3 Relativistic Density Functional Theory

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3.1 Summary

In these lectures on relativistic density functional theory I had the choice to provide a kind of survey, or to concentrate on a few specific aspects in greater detail. I chose the first option. In order to give you the opportunity to fill in the (often gory) details, I will distribute a list of references, augmented by suitable comments on the contents of the papers cited.

In my lectures I will cover the topics:
1. Introduction, giving a brief summary of why one should work with quantum electrodynamics (QED) if one is interested in the density functional theory of relativistic Coulomb systems.
2. Foundation, containing some comments on the relativistic Hohenberg-Kohn theorem and indicating how the exact (but not easily solvable) relativistic Kohn-Sham equations (containing radiative corrections and all that) can be reduced to the standard approximate variant.
3. Functionals, with a mini-survey of the relativistic functionals that have been considered. The headings are well known from the non-relativistic case: LDA, GGA, OPM, etc.
4. Results, giving an indication of the performance of these functionals for a number of systems (mainly atoms) and a brief statement on some particular systems (molecules, solids).

A few words are also necessary concerning notation. Relativistic units with

\[ h = c = 1 ; \quad m_0 = m ; \quad e . \]

will be used. This choice is debatable (e.g., if one considers expansions in \( 1/c \)), but in general use. I shall use the standard conventions of relativistic
theory, as found in most textbooks on relativistic quantum mechanics, e.g.,

$$\sum_{\mu=0}^{3} a_\mu b_\mu \rightarrow a_\mu b_\mu ,$$

with the metric

$$g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

for time (0) and space (1–3) coordinates, or the Feynman dagger notation

$$\hat{a} = \gamma_\mu a^\mu .$$

Relativistic corrections to the ground state energies of many particle systems are expected in two places. First there is the kinematic correction. The non-relativistic kinetic energy has to be replaced by its relativistic equivalent

$$-\frac{\nabla^2}{2m} \rightarrow -i \nabla \cdot \gamma . \quad (3.1)$$

The second correction is a modification of the interaction energies. On the level of relativistic density functional theory for Coulomb systems this means, for instance, the replacement of the standard Hartree energy by its covariant form involving electron four-currents, $j^\mu$ and the photon propagator, $D^{(0)}_{\mu\nu}$,

$$\frac{e^2}{2} \int d^3x \int d^3y \frac{n(x)n(y)}{|x-y|} \rightarrow \frac{1}{2} \int d^3x \int d^4y j^\mu(x)D^{(0)}_{\mu\nu}(x-y)j^\nu(y) . \quad (3.2)$$

A corresponding change applies to the other interaction terms.

The appropriate starting point for the discussion of relativistic Coulomb systems is QED [123]. The reason for using the full quantum field theory rather than just the Dirac equation is twofold: (i) With a quantum field theory the anti-particle sector is sorted correctly. This statement is illustrated by the small table comparing the free particle versions of the two options:

<table>
<thead>
<tr>
<th>charge</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirac</td>
<td>negative definite</td>
</tr>
<tr>
<td>QED</td>
<td>negative / positive</td>
</tr>
</tbody>
</table>

The experimental situation with positive energies and oppositely charged particles and anti-particles is obviously described correctly by field theory. (ii) Possible questions of renormalization are quite apparent. I illustrate this remark by one example. The four-current of an electron in an external field is given by

$$j^\mu(x) = -i \lim_{y \to \mathbf{x}} \text{Tr} [S_F(x,y)\gamma^\mu] . \quad (3.3)$$
This is the analogue of the non-relativistic case where, e.g., the density is the equal time, equal space limit of the Green function. The slightly more complicated symmetric limit

\[ \lim_{y \to x} \left( \frac{1}{2} \left( \lim_{y \to x, y^0 > x^0} + \lim_{x \to y, y^0 < x^0} \right) \right)_{(x-y)^2 \geq 0} \]  

is due to the requirement of charge conjugation invariance of the relativistic theory. In diagrammar the Green function is given by

\[ \begin{align*}
\begin{array}{c}
\includegraphics{diagram1} \\
\end{array}
\end{align*} = \begin{align*}
\begin{array}{c}
\includegraphics{diagram2} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram3} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram4} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram5} \\
\end{array} + \ldots
\end{align*} \tag{3.5} \]

The fermion (say electron) interacts in the sense of the Born approximation with an external source. Taking the symmetric limit corresponds to closing the lines on themselves

\[ -ij^\mu = \begin{align*}
\begin{array}{c}
\includegraphics{diagram6} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram7} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram8} \\
\end{array} + \begin{array}{c}
\includegraphics{diagram9} \\
\end{array} + \ldots
\end{align*} \tag{3.6} \]

One immediately recognizes that the second diagram contains the lowest order vacuum polarization

\[ -i\Pi^{(0)}_{\mu\nu}(q) = \begin{align*}
\begin{array}{c}
\includegraphics{diagram10} \\
\end{array}
\end{align*}, \tag{3.7} \]

which is one of the three basic divergence contributions of QED. It has to, and can, be renormalized. It remains to say that attempts to set up extended Thomas-Fermi-type models for relativistic systems have been thwarted for quite some years by not recognizing this feature.

I will not dwell on the field theoretical details in the following, but we have to take note of the starting point, the QED Hamiltonian

\[ \hat{H} = \int d^3x \slashed{\partial} \psi(x) (-i\gamma \cdot \nabla + m) \psi(x) \]

\[ + e \int d^3x \slashed{j}^\mu(x) \hat{A}_\mu(x) + \int d^3x \slashed{j}^\mu(x)v_{\text{ext}}(x) \]

\[ - \frac{1}{8\pi} \int d^3x \left\{ \left[ \partial^\nu \hat{A}_\mu(x) \right] \left[ \partial^\nu \hat{A}^\mu(x) \right] + \nabla \hat{A}_\mu(x) \cdot \nabla \hat{A}^\mu(x) \right\}. \tag{3.8} \]
We have fermions interacting via an electromagnetic field and with external sources and the Hamiltonian of the electromagnetic field. The renormalized Hamiltonian is

$$\hat{H}_{\text{ren}} = \hat{H} - \text{VEV} + \text{CT}.$$  

(3.9)

It involves the trivial renormalization, the subtraction of vacuum expectation values (VEV), and the serious renormalization (see above) which can be handled by the counter-term (CT) technique [4].

### 3.2 Foundations

The relativistic Hohenberg-Kohn theorem was first formulated by Rajagopal and Callaway [5,6] and by McDonald and Vosko [7]. As expected for a Lorentz covariant situation it states that the ground-state energy is a unique functional of the ground-state four-current

$$E_0[j^\mu] = F[j^\mu] + \int d^3x j^\mu(x) v_{\text{ext}}^\mu(x),$$  

(3.10)

where $F$ is an universal functional of $j^\mu$, and the simplest contribution, the coupling to the external sources, is (as usual) made explicit. The proof has been re-examined by Engel et al. [8], who demonstrated that field theoretical aspects (that were not considered by the previous authors) do not invalidate the conclusion. The final statement is: All ground-state observables can be expressed as unique functionals of the ground-state four-current as:

$$O[j^\mu] = \langle \Phi_0[j^\mu]|\hat{O}|\Phi_0[j^\mu]\rangle + \Delta O_{\text{CT}} - \text{VEV}.$$  

(3.11)

Again counter-terms and subtraction of vacuum expectation values have to be taken care of.

In practical applications the question arises: What is the situation if the external potential is electrostatic \(\{v_{\text{ext}}^\mu(x)\} = \{v_0^\mu(x), 0\}\)? The answer is: All ground-state variables, including the spatial components of the four-current, are then functionals of the charge density alone, e.g.,

$$j^\mu([n], x) = \langle \Phi_0[n]|\hat{j}^\mu(x)|\Phi_0[n]\rangle.$$  

(3.12)

The question whether these functionals are known is a different story.

The relativistic Kohn-Sham scheme starts, in complete analogy to the non-relativistic case, with a representation of the four-current and of the non-interacting kinetic energy in terms of auxiliary spinor orbitals [8]. If one calculates the four-current of a system of fermions in an external potential (as indicated above), one obtains

$$j^\mu(x) = j_{\text{vac}}^\mu(x) + j_{\text{D}}^\mu(x).$$  

(3.13)
The vacuum polarization current (which arises from the symmetric limit) is given by the solution of a Dirac equation by

\[
\mathbf{j}^\mu_{\text{vac}}(\mathbf{x}) = \frac{1}{2} \left[ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\mathbf{x}) \gamma^\mu \varphi_k(\mathbf{x}) - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) \gamma^\mu \varphi_k(\mathbf{x}) \right].
\] (3.14)

It contains negative energy solutions as well as bound states and positive energy solutions. The current due to the occupied orbitals is

\[
\mathbf{j}^\mu_{\text{D}}(\mathbf{x}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) \gamma^\mu \varphi_k(\mathbf{x}).
\] (3.15)

The non-interacting kinetic energy, including the trivial rest mass term, has a corresponding structure

\[
T_s[j^\mu] = T_{s,\text{vac}}[j^\mu] + T_{s,\text{D}}[j^\mu].
\] (3.16)

The contributions are obtained from the formulae given for \(j^\mu\) by the replacement

\[
\gamma^\mu \rightarrow -i \gamma \cdot \nabla + m.
\] (3.17)

The full Kohn-Sham scheme is obtained by writing the ground-state energy as

\[
E_0[j^\mu] = T_s[j^\mu] + E_{\text{ext}}[j^\mu] + E_{\text{Hartree}}[j^\mu] + E_{\text{xc}}[j^\mu],
\] (3.18)

where the xc energy is defined as the difference

\[
E_{\text{xc}} = F - T_s - E_{\text{Hartree}}.
\] (3.19)

The Hartree energy is the covariant version

\[
E_{\text{Hartree}}[j^\mu] = \frac{1}{2} \int d^3x \int d^4y j^\mu(x) D^{(0)}_{\mu\nu}(x-y) j^\nu(y),
\] (3.20)

which reduces to

\[
E_{\text{Hartree}}[j^\mu] = \frac{\epsilon^2}{2} \int d^3x \int d^3y \frac{j^\mu(x) j^\mu(y)}{|x-y|}
\] (3.21)

for stationary currents.

The philosophy behind this addition and subtraction both in the non-relativistic as well as in the relativistic case is to isolate the (in principle) tractable, dominant contributions. The xc-energy becomes then the key quantity concerning serious many-body effects.

Minimization of the ground-state energy with respect to the auxiliary spinor orbitals leads to the general Kohn-Sham equations:

\[
\gamma^0 \left\{ -i \gamma \cdot \nabla + m + \not{\mathbf{v}}_{\text{ext}}(\mathbf{x}) + \not{\mathbf{v}}_{\text{Hartree}}(\mathbf{x}) + \not{\mathbf{v}}_{\text{xc}}(\mathbf{x}) \right\} \varphi_k(\mathbf{x}) = \epsilon_k \varphi_k(\mathbf{x}).
\] (3.22)
This is a Dirac equation with the effective potentials

\[
\begin{align*}
\gamma^\mu \nu Hartree(x) &= \frac{e^2}{\left| x - y \right|} \int d^3y \, j^\mu(y), \\
\gamma^\mu \nu xc(x) &= \gamma^\mu \frac{\delta E_{xc}[j^\mu]}{\delta j^\mu(x)},
\end{align*}
\]

which has to be solved self-consistently.

So far nobody has solved the indicated problem. The evaluation of the vacuum contributions (in \(j^\mu\) and \(T_s\)) includes the full set of solutions of the Dirac equation and renormalization at each step of the self-consistency procedure.

In the discussion of “practical” problems some approximations are commonly applied: (i) The “no-sea” approximation, where one neglects all radiative corrections

\[
j^\mu_{vac} = T_{s,vac} = E_{xc,vac} = 0.
\]

If these corrections are of interest, they can be calculated perturbatively with the final self-consistent solutions. (ii) The situation encountered most often in electronic structure calculations is the one where the external potential is purely electrostatic. In this case, the charge density is the only variable (see above) and one has

\[
\begin{align*}
\hat{E}_{\text{Hartree}}[n] &\equiv E_{\text{Hartree}}[n, j[n]] \\
\hat{E}_{xc}[n] &\equiv E_{xc}[n, j[n]].
\end{align*}
\]

As a consequence, the effective potentials are also electrostatic, e.g.,

\[
\{v^\mu_{\text{Hartree}}(x)\} = \{v_{\text{Hartree}}(x), 0\},
\]

with

\[
v_{\text{Hartree}}(x) = \frac{\delta E_{\text{Hartree}}[j^\mu]}{\delta n(x)} + \sum_{k=1}^{3} \int d^3x' \frac{\delta E_{\text{Hartree}}[j^\mu]}{\delta j^k(x')} \frac{\delta j^k(x)}{\delta n(x)}.
\]

The additional term arises as there is an explicit functional dependence of \(j^k\) on \(n\).

The resulting electrostatic no-sea approximation is the standard version applied in practice. It is usually written as

\[
\{-i\alpha \cdot \nabla + m\beta + v_{\text{ext}}(x) + v_{\text{Hartree}}(x) + v_{\text{xc}}(x)\} \varphi_k(x) = \epsilon_k \varphi_k(x),
\]

where the density is given by

\[
n(x) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi^\dagger_k(x) \varphi_k(x).
\]
Usually the exact current \( j[n] \) (wherever it occurs) is replaced by the Kohn-Sham current

\[
j(x) = \sum_{-m < \epsilon_k \leq \epsilon_p} \phi_k^\dagger(x) \alpha \phi_k(x) . \tag{3.32}
\]

The differences that might occur due to this replacement have not been explored.

Further possible approximations rely on the fact that the free photon propagator, which mediates the interaction between the fermions, can be split into a longitudinal (Coulomb) and a transverse part

\[
D^{(0)}_{\mu\nu}(x-y) = g_{\mu 0} g_{\nu 0} \frac{e^2}{|x-y|} \delta(x^0 - y^0) + D^T_{\mu\nu}(x-y) . \tag{3.33}
\]

If one neglects the transverse contribution, one arrives at what is termed the Dirac-Coulomb approximation (a standard in quantum chemistry). Inclusion of the transverse term, which describes retardation and magnetic effects, in perturbation theory (weakly relativistic limit) leads to the Dirac-Coulomb-Breit Hamiltonian.

As a conclusion of this section, I just state that the full, weakly relativistic limit of the electrostatic, no-sea approximation (obtained with techniques such as the Fouldy-Wouthuysen transformation) makes contact with non-relativistic current-density functional theory (as formulated by Rasolt and Vignale [9]).

### 3.3 Functionals

The standard relativistic density functional expression for the ground-state energy is

\[
E_0[j^\mu] = T_s[j^\mu] + E_{\text{ext}}[j^\mu] + E_{\text{Hartree}}[j^\mu] + E_{\text{xc}}[j^\mu] . \tag{3.34}
\]

The functional dependence of \( T_s \) and \( E_{\text{xc}} \) on \( j^\mu \) needs to be established. In Kohn-Sham applications, \( T_s \) is expressed directly in terms of spinor orbitals, so only \( E_{\text{xc}} \) has to be considered. If one is aiming at setting up relativistic extensions of extended Thomas-Fermi models, one also has to consider dependence of \( T_s \) on the four-current. I shall present a few remarks on the density functional form of \( T_s \), but first we look at the exchange and correlation energy.

The simplest approximation is the local density approximation (LDA), which is obtained from the energy density of the relativistic homogeneous electron gas (RHEG)

\[
E_{\text{xc}}^{\text{LDA}}[n] = \int d^3 x \ e_{\text{xc}}^{\text{RHEG}}(n_0) \big|_{n_0=n(x)} . \tag{3.35}
\]
Two remarks apply: (i) For this homogeneous system the spatial current vanishes $j_{\text{RHEG}} = 0$, so there is only a dependence on the density. (ii) Knowledge of the ground-state energy of the RHEG is much less developed than for its non-relativistic counterpart. There are, for instance, no Monte Carlo results for $e_{\text{RHEG}}^x$. The functionals that are available in this approximation are thus obtained by painstaking evaluation of the simplest diagrammatic contributions to the ground-state energy. The details are more involved than in the non-relativistic case, partly due to questions of renormalization, partly due to the Minkowski space structure. I shall only indicate the genesis of the results in terms of the corresponding diagrams.

The $x$ contribution has been worked out as early as 1960. One can show that after proper renormalization only the contribution

$$ e_{\text{RHEG}}^x = \frac{i}{2} \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} $$

(3.36)

which is the diagram with the finite contribution of the free electron propagator, remains. The arguments leading to this result can be summarized as follows. In the RLDA the $x$-energy density is given by

$$ e_{\text{RHEG}}^x = \frac{1}{2} \int d^4y \, D^{(0)}_{\mu\nu}(x-y) \text{Tr} \left[ S^{(0)}_F(x-y)\gamma^\nu S^{(0)}_F(y-x)\gamma^\mu \right] + \text{CT} + \text{VEV} . $$

(3.37)

In diagrammar the loop integral looks like this

$$ e_{\text{RHEG(1)}}^x = \frac{i}{2} \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} . $$

(3.38)

The double line stands for the free photon propagator $D^{(0)}_{\mu\nu}$, and the wiggly line for the lowest order fermion propagator of the RHEG, $S^{(0)}_F$. The photon propagator can be split into a vacuum contribution and a direct contribution due to the occupied electron states

$$ \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} = \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} + \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} \equiv \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} + \begin{array}{c} \includegraphics[width=0.2\textwidth]{dia.png} \end{array} . $$

(3.39)
The loop integral then consists of four contributions

\[
\begin{align*}
\text{\begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture}\right)} &= \begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture} + \begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture} + \begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture} + \begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture} + \begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture}.
\end{align*}
\]

(3.40)

The first contribution is divergent but is removed by the subtraction of the vacuum, while the next two diagrams contain the lowest order self-energy

\[
\begin{align*}
\text{\begin{tikzpicture}
  \filldraw[black] (0,0) circle (0.05cm);
  \filldraw[black] (1,0) circle (0.05cm);
  \draw[->,thick] (0,0) -- (1,0);
  \draw[->,thick] (1,0) -- (0,0);
  \end{tikzpicture}\right)} &= \Sigma^{(1)}_{\text{vac}, \text{ren}},
\end{align*}
\]

(3.41)

which has still to be renormalized to yield \(\Sigma^{(1)}_{\text{vac}, \text{ren}}\). However, the terms vanish as the self-energy satisfies the on-shell condition

\[
\left[ (\not{p} + m) \Sigma^{(1)}_{\text{vac}, \text{ren}} \right]_{p^2 = m^2} = 0.
\]

(3.42)

The factor \((\not{p} + m)\) is supplied by the remaining propagator. So, finally, only the contribution due to the occupied electron states remains.

The relativistic corrections are more readily discussed if one writes

\[
\begin{align*}
\epsilon_{\text{RHEG}}^x &= \epsilon_{\text{NRHEG}}^x \Phi_x \left( \frac{k_F}{m} \right),
\end{align*}
\]

(3.43)

where the relativistic correction factor can be split (due to the structure of the free photon propagator, see above) into

\[
\begin{align*}
\epsilon_{\text{RHEG}}^x &= \epsilon_{\text{NRHEG}}^x \left[ \Phi_L^x \left( \frac{k_F}{m} \right) + \Phi_T^x \left( \frac{k_F}{m} \right) \right].
\end{align*}
\]

(3.44)

One finds that the longitudinal part (L) does not differ very much from the non-relativistic limit. The transverse correction (T) is negative and it is small for low densities, but grows sufficiently in magnitude, so that the x energy density changes sign at \(\beta = k_F/m \approx 2.5\) (one should keep in mind that the maximal density in the Hg atom – in the inner shells – amounts to \(\beta \approx 3\)).

The transverse correction factor can be decomposed into a magnetic and a retardation contribution with opposite signs. The magnetic contribution dominates at higher densities. The expansion of \(\epsilon_{\text{RHEG}}^x\) in the weakly relativistic limit gives the Breit contribution to \(\epsilon_x\), that reproduces the full transverse correction factor quite closely over the relevant range of \(0 \leq \beta \leq 3\).
Concerning correlations, the only contribution that has been worked out is the random phase (RPA) limit \([10,12,14,15]\). After renormalization, one can write the RPA correlation energy contribution as

\[
e_{\text{c}}^{\text{RPA}} = i \left\{ \begin{array}{c}
\begin{array}{c}
\text{D} \\
\text{D}
\end{array}
\end{array} + \right. \\
+ \begin{array}{c}
\begin{array}{c}
\text{D} \\
\text{D}
\end{array}
\end{array}
\right. + \ldots \right\}. \tag{3.45}
\]

The loops of the (fermion) polarization insertion involve only the direct contribution

\[
\begin{array}{c}
\text{D} \\
\end{array} = \begin{array}{c}
\begin{array}{c}
\text{D} \\
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{D} \\
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{D} \\
\end{array}
\end{array} \tag{3.46}
\]

The interaction lines correspond to the full vacuum photon propagator that is obtained by re-summation of the series

\[
\begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} = \begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} + \ldots \right\}. \tag{3.47}
\]

in terms of the renormalized vacuum polarization insertion.

The final evaluation (involving one numerical integration) has only been achieved within two further approximations: (i) In the no-sea approximation, the full photon propagator is replaced by the free propagator

\[
\begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} \approx \begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} \right\}. \tag{3.48}
\]

(ii) In the no-pair approximation (a kind of standard in quantum chemistry) one also uses the free propagator

\[
\begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} \approx \begin{array}{c}
\begin{array}{c}
\text{ren}
\end{array}
\end{array} \right\}. \tag{3.49}
\]
and in addition evaluates the polarization insertion with the electron propagator

\[ D \approx \begin{array}{c}
\oplus \\
\oplus
\end{array} \quad (3.50) \]

There is a conceptual difference in the sense that the no-pair approximation is gauge dependent, but in the final reckoning there is only a slight difference in the results. The result can (as for exchange) be written in the form

\[ e_{c,RPA}^{\text{RHEG}} = e_{c,RPA}^{\text{NRHEG}} \phi_c (\frac{k_F}{m}) \quad (3.51) \]

The correction factor can be represented quite accurately by

\[ \phi_c (\beta) = 1 + a_1 \beta^3 \ln \beta + a_2 \beta^4 + a_3 (1 + \beta^2)^2 \beta^4 + b_1 \beta^3 \ln \beta + b_2 \beta^4 + b_3 (A \ln \beta + B) \beta^7, \quad (3.52) \]

which incorporates the exact large density limit as well as the non-relativistic limit. A plot shows that the relativistic corrections can become quite substantial for higher densities.

There is no systematic treatment of other contributions to the ground-state energy of the RHEG. This remark also pertains to the construction of gradient expansion approximations (GEA), which in the x-only limit involves, to lowest order, the four-point contributions

\[ \begin{array}{c}
\oplus \\
\oplus
\end{array} + \begin{array}{c}
\oplus \\
\oplus
\end{array} + \begin{array}{c}
\oplus \\
\oplus
\end{array} \quad (3.53) \]

(You should, however, note that the proper evaluation in the non-relativistic limit took the better part of 10 years).

As the hopes placed in the GEA did not materialize (in the non-relativistic case), one turned to the construction of generalized gradient approximations (GGA). These are based on the following “philosophy”: (i) Use available “exact” results for atoms (x-only or on the basis of CI calculations) and fit them to a functional of the form

\[ F_{xc}^{\text{GGA}} = \int d^3 x e_{xc}^{\text{LDA}} F_{xc}(n, \zeta) \quad (3.54) \]

with the dimensionless gradient

\[ \zeta = \frac{(\nabla n)^2}{4n^2 (3\pi^2 n)^{2/3}} \quad (3.55) \]
(ii) Incorporate (depending on the philosophy) some exact properties as, e.g., the correct weakly inhomogeneous limit, etc.; (iii) Use this functional for the discussion of more complex Coulomb systems as molecules and solids (relying on the supposed universality).

If one wishes to proceed in this fashion in the relativistic case, one has to provide “accurate” atomic data. For this purpose, OPM, the optimized potential method [16] (in the present context the relativistic extension, the ROPM) is a valuable tool. The (R)OPM relies on the fact that the functional derivative with respect to the density (or the four-current) can be evaluated with the chain rule for functional derivatives if the dependence on the density is implicit via Kohn-Sham orbitals,

\[
E[n] = E[\varphi_k] = E[\varphi_k[n]]
\]

\[
v(x) = \frac{\delta E}{\delta n(x)} = \sum_k \int d^3x' \int d^3x'' \frac{\delta E}{\delta \varphi_k(x')} \frac{\delta \varphi_k(x'')}{\delta n(x)} .
\]

(3.56)

The first factor is evaluated directly from the explicit functional form, the second follows from the linear response limit of the Kohn-Sham equations as does the last one (the inverse Kohn-Sham response function).

On the basis of (3.56), an integral equation for the multiplicative potential \(v(x)\) can be derived. It has the form

\[
\int d^3x' K(x, x') v(x') = Q(x) ,
\]

(3.57)

where both the kernel, \(K(x, x')\), and the inhomogeneous term, \(Q(x)\), can be expressed in terms of Kohn-Sham orbitals.

For the x-only limit the application of the OPM is rather straightforward. One starts with the definition of the covariant x-energy

\[
E_x = \frac{1}{2} \int d^3x \int d^3y D^{(0)}_{\mu\nu}(x - y) \text{Tr} [S_F(x, y) \gamma^\nu S_F(y, x) \gamma^\mu]
\]

(3.58)

(see diagrams above) and evaluates the fermion propagators in the Kohn-Sham (that is, effective single particle) limit. If, in addition, one applies the electrostatic no-sea approximation, one obtains

\[
E_{KS}^x[n] = -\frac{e^2}{2} \int d^3x \int d^3y \sum_{-\epsilon_k \leq \epsilon \leq \epsilon_F} \frac{\cos (|\epsilon_k - \epsilon||x - y|)}{|x - y|} \hat{\varphi}_k(x) \gamma^\mu \hat{\varphi}_i(x) \gamma^\mu \hat{\varphi}_i(y) .
\]

(3.59)

For a corresponding correlation contribution, e.g.,

\[
E_{xc}^x[n] = E_{xc}[n] - E_{KS}^x[n]
\]

(3.60)

only some variants of perturbation theory on the basis of the Kohn-Sham Hamiltonian are available like, e.g., a straightforward second order perturbation theory (in the spirit of Möller-Plesset perturbation theory) or some partially re-summed versions. I shall not present the relevant equations.
The numerical implementation of the OPM scheme is rather involved. For this reason, one often applies the Krieger-Li-Iaffrate (KLI) approximation, which turns out to be (as in the non-relativistic case) rather accurate.

From the solution of the relativistic OPM problem (or some other “exact” equivalent) for atoms, one may construct relativistic GGA-type functionals following the procedure used in non-relativistic theory. One sets, for instance in the \(x\)-only limit
\[
F_x(n, \zeta) = \Phi_{x,0}(\beta) + g(\zeta)\Phi_{x,2}(\beta) .
\] (3.61)

One then uses non-relativistic forms of the gradient correction factor \(g\) (The different forms found in the literature do give results that vary only marginally). For the relativistic correction factor \(\Phi_{x,2}\) a flexible \([2,2]\) Padé approximant
\[
\Phi_{x,2}(\beta) = \frac{a_0 + a_1\beta^2 + a_2\beta^4}{1 + b_1\beta^2 + b_2\beta^4}
\] (3.62)
proved to be sufficient to reproduce ROPM results to high accuracy. Both the longitudinal as well as the transverse contribution can be accommodated with this ansatz. The correct weakly relativistic limit is obtained with
\[
a_0^L = 1 , \quad a_0^T = 0 , \quad \text{and} \quad \beta \approx 0 .
\] (3.63)

As a conclusion of this section I offer a few remarks on the functional \(T_s[j^\mu]\). This functional is used in relativistic, extended Thomas-Fermi models, which are based on the direct variational principle
\[
\frac{\delta}{\delta j^\mu(x)} \left\{ E_0[j^\nu] + \mu_{\text{chem}} \int d^3y j^0(y) \right\} = 0 .
\] (3.64)

In contrast to the Kohn-Sham scheme, no auxiliary orbitals are involved. Unfortunately, the presently available approximations to \(T_s[j^\mu]\) are only adequate for general estimates (rather than for results of chemical accuracy).

The functional in question is derived from the exact kinetic energy
\[
T_s[j^\mu] = -i \int d^3x \lim_{y \to x} \text{Tr} [\frac{\partial}{\partial x} \cdot \nabla + m] S_F(x, y) - \text{VEV} + \text{CT} ,
\] (3.65)
where the exact fermion propagator is replaced by the Kohn-Sham propagator
\[
\left[ \frac{i\partial}{\partial x} - m - \not{v}_{\text{KS}}(x) \right] S_{\text{KS}}^F(x, y) = \delta^{(4)}(x - y) .
\] (3.66)

As indicated, renormalization is necessary. Results are available to fourth order in the gradient of the density in the electrostatic limit
\[
T_s^{\text{el,stat}}[n] = T_s^{[0]}[n] + T_s^{[2]}[n] + T_s^{[4]}[n] + \ldots
\] (3.67)
and to second order in the gradients of the four-current for the more general case
\[
T_s[n, j] = T_s^{[0]}[n] + T_s^{[2]}[n, j] + \ldots
\] (3.68)
Table 3.1. Longitudinal ground state energies ($-E_{L\text{tot}}$) and highest occupied eigenvalues ($-\epsilon_{Lmk}$) for closed sub-shell atoms from non-relativistic OPM (NROPM [17]), relativistic OPM (ROPM [18]) and relativistic HF (RHF [19]) calculations (all energies are in hartree)

<table>
<thead>
<tr>
<th>Atom</th>
<th>NROPM</th>
<th>ROPM</th>
<th>RHF</th>
<th>NROPM</th>
<th>ROPM</th>
<th>RHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>He (1S1/2)</td>
<td>2.862</td>
<td>2.862</td>
<td>2.862</td>
<td>0.918</td>
<td>0.918</td>
<td>0.918</td>
</tr>
<tr>
<td>Be (2S1/2)</td>
<td>14.572</td>
<td>14.575</td>
<td>14.576</td>
<td>0.309</td>
<td>0.309</td>
<td>0.309</td>
</tr>
<tr>
<td>Ne (2P3/2)</td>
<td>128.545</td>
<td>128.690</td>
<td>128.692</td>
<td>0.851</td>
<td>0.848</td>
<td>0.848</td>
</tr>
<tr>
<td>Mg (3S1/2)</td>
<td>199.611</td>
<td>199.932</td>
<td>199.935</td>
<td>0.253</td>
<td>0.253</td>
<td>0.253</td>
</tr>
<tr>
<td>Ar (3P3/2)</td>
<td>526.812</td>
<td>528.678</td>
<td>528.684</td>
<td>0.591</td>
<td>0.587</td>
<td>0.588</td>
</tr>
<tr>
<td>Ca (4S1/2)</td>
<td>676.751</td>
<td>679.704</td>
<td>679.710</td>
<td>0.196</td>
<td>0.196</td>
<td>0.196</td>
</tr>
<tr>
<td>Zn (4S1/2)</td>
<td>1777.828</td>
<td>1794.598</td>
<td>1794.613</td>
<td>0.293</td>
<td>0.299</td>
<td>0.299</td>
</tr>
<tr>
<td>Kr (4P3/2)</td>
<td>2752.028</td>
<td>2788.848</td>
<td>2788.861</td>
<td>0.523</td>
<td>0.515</td>
<td>0.514</td>
</tr>
<tr>
<td>Sr (5S1/2)</td>
<td>3131.514</td>
<td>3178.067</td>
<td>3178.080</td>
<td>0.179</td>
<td>0.181</td>
<td>0.181</td>
</tr>
<tr>
<td>Pd (4D5/2)</td>
<td>4937.858</td>
<td>5044.384</td>
<td>5044.400</td>
<td>0.335</td>
<td>0.319</td>
<td>0.320</td>
</tr>
<tr>
<td>Cd (5S1/2)</td>
<td>5465.056</td>
<td>5593.299</td>
<td>5593.319</td>
<td>0.266</td>
<td>0.282</td>
<td>0.281</td>
</tr>
<tr>
<td>Xe (5P3/2)</td>
<td>7232.018</td>
<td>7446.876</td>
<td>7446.895</td>
<td>0.456</td>
<td>0.439</td>
<td>0.440</td>
</tr>
<tr>
<td>Ba (6S1/2)</td>
<td>7883.404</td>
<td>8135.625</td>
<td>8135.644</td>
<td>0.158</td>
<td>0.163</td>
<td>0.163</td>
</tr>
<tr>
<td>Yb (6S1/2)</td>
<td>13391.070</td>
<td>14067.621</td>
<td>14067.669</td>
<td>0.182</td>
<td>0.196</td>
<td>0.197</td>
</tr>
<tr>
<td>Hg (6S1/2)</td>
<td>18408.313</td>
<td>19648.826</td>
<td>19648.865</td>
<td>0.262</td>
<td>0.329</td>
<td>0.328</td>
</tr>
<tr>
<td>Rn (7S1/2)</td>
<td>23093.258</td>
<td>25028.027</td>
<td>25028.061</td>
<td>0.149</td>
<td>0.167</td>
<td>0.166</td>
</tr>
<tr>
<td>No (7S1/2)</td>
<td>32787.471</td>
<td>36740.625</td>
<td>36740.682</td>
<td>0.171</td>
<td>0.209</td>
<td>0.209</td>
</tr>
</tbody>
</table>

3.4 Results

I shall first show some results for atoms in order to illustrate the magnitude of relativistic effects and to compare the performance of the various relativistic functionals.

The first set of tables deals with the x-only limit, where in addition a direct comparison with relativistic Hartree-Fock (RHF) results is possible. Total ground-state energies for closed sub-shell atoms (Table 3.1) calculated with the longitudinal x-contribution (the straightforward Coulomb interaction), show the following features: Comparing NROPM to ROPM results one notices the growing importance of relativistic corrections as the central charge is increased (The difference between relativistic and non-relativistic energies is nearly 4000 hartree). One also notices that there is hardly any difference between ROPM and RHF energies, although in the first case the effective potential is multiplicative while in the latter it is non-local. The second column gives the energies of the highest occupied orbitals. Even the outermost orbitals experience some effect of relativity (due to the change of the effective potential generated by the inner orbitals).
The full situation for the orbital energies is illustrated in Table 3.2 for the Hg atom (also in the longitudinal x-only limit). Comparing the orbital energies obtained from NROPM and ROPM calculations one sees once more the effect of relativistic corrections. One also notices that the orbital energies obtained from ROPM and RHF are quite different, with the exception of the last occupied orbitals, even if the total energies agree very closely. This stresses the fact that the orbitals (and their energies) are only auxiliary quantities that should be interpreted with some care (one should, e.g., not calculate excited state energies by just promoting particles from occupied to unoccupied orbitals). The exception is the highest occupied orbital whose energy corresponds (in principle) to the first ionization potential. Included in the table are Dirac-Fock-Slater (DFS) results (using the non-relativistic Slater potential in the Dirac equation) and RLDA results (using the relativistic longitudinal x-potential). These are basically two similar versions of LDA-type Kohn-Sham calculations. One sees that the differences in the orbital energies are small for the inner orbitals and become even smaller for the

<table>
<thead>
<tr>
<th>Level</th>
<th>NROPM</th>
<th>ROPM</th>
<th>RHF</th>
<th>DFS</th>
<th>RLDA</th>
<th>RWDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S1/2</td>
<td>2756.925</td>
<td>3047.430</td>
<td>3074.228</td>
<td>3047.517</td>
<td>3044.410</td>
<td>3051.995</td>
</tr>
<tr>
<td>2S1/2</td>
<td>461.647</td>
<td>540.056</td>
<td>550.251</td>
<td>539.713</td>
<td>539.250</td>
<td>540.530</td>
</tr>
<tr>
<td>2P1/2</td>
<td>444.015</td>
<td>446.682</td>
<td>526.855</td>
<td>518.164</td>
<td>517.746</td>
<td>519.244</td>
</tr>
<tr>
<td>2P3/2</td>
<td>108.762</td>
<td>128.272</td>
<td>133.113</td>
<td>128.001</td>
<td>127.905</td>
<td>128.292</td>
</tr>
<tr>
<td>3S1/2</td>
<td>100.430</td>
<td>118.350</td>
<td>122.639</td>
<td>118.228</td>
<td>118.148</td>
<td>118.592</td>
</tr>
<tr>
<td>4D5/2</td>
<td>4.250</td>
<td>3.756</td>
<td>4.473</td>
<td>3.556</td>
<td>3.559</td>
<td>3.665</td>
</tr>
<tr>
<td>5S1/2</td>
<td>3.501</td>
<td>4.403</td>
<td>5.103</td>
<td>4.290</td>
<td>4.286</td>
<td>4.349</td>
</tr>
<tr>
<td>5P1/2</td>
<td>2.344</td>
<td>3.012</td>
<td>3.538</td>
<td>2.898</td>
<td>2.896</td>
<td>2.955</td>
</tr>
<tr>
<td>5P3/2</td>
<td>2.344</td>
<td>2.363</td>
<td>2.842</td>
<td>2.219</td>
<td>2.218</td>
<td>2.265</td>
</tr>
<tr>
<td>5D3/2</td>
<td>0.538</td>
<td>0.505</td>
<td>0.650</td>
<td>0.363</td>
<td>0.363</td>
<td>0.397</td>
</tr>
<tr>
<td>5D5/2</td>
<td>0.538</td>
<td>0.439</td>
<td>0.575</td>
<td>0.296</td>
<td>0.296</td>
<td>0.328</td>
</tr>
<tr>
<td>6S1/2</td>
<td>0.262</td>
<td>0.329</td>
<td>0.328</td>
<td>0.222</td>
<td>0.222</td>
<td>0.254</td>
</tr>
</tbody>
</table>
Table 3.3. Longitudinal (Coulomb) x-only energies ($-E^x_L$) for closed sub-shell atoms from NROP, ROPM, RHF, DFS, RLDA, and RWDA-calculations [18] (all energies are in hartree)

<table>
<thead>
<tr>
<th>Atom</th>
<th>NROP</th>
<th>ROPM</th>
<th>RHF</th>
<th>DFS</th>
<th>RLDA</th>
<th>RWDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.026</td>
<td>1.026</td>
<td>1.026</td>
<td>0.853</td>
<td>0.853</td>
<td>1.026</td>
</tr>
<tr>
<td>Be</td>
<td>2.666</td>
<td>2.667</td>
<td>2.668</td>
<td>2.278</td>
<td>2.278</td>
<td>2.706</td>
</tr>
<tr>
<td>Ne</td>
<td>12.105</td>
<td>12.120</td>
<td>12.123</td>
<td>10.952</td>
<td>10.944</td>
<td>12.843</td>
</tr>
<tr>
<td>Mg</td>
<td>15.988</td>
<td>16.017</td>
<td>16.023</td>
<td>14.564</td>
<td>14.550</td>
<td>17.093</td>
</tr>
<tr>
<td>Ar</td>
<td>30.175</td>
<td>30.293</td>
<td>30.303</td>
<td>27.897</td>
<td>27.844</td>
<td>32.419</td>
</tr>
<tr>
<td>Ca</td>
<td>35.199</td>
<td>35.371</td>
<td>35.383</td>
<td>32.702</td>
<td>32.627</td>
<td>37.967</td>
</tr>
<tr>
<td>Zn</td>
<td>69.619</td>
<td>70.245</td>
<td>70.269</td>
<td>66.107</td>
<td>65.834</td>
<td>75.604</td>
</tr>
<tr>
<td>Kr</td>
<td>93.833</td>
<td>95.048</td>
<td>95.072</td>
<td>89.784</td>
<td>89.293</td>
<td>102.095</td>
</tr>
<tr>
<td>Sr</td>
<td>101.926</td>
<td>103.404</td>
<td>103.429</td>
<td>97.836</td>
<td>97.251</td>
<td>111.133</td>
</tr>
<tr>
<td>Pd</td>
<td>139.113</td>
<td>141.898</td>
<td>141.930</td>
<td>134.971</td>
<td>133.887</td>
<td>152.275</td>
</tr>
<tr>
<td>Cd</td>
<td>148.879</td>
<td>152.143</td>
<td>152.181</td>
<td>144.931</td>
<td>143.687</td>
<td>163.321</td>
</tr>
<tr>
<td>Xe</td>
<td>179.062</td>
<td>184.083</td>
<td>184.120</td>
<td>175.926</td>
<td>174.102</td>
<td>197.564</td>
</tr>
<tr>
<td>Ba</td>
<td>189.065</td>
<td>194.804</td>
<td>194.841</td>
<td>186.417</td>
<td>184.363</td>
<td>209.171</td>
</tr>
<tr>
<td>Yb</td>
<td>276.143</td>
<td>288.186</td>
<td>288.265</td>
<td>278.642</td>
<td>274.386</td>
<td>310.268</td>
</tr>
<tr>
<td>Hg</td>
<td>345.240</td>
<td>365.203</td>
<td>365.277</td>
<td>354.299</td>
<td>347.612</td>
<td>392.339</td>
</tr>
<tr>
<td>Rn</td>
<td>387.445</td>
<td>414.082</td>
<td>414.151</td>
<td>402.713</td>
<td>394.102</td>
<td>444.584</td>
</tr>
<tr>
<td>Ra</td>
<td>401.356</td>
<td>430.597</td>
<td>430.664</td>
<td>419.218</td>
<td>409.871</td>
<td>462.365</td>
</tr>
<tr>
<td>No</td>
<td>511.906</td>
<td>564.309</td>
<td>564.415</td>
<td>554.242</td>
<td>538.040</td>
<td>606.216</td>
</tr>
</tbody>
</table>

outer ones. This indicates that one is dealing with a density range for which the relativistic corrections to the longitudinal x-energy are not too large. On the other hand there are definite differences between these LDA results and the results that treat the x-effects exactly.

Corresponding results for the Coulomb energies of the closed sub-shell atoms (Table 3.2) are also of interest. Again, ROPM and RHF results agree quite closely, but one also notices that the differences between NROP and ROPM results are not too large (of the order of 50 hartree for No, compared to the 4000 hartree for the total ground-state energy). The major part of the relativistic correction is kinetic rather than due to the structure of the interaction functionals. The RLDA versions do not perform optimally, although they reproduce the trend of the relativistic corrections.

In Table 3.3 (still in the longitudinal x-only limit) some RGGA results are included. The corresponding functional is obtained by fitting ROPM results to the parameterization that I have discussed. i.e., $g(\zeta)$ is written in a non-local PW91 form [20], and $\Phi_{x,2}$ in the [2,2] Padé form.

The results show that the ROPM results (which are not that easily generated) can be reproduced with very reasonable accuracy by the RGGA parameterization.
Table 3.4. Longitudinal x-only ground-state energies: Self-consistent ROPM, RHF, RLDA and RGGA results for neutral atoms with closed sub-shells (in hartree)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$-E_{\text{tot}}^L$</th>
<th>$E_{\text{tot}}^L - E_{\text{tot}}^{\text{ROP}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROPM</td>
<td>RHF</td>
</tr>
<tr>
<td>He</td>
<td>2.862</td>
<td>0.000</td>
</tr>
<tr>
<td>Be</td>
<td>14.575</td>
<td>$-0.001$</td>
</tr>
<tr>
<td>Ne</td>
<td>128.690</td>
<td>$-0.002$</td>
</tr>
<tr>
<td>Mg</td>
<td>199.932</td>
<td>$-0.003$</td>
</tr>
<tr>
<td>Ar</td>
<td>528.678</td>
<td>$-0.005$</td>
</tr>
<tr>
<td>Ca</td>
<td>679.704</td>
<td>$-0.006$</td>
</tr>
<tr>
<td>Zn</td>
<td>1794.598</td>
<td>$-0.014$</td>
</tr>
<tr>
<td>Kr</td>
<td>2788.848</td>
<td>$-0.013$</td>
</tr>
<tr>
<td>Sr</td>
<td>3178.067</td>
<td>$-0.013$</td>
</tr>
<tr>
<td>Pd</td>
<td>5044.384</td>
<td>$-0.016$</td>
</tr>
<tr>
<td>Cd</td>
<td>5593.299</td>
<td>$-0.020$</td>
</tr>
<tr>
<td>Xe</td>
<td>7446.876</td>
<td>$-0.019$</td>
</tr>
<tr>
<td>Ba</td>
<td>8135.625</td>
<td>$-0.019$</td>
</tr>
<tr>
<td>Yb</td>
<td>14067.621</td>
<td>$-0.048$</td>
</tr>
<tr>
<td>Hg</td>
<td>19648.826</td>
<td>$-0.039$</td>
</tr>
<tr>
<td>Rn</td>
<td>23601.969</td>
<td>$-0.035$</td>
</tr>
<tr>
<td>Ra</td>
<td>25028.027</td>
<td>$-0.034$</td>
</tr>
</tbody>
</table>

Table 3.5 includes the transverse x-contribution. For the column labeled RHF, the additional term is evaluated with the RHF density and added to the RHF ground-state energy. Otherwise one finds a similar story: RGGA results agree well with the ROPM standard while RLDA results do not. Looking at the transverse x-energy contribution (Table 3.6) one finds that any of the corrected non-relativistic GGA functionals (here ECMV92\cite{21} and B88\cite{22}) perform equally well.

I will not show any results that indicate that ROPM x-only results can be reproduced in a satisfactory fashion with the KLI approximation.

The discussion of correlation effects is more demanding. The first statement is: The RLDA does not give very satisfactory results. The functional that was used had the form (no-sea, electrostatic)

$$E_{\text{c}}^{\text{RLDA}}[n] = E_{\text{c,rel}}^{\text{RPA}}[n] - E_{\text{c,nonrel}}^{\text{RPA}}[n] + E_{\text{c,nonrel}}^{\text{LDA}}[n].$$

(3.69)

Only the relativistic correction to the RPA is used and added to a more accurate non-relativistic functional (e.g., from parameterization of Monte Carlo results). For low densities the first two terms cancel, so that the correlation energy is given by the more adequate non-relativistic contribution. For high densities the non-relativistic RPA contributions cancel, so that this functional contains the relativistic RPA contribution plus the non-relativistic non-RPA terms. The failure is illustrated in Table 3.7 where RLDA results are com-
Table 3.5. Total relativistic x-only ground state energies: Self-consistent ROPM, RLDA and (R)GGA results for neutral atoms with closed sub-shells in comparison with perturbative RHF data (in hartree)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(-E_{\text{tot}}^{L+T})</th>
<th>(E_{\text{tot}}^{L+T} - E_{\text{tot}}^{L+T,\text{ROPM}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROPM</td>
<td>RHF(p)</td>
</tr>
<tr>
<td>He</td>
<td>2.862</td>
<td>0.000</td>
</tr>
<tr>
<td>Be</td>
<td>14.575</td>
<td>-0.001</td>
</tr>
<tr>
<td>Ne</td>
<td>128.674</td>
<td>-0.002</td>
</tr>
<tr>
<td>Mg</td>
<td>199.900</td>
<td>-0.003</td>
</tr>
<tr>
<td>Ar</td>
<td>528.546</td>
<td>-0.005</td>
</tr>
<tr>
<td>Ca</td>
<td>679.513</td>
<td>-0.006</td>
</tr>
<tr>
<td>Zn</td>
<td>1793.840</td>
<td>-0.014</td>
</tr>
<tr>
<td>Kr</td>
<td>2787.429</td>
<td>-0.012</td>
</tr>
<tr>
<td>Sr</td>
<td>3176.358</td>
<td>-0.012</td>
</tr>
<tr>
<td>Pd</td>
<td>5041.098</td>
<td>-0.013</td>
</tr>
<tr>
<td>Cd</td>
<td>5589.495</td>
<td>-0.016</td>
</tr>
<tr>
<td>Xe</td>
<td>7441.172</td>
<td>-0.012</td>
</tr>
<tr>
<td>Ba</td>
<td>8129.160</td>
<td>-0.010</td>
</tr>
<tr>
<td>Yb</td>
<td>14053.748</td>
<td>-0.023</td>
</tr>
<tr>
<td>Hg</td>
<td>19626.702</td>
<td>0.005</td>
</tr>
<tr>
<td>Rn</td>
<td>23573.351</td>
<td>0.026</td>
</tr>
<tr>
<td>Ra</td>
<td>24996.942</td>
<td>0.034</td>
</tr>
</tbody>
</table>

pared to results of second order perturbation theory (relativistic). Even if one estimates a conservative error of 50% in the perturbative results, obviously the RLDA does not perform too well. Improvements can, however, be expected via Kohn-Sham perturbation theory on the basis of x-only ROPM results. Further work remains to be done.

3.5 Further Results

In this section I will just list some additional available results in relativistic density functional theory:

1. Relativistic spin-density functional theory has been explored. In this case, charge as well as magnetic densities are calculated, but one has to deal with rather tricky numerical problems. Among the quantities calculated are Kohn-Sham orbital energies, ground-state energies, and the (approximate) exchange-correlation magnetic potential.

2. Relativistic DFT calculations have been performed for the noble metal dimers Cu\(_2\) and Au\(_2\) as well as for the transition metal compounds Fe\(_2\) and FeO. Separation energies, equilibrium separations, and the oscillator frequency are compared: non-relativistic versus relativistic, all electron versus pseudo-potential and LDA versus GGA results.
Table 3.6. Transverse x-only energies ($E_{Tx}$) for closed sub-shell atoms: ROPM results in comparison with the values obtained by insertion of ROPM densities into the relativistic LDA (RLDA) and two relativistic GGAs (RECMV92 and RB88) (all energies are in hartree [23])

<table>
<thead>
<tr>
<th>Atom</th>
<th>ROPM</th>
<th>RLDA</th>
<th>RECMV92</th>
<th>RB88</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.000064</td>
<td>0.000159</td>
<td>0.000060</td>
<td>0.000061</td>
</tr>
<tr>
<td>Be</td>
<td>0.00070</td>
<td>0.00176</td>
<td>0.00071</td>
<td>0.00072</td>
</tr>
<tr>
<td>Ne</td>
<td>0.0167</td>
<td>0.0355</td>
<td>0.0166</td>
<td>0.0167</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0319</td>
<td>0.0654</td>
<td>0.0319</td>
<td>0.0319</td>
</tr>
<tr>
<td>Ar</td>
<td>0.132</td>
<td>0.251</td>
<td>0.132</td>
<td>0.132</td>
</tr>
<tr>
<td>Ca</td>
<td>0.191</td>
<td>0.356</td>
<td>0.191</td>
<td>0.191</td>
</tr>
<tr>
<td>Zn</td>
<td>0.759</td>
<td>1.328</td>
<td>0.760</td>
<td>0.759</td>
</tr>
<tr>
<td>Kr</td>
<td>1.420</td>
<td>2.410</td>
<td>1.421</td>
<td>1.419</td>
</tr>
<tr>
<td>Sr</td>
<td>1.711</td>
<td>2.878</td>
<td>1.712</td>
<td>1.710</td>
</tr>
<tr>
<td>Cd</td>
<td>3.809</td>
<td>6.180</td>
<td>3.809</td>
<td>3.809</td>
</tr>
<tr>
<td>Xe</td>
<td>5.712</td>
<td>9.114</td>
<td>5.712</td>
<td>5.713</td>
</tr>
<tr>
<td>Hg</td>
<td>22.169</td>
<td>34.257</td>
<td>22.169</td>
<td>22.169</td>
</tr>
<tr>
<td>Rn</td>
<td>28.679</td>
<td>44.382</td>
<td>28.681</td>
<td>28.680</td>
</tr>
<tr>
<td>Ra</td>
<td>31.151</td>
<td>48.275</td>
<td>31.149</td>
<td>31.151</td>
</tr>
</tbody>
</table>

Table 3.7. Comparison of LDA [18], CI (estimated from non-relativistic CI-calculations for the three innermost electrons and the experimental ionization potentials of all other electrons [24]) and MBPT2 [26] correlation energies for neutral atoms: $E_{NREL}^{\text{CI}}$ – non-relativistic correlation energy, $\Delta E_{cL}^{L}$ – relativistic contribution in the longitudinal correlation energy, $E_{cT}^{T}$ – transverse correlation energy (in the case of the MBPT2 only the dominating Breit contribution to $E_{cT}^{T}$ is given (all energies are in mhartree))

<table>
<thead>
<tr>
<th>Atom</th>
<th>$-E_{cL}^{NREL}$</th>
<th>$-\Delta E_{cL}^{L}$</th>
<th>$-E_{cT}^{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MBPT2 CI LDA</td>
<td>MBPT2 LDA</td>
<td>MBPT2 LDA</td>
</tr>
<tr>
<td>He</td>
<td>37.14</td>
<td>42.04</td>
<td>111.47</td>
</tr>
<tr>
<td>Be</td>
<td>94.34</td>
<td>224.44</td>
<td>222.44</td>
</tr>
<tr>
<td>Ne</td>
<td>383.19</td>
<td>390.47</td>
<td>743.38</td>
</tr>
<tr>
<td>Mg</td>
<td>438.28</td>
<td>891.42</td>
<td>891.42</td>
</tr>
<tr>
<td>Ar</td>
<td>697.28</td>
<td>722.16</td>
<td>1429.64</td>
</tr>
<tr>
<td>Zn</td>
<td>1650.61</td>
<td>2666.20</td>
<td>2666.20</td>
</tr>
<tr>
<td>Kr</td>
<td>1835.43</td>
<td>3282.95</td>
<td>3282.95</td>
</tr>
<tr>
<td>Cd</td>
<td>2618.11</td>
<td>4570.56</td>
<td>4570.56</td>
</tr>
<tr>
<td>Xe</td>
<td>2921.13</td>
<td>5200.19</td>
<td>5200.19</td>
</tr>
<tr>
<td>Hg</td>
<td>5086.24</td>
<td>8355.68</td>
<td>8355.68</td>
</tr>
<tr>
<td>Rn</td>
<td>5392.07</td>
<td>9026.90</td>
<td>9026.90</td>
</tr>
</tbody>
</table>
3. A number of solids with heavy constituents have been treated in relativistic DFT. For Au and Pt the linearized augmented plane-wave (LAPW) method has been implemented in order to study relativistic effects in solids (relativistic versus non-relativistic, LDA versus GGA results). Similarly, effects of spin-orbit-coupling have been investigated in bulk W, Ir and Au on the basis of relativistic LDA-LAPW approaches.

4. On the basis of quantum hadron-dynamics, a field theoretical meson exchange model, Kohn-Sham and extended Thomas-Fermi investigations of nuclei, in particular trans-uranic systems, have been carried out.

Detailed results of relativistic DFT and a full list of references can be found in [27,28].

Acknowledgments

As I am about to retire from “active service”, I would like to take this opportunity to thank all the people with whom I had the pleasure to work during the last 40 years. In particular, I would like to thank my Portuguese friends Carlos Fiolhais, João da Providência and José Urbano for a continuing exchange of ideas over many years. Finally, I would like to thank the organizers of this fascinating Summer School, which attracted young people from all over Europe.

References

16. See chapter by E. Engel in this volume and references therein.
23. In all our calculations the nuclei were represented by uniformly charged spheres with nuclear radii given by $R_{\text{nuc}} = 1.079A^{1/3} + 0.73587F$, $A$ being the atomic mass (weighted by isotopic abundance) taken from Table III.7 of [24] unless explicitly stated otherwise. The speed of light has been set to $c = 137.0539895$.