DENSITY FUNCTIONAL THEORY OF FIELD THEORETICAL SYSTEMS

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Abstract

The field theoretical background of relativistic density functional theory is emphasized and its consequences for relativistic Kohn-Sham equations are shown. The local density approximation for the exchange energy functional is reviewed and the importance of relativistic corrections for an accurate representation of the exchange functional is demonstrated.

I. INTRODUCTION

In view of the importance of relativistic effects for the physics and chemistry of heavy elements (see e.g. [1–3]) the analysis and further development of relativistic density functional theory (DFT) is of substantial practical interest. While the effects of relativistic kinematics of the electrons on atomic structure and chemical bonds have been studied in much detail, the consequences of relativistic corrections to exchange and correlation, and in particular of the retardation of the electron-electron interaction, have gained less attention, at least in the DFT context. Moreover, considering e.g. the spectroscopy of high-Z atoms even radiative corrections can no longer be neglected, thus emphasizing the fact that the appropriate theory for a fully relativistic *ab initio* description of atoms and molecules is quantum electrodynamics (QED). As an immediate consequence any consistent formulation of relativistic DFT must also be based on QED.

A relativistic extension of the Hohenberg-Kohn (HK) theorem [4] has been given by Rajagopal and Callaway [5]. The corresponding Kohn-Sham (KS) equations [6] have been introduced by Rajagopal [7] and independently by MacDonald and Vosko [8]. However, while these relativistic extensions of DFT concepts started from QED, the additional features introduced by QED as compared to nonrelativistic many body theory have only partially been taken into account. In particular, the existence of antiparticles (negative energy states) allowing for the creation of virtual electron-positron pairs and the intrinsically related question of renormalization have not been addressed. Recently, an attempt has been made [9] to deal with these problems. The consequences, in particular for relativistic KS-equations, will be briefly reviewed in this paper. As a result of taking the field theoretical basis of relativistic DFT seriously one finds that the latter approach in principle contains all radiative effects inherent in QED, although at the price of a substantially more complicated selfconsistency scheme. In the second part of this paper the local density approximation (LDA) to the relativistic exchange-correlation energy functional [7,8,10–12] is reconsidered. On the basis of

the LDA it is shown that relativistic corrections to the functional dependence of the exchange energy functional $E_x[n]$ on the density are required for an accurate description of high-Z atoms, i.e. that using nonrelativistic approximations to $E_x[n]$ in relativistic KS-calculations introduces substantial errors. Finally, the modification of the correlation energy functional by inclusion of vacuum corrections is illustrated within the RPA.

II. FIELD THEORETICAL BASIS

The starting point for the discussion of field theoretical systems is their Lagrangian density which completely specifies the physics involved. Here we consider QED, which is the appropriate quantum field theory for the description of relativistic atomic, molecular and condensed matter systems. In order to deal with these systems in a fully covariant way one would have to associate dynamic degrees of freedom to both electrons and nuclei (at least on a classical level). As usual in the context of atomic and molecular physics, however, we restrict ourselves to treating all nuclei as fixed, time-independent external sources, thus partially breaking covariance by assumimg the existence of a common rest frame of all nuclei. The corresponding Lagrangian is given by

$$\begin{aligned}
\mathcal{L} &= \mathcal{L}_e + \mathcal{L}_\gamma + \mathcal{L}_{int} \qquad (1)\\
\mathcal{L}_e &= \frac{1}{4}\left\{\left[\hat{\overline{\psi}}, (i\vec{\partial\!\!\!/} - m)\hat{\psi}\right] + \left[\hat{\overline{\psi}}(-i\overleftarrow{\partial\!\!\!/} - m), \hat{\psi}\right]\right\}\\
\mathcal{L}_\gamma &= -\frac{1}{4}(\partial_\mu \hat{A}_\nu - \partial_\nu \hat{A}_\mu)(\partial^\mu \hat{A}^\nu - \partial^\nu \hat{A}^\mu) - \frac{\lambda}{2}(\partial_\nu \hat{A}^\nu)^2\\
\mathcal{L}_{int} &= -\, e\, \hat{j}^\nu \left(\hat{A}_\nu + V_\nu\right)\\
\hat{j}^\nu &= \frac{1}{2}\left[\hat{\overline{\psi}}, \gamma^\nu \hat{\psi}\right] \quad , \qquad (2)
\end{aligned}$$

where $\hat{\psi}$ and $\hat{A}_\mu$ denote the electron and photon field operators, respectively, while $V_\mu(\boldsymbol{x})$ represents the static potential generated by the nuclei. For the photon field we have chosen to work in the covariant gauge. Moreover, both $\mathcal{L}_e$ and the electronic four current $\hat{j}^\nu(x)$ have been written in a charge conjugation invariant form [13]. Note that due to the choice of a particular Lorentz frame in which the external sources are at rest the gauge invariance of the Lagrangian with respect to gauge transformations of the external potential has been partially broken: Only static gauge transformations are admitted within the rest frame of the nuclei.

On the basis of Noether's theorem one can easily discuss the various symmetries of the field theory at hand. First of all, the continuity equation for the energy momentum tensor obtained from (1),

$$\partial_\mu \hat{T}^{\mu 0}(x) = 0 \quad , \qquad (3)$$

which reflects stationarity in the rest frame of the nuclei, allows to identify the Hamiltonian,

$$\hat{H} \equiv \int d^3x\ \hat{T}^{00}(x) \quad . \qquad (4)$$

Moreover, the continuity equation for the four current,

$$\partial_\nu \hat{j}^\nu(x) = 0 \quad , \tag{5}$$

implies the conservation of the total charge,

$$\hat{Q} = \int d^3x \ \hat{j}^0(x) = \frac{1}{2} \int d^3x \ \left[\hat{\psi}^+(x), \hat{\psi}(x)\right] \quad . \tag{6}$$

As a consequence any ground state resulting from (1) can be classified with respect to its charge. Furthermore, an analysis of the generalized angular momentum tensor immmediatly demonstrates the intrinsic coupling of orbital angular momentum and electron spin exhibiting the fact that there is no direct relativistic analogue of spin-density functional theory. Finally, a discussion of the relevant discrete symmetry transformations (parity, charge conjugation and time reversal) shows that the ground state resulting from (1) for an external four potential V^μ without any spatial symmetries is nondegenerate in general. Consequently no degeneracies remain to be lifted by introduction of additional (artificial) couplings of the electron field to external sources (as usual in the context of nonrelativistic spin-density functional theory).

Unfortunately, the Hamiltonian (4) does not allow to prove a relativistic HK-theorem without addressing the issue of renormalization as any direct evaluation of the ground state expectation values $< \Psi|\hat{H}|\Psi >$ and $< \Psi|\hat{j}^\nu|\Psi >$ leads to various divergencies. On one hand, there is the divergent vacuum energy of noninteracting electrons and photons, i.e. the energy of all Dirac sea states in the electronic case and the zero point energy of the photons. These divergent energy contributions are usually removed by either normal ordering of the operators in the Hamiltonian or by explicit subtraction of the vacuum expectation value of the energy of free electrons and photons,

$$\hat{H}_r = \hat{H} - < 0|\hat{H}_{free}|0 > \quad , \tag{7}$$

such that $\hat{H}_r$ leads to a finite ground state energy for noninteracting homogeneous systems. On the other hand, UV-divergencies which result from the perturbative treatment of the interaction between electrons and photons as well as the external potential show up in both the ground state energy and the ground state four current. These divergencies can be taken care of by the standard renormalization procedure of quantum field theory (applied to ground state energies and four currents — see e.g. [9]), the main point being that all counterterms required to keep the ground state energy and four current finite are completely determined by specification of V^μ and do not explicitly depend on the ground state $|\Psi >$ corresponding to V^μ. This then allows to use the familiar nonrelativistic scheme [4] for the proof of the HK-theorem also in the relativistic situation where any serious proof must be based on renormalized quantities (for details see [9]).

III. RELATIVISTIC DENSITY FUNCTIONAL THEORY

A HK-theorem for relativistic systems has first been formulated by Rajagopal and Callaway [5] (see also Refs. [8,14,15,9]). On the basis of (4) one finds that the class of external four potentials just differing by (static) gauge transformations uniquely determines the associated class of ground states as well as the corresponding gauge invariant ground state

four current and vice versa,

$$\Big\{V_\nu(\boldsymbol{x})\Big|V_\nu(\boldsymbol{x})+\partial_\nu\Lambda(t,\boldsymbol{x});\Lambda(t,\boldsymbol{x})=ct+\lambda(\boldsymbol{x})\Big\}\Longleftrightarrow\Big\{|\Psi>\Big\}\Longleftrightarrow j^\nu(\boldsymbol{x})\quad .$$

In other words, choosing some suitable representative of the class of ground states, i.e. fixing the gauge once and for all, one ends up with the statement that the ground state is a unique functional of the ground state four current, $|\Psi[j^\nu]>$. Consequently also all ground state observables are unique functionals of j^ν, the most important being the ground state energy,

$$E[j^\nu]=<\Psi[j^\nu]\mid\hat{H}\mid\Psi[j^\nu]>\quad ,$$

where renormalization is implicitly understood. The minimum principle for ground state energies [16] then allows to obtain the exact j^ν by solution of a variational equation,

$$\frac{\delta}{\delta j^\nu(\boldsymbol{r})}\Big\{E[j^\nu]-\mu\int d^3x\ j^0(\boldsymbol{x})\Big\}=0\quad , \tag{8}$$

where charge conservation has been imposed. Thus the statements of the relativistic HK-theorem are rather similar to its nonrelativistic counterpart. Note, however, that relativistic DFT also includes all radiative effects.

Relativistic KS-equations have been introduced by Rajagopal [7] as well as MacDonald and Vosko [8]. As for the HK-theorem, however, the problem of radiative corrections has not been addressed until recently [9]. Thus in the following we will briefly summarize the KS-equations obtained on the field theoretical level. The starting point is a decomposition of the total energy functional into the kinetic energy functional of noninteracting particles $T_s[j^\mu]$, the external potential energy, a Hartree-like contribution $E_H[j^\mu]$ and the exchange-correlation energy functional $E_{xc}[j^\mu]$,

$$E[j^\nu]=T_s[j^\nu]+e\int d^3x\ j^\nu(\boldsymbol{x})V_\nu(\boldsymbol{x})+E_H[j^\nu]+E_{xc}[j^\nu]\quad , \tag{9}$$

which essentially represents the definition of $E_{xc}[j^\mu]$. While the functional dependence of T_s on j^μ is not known explicitly, T_s can be expressed exactly in terms of the single particle four spinors $\varphi_n(\boldsymbol{x})$ resulting from a given local potential,

$$\begin{aligned}
T_s[j^\nu]&=T_{s,V}+T_{s,D} \qquad (10)\\
T_{s,V}&=\frac{1}{2}\int d^3x\ \Big\{\sum_{\epsilon_n\le -m}\overline{\varphi}_n(\boldsymbol{x})\Big[-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}+m\Big]\varphi_n(\boldsymbol{x})\\
&\qquad\qquad -\sum_{\epsilon_n>-m}\overline{\varphi}_n(\boldsymbol{x})\Big[-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}+m\Big]\varphi_n(\boldsymbol{x})\Big\}-\delta T^{vac}_{s,hom}\\
T_{s,D}&=\int d^3x\ \sum_{-m<\epsilon_n\le\epsilon_F}\overline{\varphi}_n(\boldsymbol{x})\Big[-i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}+m\Big]\varphi_n(\boldsymbol{x})\quad .
\end{aligned}$$

Here $T_s[j^\nu]$ has been decomposed into a vacuum contribution $T_{s,V}$ and the kinetic energy $T_{s,D}$ of the real electrons bound by the local potential (characterised by their eigenvalues between $-m$ and the Fermi energy ϵ_F). Note that the difference between the kinetic energies of negative ($\epsilon_n\le -m$) and positive energy ($\epsilon_n>-m$) single particle states in $T_{s,V}$ is a consequence of the charge conjugation invariant form of the Lagrangian, Eq.(1). Of course, this

vacuum contribution requires renormalization, i.e. $\delta T^{vac}_{s,hom}$ represents the (divergent) energy of the noninteracting free Dirac sea as discussed earlier. The four current of noninteracting particles is obtained from the single particle spinors by

$$
\begin{aligned}
j^\nu(\boldsymbol{x}) &= j^\nu_V(\boldsymbol{x}) + j^\nu_D(\boldsymbol{x}) \qquad (11)\\
j^\nu_V(\boldsymbol{x}) &= \frac{1}{2}\Big\{ \sum_{\epsilon_n \le -m} \overline{\varphi}_n(\boldsymbol{x})\gamma^\nu\varphi_n(\boldsymbol{x}) - \sum_{\epsilon_n > -m} \overline{\varphi}_n(\boldsymbol{x})\gamma^\nu\varphi_n(\boldsymbol{x})\Big\}\\
j^\nu_D(\boldsymbol{x}) &= \sum_{-m<\epsilon_n\le\epsilon_F} \overline{\varphi}_n(\boldsymbol{x})\gamma^\nu\varphi_n(\boldsymbol{x}) \quad ,
\end{aligned}
$$

which is finite without additional counterterms. The direct electron-electron interaction energy (Hartree term) is given by

$$
E_H[j^\nu] = -i\frac{e^2}{2}\int d^3x \int d^4y \; j^\mu(\boldsymbol{x}) \; D^0_{\mu\nu}(x-y) \; j^\nu(\boldsymbol{y}) \quad , \qquad (12)
$$

where $D^0_{\mu\nu}$ represents the free photon propagator, such that E_H does not only contain the Coulomb interaction between the density j^0 at $\boldsymbol{x}$ and that at $\boldsymbol{y}$ but also a current-current interaction term.

Minimizing the total energy (9) on the basis of Eqs.(10-12) with respect to auxilliary single particle spinors φ_n assumed to reproduce the exact j^ν of the actually interesting interacting system then leads to the relativistic KS-equations,

$$
\gamma^0\Big\{ -i\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + m + e\not{V}(\boldsymbol{x}) + \not{\phi}_H(\boldsymbol{x}) + \not{\phi}_{xc}(\boldsymbol{x})\Big\}\varphi_n(\boldsymbol{x}) = \epsilon_n\varphi_n(\boldsymbol{x}) \quad , \qquad (13)
$$

where

$$
v^\nu_H(\boldsymbol{x}) = e^2\int d^3y \; \frac{j^\nu(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} \qquad (14)
$$

$$
v^\nu_{xc}(\boldsymbol{x}) = \frac{\delta E_{xc}[j^\mu]}{\delta j_\nu(\boldsymbol{x})} \quad . \qquad (15)
$$

Of course, in (15) $E_{xc}[j^\mu]$ is implicitly understood to be renormalized, i.e. renormalization has to be taken care of in the construction of any approximation for this functional (an explicit example for a renormalized $E_{xc}[j^\mu]$ will be given in Section IV).

Note that in order to treat the vacuum polarization current j^ν_V and the corresponding vacuum correction $T_{s,V}$ consistently not only knowledge of all occupied states is required, but also all continuum states must be known which represents an enormous difficulty in real applications. Moreover, although radiative corrections can not be ignored in spectroscopic analyses of high-Z atoms (they e.g. reduce the ground state energy of Hg by roughly $18.9a.u.$ [17] such that their contribution is much larger than the total correlation energy) one would not expect them to be relevant for chemical bonds as only the innermost orbitals are affected. Thus in practice all radiative corrections have been neglected so far (or at least dealt with perturbatively) leading to a considerable simplification of the KS-scheme. However, it should be emphasized at this point that this so-called no-sea approximation which represents a DFT-version of the projection on positive energy states can not be directly identified with the standard projection schemes due to the auxilliary character of the φ_n (although in actual applications one would expect little difference). In any case, a model study in which vacuum corrections are included selfconsistently seems interesting from a conceptual point of view in order to demonstrate the feasibility of the relativistic KS-equations, Eqs.(11,13-15).

IV. RELATIVISTIC AND RADIATIVE CORRECTIONS TO THE EXCHANGE-CORRELATION ENERGY

As a matter of principle the relativistic exchange-correlation energy functional depends on the complete four current $j^\nu = (j^0, \boldsymbol{j})$. However, in practice the only relativistic extension available to date is the local density approximation (LDA) which automatically implies vanishing $\boldsymbol{j}$ such that E_{xc} in this approximation becomes a functional of the density $j^0 = n$ only. The LDA nevertheless clearly demonstrates the importance of relativistic corrections at least for the exchange part of the functional which is briefly reviewed here.

The corresponding exchange energy density e_x^{LDA} reads

$$e_x^{LDA}(n) = \frac{ie^2}{2} \int d^4y \; D^0_{\mu\nu}(x-y) \; tr[\gamma^\mu G(x,y) \gamma^\nu G(y,x)] \quad , \tag{16}$$

where $G(x,y)$ represents the electron propagator of the noninteracting relativistic homogeneous electron gas. The remaining loop integration can be performed analytically [18–20,7,8],

$$e_x^{LDA}(n) = c_{0x} n^{\frac{4}{3}} \left\{ 1 - \frac{3}{2} \left[\frac{\eta}{\beta} - \frac{1}{\beta^2} arsinh(\beta) \right]^2 \right\} \quad , \tag{17}$$

where

$$\beta = \frac{(3\pi^2 n)^{\frac{1}{3}}}{m} \qquad ; \qquad \eta = (1+\beta^2)^{\frac{1}{2}} \quad .$$

Note that the exchange energy is of first order in the fine structure constant so that vacuum corrections do not contribute to e_x^{LDA}. In Eq.(17) e_x^{LDA} has been written as a product of its nonrelativistic limit $c_{0x} n^{\frac{4}{3}}$ and a relativistic correction factor. The latter is plotted in Fig.1 as a function of β. Also shown in Fig.1 is the standard decomposition of (16) into the nonretarded Coulomb contribution e_x^{Cou} and the remainder, the transverse term,

$$e_x^{Cou} = -\frac{e^2}{2} \int d^3y \; \frac{tr[\gamma^0 G(x,y) \gamma^0 G(y,x)]}{4\pi |\boldsymbol{x} - \boldsymbol{y}|} \Big|_{x^0 = y^0} \tag{18}$$

$$e_x^{tr} = e_x^{total} - e_x^{Cou} \quad . \tag{19}$$

Thus, while e_x^{Cou} just takes into account the relativistic kinematics of the electrons, e_x^{tr} adds in the retardation of the electron-electron interaction. Fig.1 demonstrates that in the nonrelativistic limit $\beta \to 0$ the Coulomb contribution dominates completely. However, while e_x^{Cou} is only weakly dependent on β, the tranverse part of e_x starts to increase rapidly with β and dominates in the ultrarelativistic limit in which e_x^{total} even changes its sign. In Fig.1 the β-values at the r-expectation values of the $1s$-orbitals obtained by nonrelativistic calculations for Kr and Rn are also indicated in order to give an idea to which extent these relativistic corrections actually affect the description of atomic systems. While from this comparison one would expect little effect on atoms smaller than Kr, the difference between the nonrelativistic and relativistic forms of e_x^{LDA} should definitely be relevant for high-Z atoms. Moreover, these densities seem to indicate that the sign change at about $\beta \approx 2.5$ is not really probed in atomic systems.

An analysis of the various contributions to the exchange energy of neutral Mercury listed in Table I illustrates the properties of $E_x^{LDA}[n]$ and emphasizes the importance of

a relativistic extension of $E_x[n]$ for DFT-applications to high-Z atoms. As Table I shows the relativistic correction to the Coulomb exchange energy is larger than the difference between the nonrelativistic LDA result and the exact relativistic E_x^{Cou} [21], i.e. larger than the nonlocal correction to the nonrelativistic E_x. The total relativistic correction, on the other hand, is only about $2a.u.$ as E_x^{tr} almost cancels with the relativistic correction to E_x^{Cou}. Moreover, while the latter is underestimated by the LDA, E_x^{tr} is overestimated by as much as 50% leading to a total LDA-error about twice as large as in the nonrelativistic case. Of course, the relativistic corrections to E_x are dominated by contributions from the innermost orbitals [12], i.e. by the region close to the nucleus where the density is rather inhomogeneous. It is thus not surprising that the LDA gives rather inaccurate results.

The fact that the total relativistic E_x^{HF} is not much different from the nonrelativistic exchange energy should not be interpreted as an indication that relativistic effects are irrelevant for the exchange energy functional: When going from a nonrelativistic to a relativistic treatment two effects lead to changes in the value of E_x, (i) the difference between the self-consistent relativistic and nonrelativistic densities inserted in $E_x[n]$, and (ii) the relativistic corrections in the functional dependence of $E_x[n]$ on the density. As the form of the density is rather independent of the specific $E_x[n]$ used for its calculation (i.e. is dominated by kinetic effects) the former relativistic contribution shows up in any case: For Hg this component amounts to 22a.u. (as can be seen from the third row of Table I) such that utilizing the nonrelativistic $E_x^{LDA}[n]$ in a relativistic KS-calculation overestimates the exchange energy drastically. One thus concludes that an accurate relativistic exchange energy functional must contain nonlocal relativistic corrections (one e.g. could think of a relativistic extension of the generalized gradient approximation).

While to date the inclusion of radiative corrections in approximate $E_{xc}[n]$ seems not quite appropriate in view of the inaccuracies currently remaining in nonlocal and relativistic corrections, it is nevertheless interesting from a conceptual point of view (and might even be necessary for special problems like the description of highly ionized high-Z atoms). In order to give an idea of the effect of radiative corrections on $E_{xc}[n]$ we consider the LDA for $E_c[n]$. Within the RPA one finds for the correlation energy density [22],

$$e_c^{RPA}(n) = -\frac{i}{2}\int \frac{d^4q}{(2\pi)^4}\, Tr\Bigg\{ \ln\left[g_\mu{}^\nu + e^2\frac{\Pi^{(0)}_{D,\mu}{}^\nu(q)}{q^2[1+e^2\Pi_R^{(0)}(q^2)]+i\epsilon}\right] - e^2\frac{\Pi^{(0)}_{D,\mu}{}^\nu(q)}{q^2[1+e^2\Pi_R^{(0)}(q^2)]+i\epsilon}\Bigg\} \quad , \tag{20}$$

where the response function $\Pi^{(0),\mu\nu}(q)$ of the noninteracting homogeneous electron gas has been decomposed into a vacuum contribution and the remainder,

$$\Pi^{(0),\mu\nu}(q) = \Pi_V^{(0),\mu\nu}(q) + \Pi_D^{(0),\mu\nu}(q)$$

and the tensor structure of the lowest order vacuum polarization,

$$\Pi_V^{(0),\mu\nu}(q) = \left(q^2 g^{\mu\nu} - q^\mu q^\nu\right)\Pi_R^{(0)}(q^2) \quad ,$$

has been utilized. Note that counterterms had to be included to keep both $\Pi^{(0)}(q^2)$ (indicated by the index R) and the outer loop integration in Eq.(20) finite. As to be expected

the creation of virtual electron-positron pairs represented by $\Pi_R^{(0)}$ leads to a screening of the free electron-electron interaction. However, for electronic systems the vacuum-screened correlation energy functional (20) still has to be evaluated.

ACKNOWLEDGMENTS

I would like to thank Profs. R. M. Dreizler and A. K. Rajagopal for very stimulating and helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft (project En 265/1-1) is gratefully acknowledged.

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TABLES

	E_x	E_x^{Cou}	E_x^{tr}
NRHF	—	-345.30	—
NRLDA(NRLDA)	—	-331.88	—
NRLDA(LDA)	—	-353.55	—
HF	-343.11	-365.28	22.17
LDA(LDA)	-313.09	-347.07	33.98

TABLE I. Various contributions to the relativistic exchange energy of Hg: NRHF — nonrel. HF result, NRLDA(NRLDA) — nonrel. LDA functional with nonrel. LDA density, NRLDA(LDA) — nonrel. LDA functional with rel. LDA density, HF — rel. HF results [23,24], LDA(LDA) — rel. LDA functionals with rel. LDA density [12], (all energies are in $a.u.$).

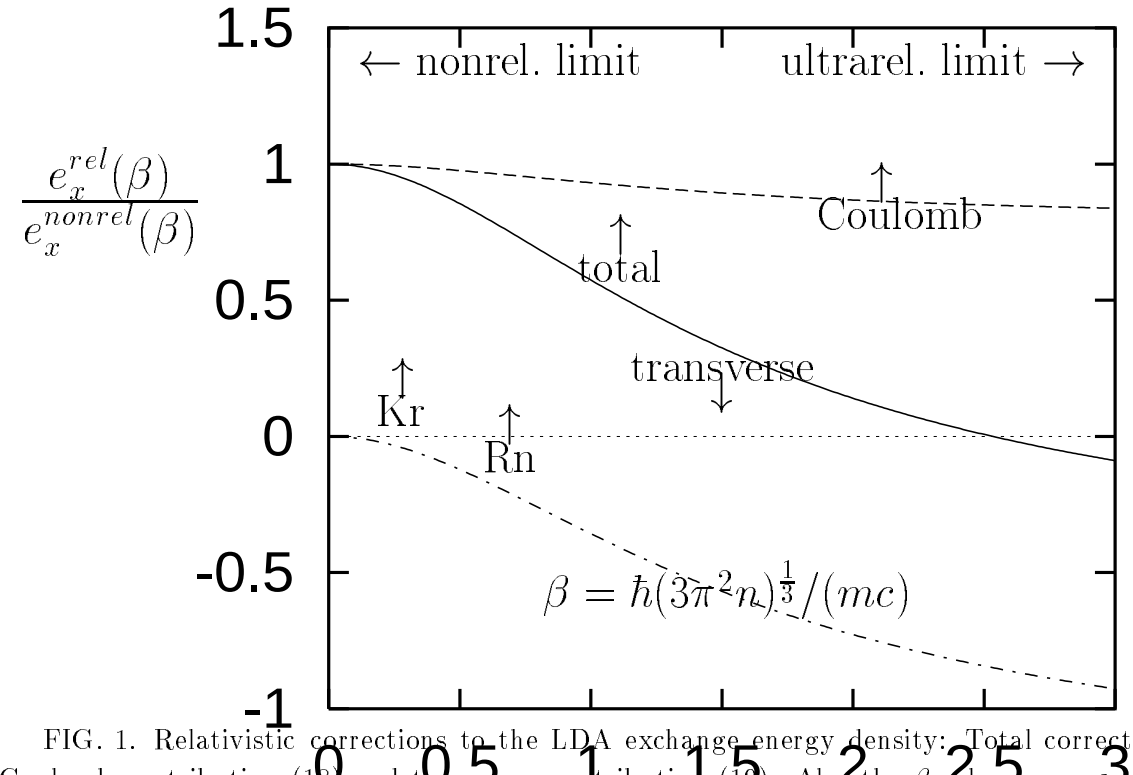

FIG. 1. Relativistic corrections to the LDA exchange energy density: Total correction (17), Coulomb contribution (18) and transverse contribution (19). Also the β-values corresponding to the densities of Kr and Rn at the r-expectation values of the 1s-orbitals are indicated.