\tilde{n}(\boldsymbol{r})$, which is related to the full density (4.33) by

$$n(\boldsymbol{r}) = \tilde{n}(\boldsymbol{r}) + \triangle n(\boldsymbol{r})\,.$$

$\tilde{n}(\boldsymbol{r})$ is expanded as

$$\tilde{n}(\boldsymbol{r}) = \sum_{i}^{N_{atom}} \sum_{j}^{M_i} \sum_{l=0}^{L_j} \sum_{m=-l}^{m=l} Q_{jm}^{il}\, |f_i^j(r_i)|^2\, Y_{lm}(\Omega_i)\,, \tag{4.62}$$

where i runs over all atoms (symmetry equivalent centers), f_i^j represents the j-th basis function at center i and j runs over all orbitals of interest. The coefficients Q_{jm}^{il} are determined by a least square fit of $\tilde{n}$ to the complete n in such a way, that the total electronic charge is conserved. In (4.35) v_H is then approximated by the electrostatic potential corresponding to (4.62),

$$\begin{aligned} \tilde{v}_H(\boldsymbol{r}) &= e^2 \sum_{ijlm} Q_{jm}^{il} \frac{4\pi}{2l+1} \frac{1}{r_i^{l+1}} Y_{lm}(\Omega_i) \\ &\quad \times \left[\int_0^{r_i} dr'\, r'^l\, |f_j^i(r'_i)|^2 \;+ r_i^{2l+1} \int_{r_i}^{\infty} dr' \frac{1}{r'^{l+1}} |f_j^i(r')|^2 \right], \end{aligned} \tag{4.63}$$

while E_H is approximated by

$$E_H \approx \int d^3r\, n(\boldsymbol{r}) \tilde{v}_H(\boldsymbol{r}) - \frac{1}{2} \int d^3r\, \tilde{n}(\boldsymbol{r}) \tilde{v}_H(\boldsymbol{r})\,,$$

so that only terms of second order in Δn are neglected. It has been shown, that this procedure not only provides an efficient computational scheme, but also yields a variationally consistent total energy (Bastug et al. 1995).

4.6.1 Results

In this section we give some exemplary results from RDVM calculations using the Slater expression for E_{xc} (with $X_\alpha = 0.7$). In Table 4.10 the spectroscopic constants of some heavy diatomic molecules obtained by the RDVM (Bastug et al. 1997a) are compared to relativistic configuration interaction (RCI) data on the basis of relativistic effective core potentials (RECP). An interesting result of this investigation is the observation that the binding energies from

Table 4.10: Spectroscopic constants of some heavy dimers: Relativistic and nonrelativistic DVM results versus RECP-RCI data. a: Christiansen (1983), b: Balasubramanian and Pitzer (1983), c: Christiansen (1984), d: Froben et al. (1983), e: Stranz and Khanna (1981), f: Huber and Herzberg (1950).

molecule	method	R_e [Bohr]	D_e [eV]	ω_e [cm^{-1}]
Tl_2	RECP-RCI^a	6.69	0.16	39
	AE-RDVM	6.13	0.63	66
	AE-DVM	6.24	1.41	76
	expt^d	5.67	0.43	80
Pb_2	RECP-RCI^b	5.61	0.88	103
	AE-RDVM	5.68	1.33	110
	AE-DVM	5.72	3.35	119
	expt^e		1.02	108
Bi_2	RECP-RCI^c	5.27	2.30	170
	AE-RDVM	5.16	2.88	175
	AE-DVM	5.23	5.51	189
	expt^f	5.03	2.04	173

relativistic calculations are smaller than their non-relativistic counterparts (AE-DVM). This can be understood by an analysis of the molecular valence orbitals: For Tl_2 and Pb_2 they are of $1/2(\sigma)$-type, for Bi_2 there are four $1/2(\sigma)$-type and two $3/2(\pi)$-type orbitals. These orbitals are mainly linear combinations of atomic $6p_{(\frac{1}{2})}$ and $6p_{(\frac{3}{2})}$ wave functions of the constituent atoms. As a result of spin-orbit splitting, the $6p_{(\frac{3}{2})}$ state is less bound which leads to a weaker bonding in the relativistic case.

In another study the geometric and electronic structures of highly symmetric neutral and multiply charged C_{60}^{x+} $(x = 0 - 7)$ fullerenes were investigated (Bastug et al. 1997b). From these calculations one can estimate that stable C_{60}^{x+} clusters should exist up to $x = 13$. This value can be compared with a value of at least $x = 9$ obtained from slow ion impact experiments (Jin et al. 1996). Another theoretical investigation predicted a critical charge of $x = 16$ (Seifert et al. 1996).

The binding energies for the molecules calculated so far systematically overestimate the experimental data, which is a hint that a better description of the xc-energy is required. For that purpose, the RDVM was extended using the xc-functionals discussed in Section 4.4. Results for some diatomic molecules have already been presented in Table 4.4.

4.6.2 Geometry optimization

To obtain equilibrium geometries for small molecules and clusters we have implemented a variable metric method which is based on a quasi-Newton scheme and widely used in optimization theory (Schlegel 1987, Lipkowitz and Boyd 1993). In this method the energy surface $E(\boldsymbol{R})$ is expanded around the present set of internuclear distances $\boldsymbol{R}_k$ up to second order. An improved geometry $\boldsymbol{R}_{k+1}$ can then be obtained by

$$\boldsymbol{R}_{k+1} = \boldsymbol{R}_k - \lambda_k H_k^{-1} \boldsymbol{g}_k \,, \tag{4.64}$$

where H denotes the matrix of the second derivatives (Hessian), $\boldsymbol{g} = dE/d\boldsymbol{R}$ and λ is a step-length parameter. Due to the huge computational effort required, H cannot be calculated directly. It can, however, be approximated by the displacements and the gradients of previous steps. Iterative use of (4.64) finally leads to the equilibrium geometry.

For the calculation of the energy gradient we follow the computational scheme applied in non-relativistic codes (Satoko 1981, 1984, Versluis and Ziegler 1988, Fournier et al. 1989). The only contribution to the total energy which explicitly depends on the nuclear coordinates is the energy (4.61). The force on nucleus α can thus be obtained by calculating the first derivative of (4.61) with respect to the nuclear coordinates $\boldsymbol{R}_\alpha$,

$$\left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{HFF} = \int d^3r \frac{Z_\alpha e^2 \; n(\boldsymbol{r})}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|^3}(\boldsymbol{R}_\alpha - \boldsymbol{r}) - \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\,\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta\,|^3}(\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta)\,. \tag{4.65}$$

This so-called Hellmann-Feynman force (HFF) represents the electrostatic interaction between the negatively charged electrons and the nuclei as well as the interaction among the nuclei. Eq.(4.65) would describe the forces correctly for an exact solution of the Dirac equation. However, in practical calculations one has to introduce approximations which have a rather large influence on the forces. There are two such 'artificial' forces resulting from:

A. Finite basis sets: The molecular wavefunctions are represented as a finite sum of atom-centered four-component basis functions, which causes a spurious force often called orbital basis correction (OBC) (also known as Pulay force (Pulay 1983)). For an atom centered at $\boldsymbol{R}_\alpha$ it reads

$$\begin{aligned}\left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{OBC} &= \sum_i \Theta_i \sum_{\mu\nu} c^*_{i\mu} c_{i\nu} \int d^3r \frac{\partial \xi^\dagger_\mu}{\partial \boldsymbol{R}_\alpha}\Big([-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + (\beta - \mathbf{1})mc^2] \\ &\quad + v_{ext} + \tilde{v}_H + v_{xc} - \epsilon_i\Big)\xi_\nu + c.c.\,.\end{aligned}$$

Here, μ runs over the basis functions centered at position $\boldsymbol{R}_\alpha$, while ν runs over all basis functions.

Table 4.11 Analytical versus numerical gradient for Au_2.

		force [Hartree/Bohr]				
R [Bohr]	D_e [eV]	numerical	analytical	HFF	OBC	DFC
4.5	-2.977	-0.038	-0.037	1.954	-1.905	-0.087
4.6	-3.051	-0.018	-0.018	2.091	-2.028	-0.081
4.65	-3.069	-0.009	-0.009	2.147	-2.078	-0.078
4.7	-3.076	-0.001	-0.001	2.194	-2.122	-0.075
4.75	-3.074	0.005	0.004	2.236	-2.159	-0.072
4.8	-3.064	0.011	0.011	2.270	-2.190	-0.069
4.9	-3.023	0.020	0.020	2.320	-2.237	-0.063

B. Charge density fit: The approximation of v_H by (4.63) leads to the density fit correction (DFC) (again for an atom at $\boldsymbol{R_\alpha}$),

$$\left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{DFC} = \int d^3r \left(n(\boldsymbol{r}) - \tilde{n}(\boldsymbol{r})\right) \frac{\partial \tilde{v}_H}{\partial \boldsymbol{R}_\alpha} .$$

The total energy gradient used in (4.64) is thus given by

$$\frac{dE}{d\boldsymbol{R}_\alpha} = \left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{HFF} + \left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{OBC} + \left(\frac{dE}{d\boldsymbol{R}_\alpha}\right)_{DFC} . \tag{4.66}$$

To check the accuracy of the analytical energy gradient (4.66) we have calculated both (4.66) and the numerical gradient for Au_2 (using the RLDA). In this case, the numerical force can be obtained easily by numerical differentiation of $E(\boldsymbol{R})$ via a two-point formula. As can be seen from Table 4.11, the analytical gradient is in very good agreement with the numerical gradient. Moreover, the force vanishes at the minimum of the binding energy at about 4.71 Bohr. It is worth noting that the artificial gradient terms are of the same order of magnitude as the physical Hellmann-Feynman force. They exactly compensate the errors introduced by the use of finite atom-centered basis sets and the approximate treatment of v_H.

In Table 4.12 our results of geometry optimizations for the hexafluoride actinide compounds UF_6, NpF_6 and PuF_6 are compared with results of RECP calculations, using different xc-functionals. The optimized bond lengths obtained with the RDVM on the level of the RLDA are in very good agreement with the experimental data. Moreover, the RLDA result for UF_6 is very close to the value of 3.77 Bohr obtained by a DCB calculation (Jong and Nieuwpoort 1996). The RECP values, on the other hand, overestimate the bond lengths substantially. In addition, the bond length reduction from UF_6 to NpF_6 is not reproduced by the RECP calculations.

Table 4.12: Estimated M–F bond lengths (in Bohr) of MF_6 compounds (M = U, Np, Pu). The calculations were performed in O_h-symmetry. In the RECP-calculations the Becke-Lee-Yang-Parr GGA has been applied. a: Gagliardi et al. (1998), b: Hay and Martin (1998), c: Weinstock and Goodman (1965)

method	UF_6	NpF_6	PuF_6
AE-RLDA	3.79	3.76	3.76
RECP-LDA[a]	3.87		3.81
RECP-GGA[a]	3.97		
RECP-GGA[b]	3.86	3.87	3.82
expt.[c]	3.77	3.74	3.72

4.6.3 Adsorption on surfaces

Another investigation was dedicated to the question whether the RDVM is able to describe adsorption processes on surfaces. In a first conceptual study we have calculated the binding energy of a single Barium adatom on a Barium(110) surface, varying the distance perpendicular to the surface (Geschke et al. 2000) (within the Slater-X_α approximation for E_{xc}). A first investigation showed that the adatom is preferably adsorbed at a hollow position, as shown in Fig.4.7. The Ba surface was modeled by an atomic cluster, consisting of four first and five second layer atoms in the most restricted case. The internuclear distances in the cluster were kept fixed at the bulk values, i.e. relaxation effects were not considered. In order to check the sensitivity of the results to the size of the cluster the number of atoms in the first layer was further increased laterally up to 12 atoms. As can be seen from Figure 4.7, which shows the binding energy of the adatom as a function of the distance to the surface, the cluster approach is justified at least for the system chosen here. The differences of the potential energy curves around the equilibrium distance between the simulation of the surface by a 13-atom cluster and that by a 17-atom cluster are marginal.

We have also investigated the adsorption of a carbon oxide molecule on a Platinum (111)-surface, comparing different adsorption sites. Due to its catalytic properties there exists an enormous interest in the chemistry of Pt surfaces. In particular, the adsorption of CO on Pt(111) has been extensively studied both experimentally (Ertl et al. 1977, Froitzheim et al. 1977, Seebauer et al. 1982) and theoretically (Hammer et al. 1996, Kopalj and Causà 1999, Brako and Şokçević 1998, Lynch and Hu 2000). Our results are consistent with the experimental observation that the CO molecule is preferably adsorbed in an on-top position, in which the internuclear axis of CO is perpendicular to the surface and the Carbon atom sits directly above a Pt surface atom (Seebauer et al. 1982). This result emphasizes the importance of relativity,

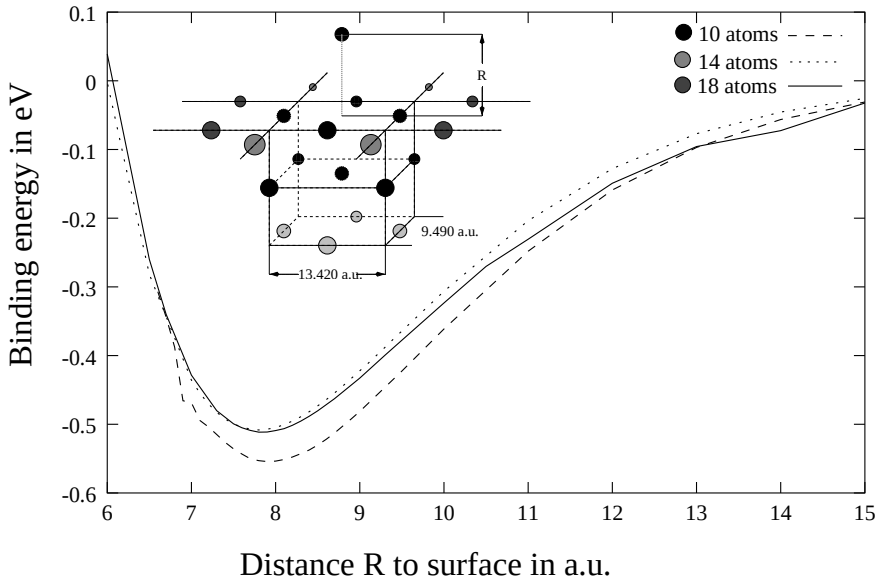

Figure 4.7: Potential energy curves of an adsorbed Ba atom in the hollow position on a Ba(110) surface for different cluster sizes.

as a corresponding nonrelativistic calculation predicts a bridge position to be energetically preferred (Philipsen et al. 1997). Detailed data are given for the on-top position in Table 4.13. In our calculations for this geometry the surface was modeled by an atomic cluster with 7 atoms in a first layer and 6 atoms representing a second layer. The RLDA value for the distance between the C atom and the closest Pt atom in the surface is in very good agreement with experiment. On the other hand, the binding energy is overestimated by the RLDA, even though, in view of the influence of the coverage, the recent experimental value of $1.89 \pm 0.20\,\mathrm{eV}$ (Yeo et al. 1997) obtained for low coverages has to be taken with a grain of salt. This deviation is significantly reduced by use of the RGGA (employing the relativistic form (4.56) of the Becke GGA (Becke 1988a) for E_x and the Perdew GGA for E_c (Perdew 1986)). From the results given in this paragraph one can conclude that the RDVM gives realistic data within a reasonable computing time even for such complex systems.

4.6.4 Improved numerical integration scheme

The most time consuming step in RDVM calculations is the numerical evaluation of multicenter matrix elements. Although the Baerends integration scheme used so far (te Velde and Baerends 1992) is rather accurate and ef-

Table 4.13: Distance of C atom to closest Pt atom in the surface ($R_{\mathrm{Pt-C}}$) and binding energy (E_b) for CO adsorbed on Pt(111) in on-top position: RDVM results versus complete active space self-consistent-field data (CASSCF) (Roszak and Balasubramanian 1995) and GGA results within the zeroth order regular approximation (ZORA) (Philipsen et al. 1997). expt.: Ogletree et al. (1986).

method	$R_{\mathrm{Pt-C}}$ [Bohr]	E_b [eV]	model
RDVM RLDA	3.50	3.25	2 layers cluster
RDVM RGGA	3.57	2.30	2 layers cluster
CASSCF	3.84	1.44	
ZORA GGA	3.59	1.41	2 layers slab
expt.	3.49±0.19	1.89 ± 0.20	

ficient due to the partitioning of the complete integration area into smaller subregions, this scheme still suffers from the discontinuities between different subregions. In order to avoid numerical inaccuracies a large number of sample points is necessary in these critical regions. Hence, for very large systems or for molecules of low symmetry too many sample points are required.

We have implemented a new integration scheme which requires fewer grid points (Heitmann et al. 2001). We followed the basic concept of decomposing the whole space into smaller subregions via overlapping cell functions $z_A(\boldsymbol{r})$ (Becke 1988b, Becke and Dickinson 1988, Perez-Jorda et al. 1994) in order to reduce the multicenter integrals to integrals of lower dimensions (Ishikawa et al. 1999),

$$\int F(\boldsymbol{r}) d^3r = \sum_A \int d^3r F(\boldsymbol{r}) z_A(\boldsymbol{r}) = \sum_A I_A \quad ; \quad \sum_A z_A(\boldsymbol{r}) = 1 \, .$$

The $z_A(\boldsymbol{r})$ are chosen so that they tend to 1 in the vicinity of atom A but drop to zero in the direction of all other nuclei. Thus, even for integrals involving atomic basis functions of two different atoms the integrand of each contribution I_A has no more than one singular point. The integration can be further simplified by suitable transformations to intrinsic coordinates, e.g. elliptic-hyperbolic coordinates for diatomic molecules or spherical coordinates for polyatomic systems.

In Table 4.14 the performance of this new integration scheme is compared to that of the Baerends method for the case of $RfCl_4$ (for fixed T_d symmetry), focusing on the most basic properties, the total charge and energy. Since Rf is the first transactinide element with nuclear charge $Z = 104$, this 'test system' offers the possibility to study the performance of the integration scheme in the

Table 4.14: Comparison of the Baerends integration scheme with new method: Total charge and energy of neutral $RfCl_4$ (172 electrons) for different numbers of sample points n_{tot} (δ_B: relative accuracy in the Baerends method, δ_Ω: relative accuracy in the angular integration of new scheme). The values in parentheses denote the number of radial points used in the new scheme.

	δ	n_{tot}	Q	$-E_{tot}$ [Hartree]
	$1.0{\cdot}10^{-6}$	4442	172.00076	40491.4
δ_B	$1.0{\cdot}10^{-8}$	8753	172.0000024	40490.991
	$1.0{\cdot}10^{-10}$	15716	172.00000047	40490.93052
	$1.0{\cdot}10^{-11}$	25934	172.00000040	40490.930497
	$1.0{\cdot}10^{-3}$	589 (42)	171.99910	40490.88
	$1.0{\cdot}10^{-5}$	2646 (80)	172.000016	40490.9294
δ_Ω	$0.3{\cdot}10^{-6}$	8776 (109)	172.0000011	40490.930435
	$1.0{\cdot}10^{-7}$	14125 (119)	172.00000038	40490.930433
	$0.3{\cdot}10^{-7}$	22247 (128)	172.000000019	40490.930414

high-Z regime. It can be seen that with the new method the same accuracy is reached for both Q and E_{tot} with half as many grid points as in the case of the Baerends scheme.

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