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RELATIVISTIC CORRECTIONS TO THE EXCHANGE-CORRELATION ENERGY FUNCTIONAL

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INTRODUCTION

During recent years the development of fully relativistic methods for electronic structure calculations has been a major trend both in atomic physics and computational quantum chemistry (see e.g.[1, 2, 3, 4, 5]). Looking at Gold as the prime candidate for relativistic effects this trend is easy to understand: When going from a nonrelativistic to a relativistic treatment the ionization potential of Au increases by 30% [6], the bond length of AuH is contracted by 13% and its dissociation energy increases by about 50% [6]. The differences are even more dramatic for the electron affinity: For Au a nonrelativistic CI-calculation [7] gives a value of 1.02 eV compared with 2.28 eV obtained with a fully relativistic Coupled-Cluster calculation [4]. Moreover, the fact that the relativistic Hartree-Fock (RHF) approach leads to 7.48 eV [4] for the electron affinity of Au while the nonrelativistic HF value is 0.10 eV, clearly demonstrates that relativistic and exchange-correlation (xc) effects are nonadditive.

Since the introduction of Generalized Gradient Approximations (GGAs) [8, 9, 10] density functional theory (DFT) has gained considerable attraction in the quantum chemistry community. In fact, it has been shown by studying a variety of small molecules with light constituents [11, 12] that for binding geometries and atomization energies DFT methods can successfully compete with the traditional *ab initio* approaches. As soon as heavy elements are involved, however, the situation is not as clear. All applications of relativistic DFT (RDFT) [13, 14, 15, 16] have so far essentially been restricted to a relativistic treatment of the DFT kinetic energy, thus ignoring the nonadditivity of relativistic and xc-effects. Although the relativistic Local Density Approximation (RLDA) has been evaluated rather early [14, 15, 17] its application is hampered by both the well-known deficiencies of the nonrelativistic LDA and its inaccurate description of relativistic corrections [18, 19]. This is e.g. obvious from the 50% overestimation of the Au₂ dissociation energy, found in a fully relativistic LDA-KS-calculation [20]. Only very recently has a relativistic extension of the GGA (RGGA) for the exchange-only (x-only) energy been put forward [21], applications to molecules in fully relativistic Kohn-Sham (KS) calculations are not yet available.

In this contribution we analyze the RGGA on the basis of exact relativistic x-only

results obtained with the relativistic Optimized-Potential-Method (ROPM) [22, 23, 24, 19] (after a brief review of RDFT, which serves to define the various concepts involved, and an outline of our RGGA approach). In particular, we present first selfconsistent ROPM calculations including the complete transverse interaction (usually only taken into account on the weakly relativistic Breit level or evaluated perturbatively*) and use the resulting x-only potentials to investigate the accuracy of the RGGA on a microscopic level. In response to the deficiencies of the RLDA for the correlation energy we extend the RGGA to include relativistic correlation effects. Moreover, by applying the relativistic extension scheme to different nonrelativistic GGAs its general validity is demonstrated.

RELATIVISTIC KOHN-SHAM EQUATIONS

The starting point for the derivation of relativistic KS-equations is the standard QED Hamiltonian \hat{H}_e augmented by an external potential term, representing the nuclei and, if present, applied static electric and/or magnetic fields (we use $\hbar = c = 1$ throughout),

$$\hat{H} = \hat{H}_e + \int d^3r v_{ext}^\mu \hat{j}_\mu \quad ; \quad \hat{j}_\mu = \frac{1}{2} [\hat{\psi}, \gamma_\mu \hat{\psi}] , \quad (1)$$

where the current operator \hat{j}_μ has been written in a charge conjugation 'invariant' form. As usual in relativistic quantum field theory both \hat{H} and \hat{j}_μ require renormalization. The energy of the negative continuum states can e.g. be eliminated via

$$\hat{H}_R = \hat{H} - \langle 0 | \hat{H}_e | 0 \rangle ,$$

where $|0\rangle$ represents the vacuum corresponding to \hat{H}_e . Additional counterterms are necessary to deal with the UV-divergencies. In the subsequent discussion we will always assume that the quantities involved are renormalized without explicitly displaying the relevant counterterms.

On the basis of the assumption that there exists a minimum principle[†] for the renormalized ground state energy E_{tot} one can then directly establish a Hohenberg-Kohn theorem [13, 14, 15]: E_{tot} is a unique functional of the (renormalized) ground state four current j_μ which can be written as

$$E_{tot}[j_\mu] = F[j_\mu] + \int d^3r v_{ext}^\mu j_\mu , \quad (2)$$

with $F[j_\mu]$ being a universal functional of j_μ . Note that the gauge dependence of the corresponding QED ground state is not transferred into $E_{tot}[j_\mu]$ as the ground state energy and four current are gauge invariant quantities (up to trivial energy shifts[‡]).

One can then represent the exact current j_μ of the interacting system via auxiliary single particle four spinors,

$$j^\nu(\mathbf{x}) = j_V^\nu(\mathbf{x}) + j_D^\nu(\mathbf{x}) \quad (3)$$

$$j_V^\nu(\mathbf{x}) = \frac{1}{2} \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) \right\} \quad (4)$$

$$j_D^\nu(\mathbf{x}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) , \quad (5)$$

*Inclusion of the complete orbital-dependent transverse RHF exchange potential would lead to gauge dependent results.

[†]Note that its existence is the guiding principle in the construction of the standard renormalization scheme.

[‡]Only static gauge transformations are relevant in this context.

and define the corresponding noninteracting kinetic energy

$$T_s[j^\nu] = T_{s,V}[j^\nu] + T_{s,D}[j^\nu] \quad (6)$$

$$T_{s,V}[j^\nu] = \frac{1}{2} \int d^3x \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\mathbf{x}) [-i\boldsymbol{\gamma} \cdot \nabla + m] \varphi_k(\mathbf{x}) \right. \\ \left. - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) [-i\boldsymbol{\gamma} \cdot \nabla + m] \varphi_k(\mathbf{x}) \right\} \quad (7)$$

$$T_{s,D}[j^\nu] = \int d^3x \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) [-i\boldsymbol{\gamma} \cdot \nabla + m] \varphi_k(\mathbf{x}) . \quad (8)$$

Here j_V^ν represents the KS-equivalent of the usual vacuum polarization current and $T_{s,V}$ is the kinetic contribution to the KS Casimir energy. j_D^ν and $T_{s,D}$, on the other hand, result from the discrete bound 'electrons'. Minimizing E_{tot} with respect to the φ_k one finds the relativistic KS-equations in their most general form,

$$\gamma^0 \left\{ -i\boldsymbol{\gamma} \cdot \nabla + m + \gamma_\nu [v_{ext}^\nu(\mathbf{x}) + v_H^\nu(\mathbf{x}) + v_{xc}^\nu(\mathbf{x})] \right\} \varphi_k(\mathbf{x}) = \epsilon_k \varphi_k(\mathbf{x}) , \quad (9)$$

where the relativistic Hartree and xc-potentials are given by[§]

$$v_H^\nu(\mathbf{x}) = e^2 \int d^3y \frac{j^\nu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \quad ; \quad v_{xc}^\nu(\mathbf{x}) = \frac{\delta E_{xc}[j^\mu]}{\delta j_\nu(\mathbf{x})} \quad (10)$$

$$E_{xc}[j^\mu] = F[j^\mu] - T_s[j^\mu] - \frac{e^2}{2} \int d^3x \int d^3y \frac{j^\nu(\mathbf{x}) j_\nu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} . \quad (11)$$

This set of equations has to be solved selfconsistently, leading to the exact ground state four current and energy, in principle.

Due to the four component structure of the relativistic KS potential and in particular the selfconsistent treatment of radiative corrections Eqs.(3-10) are not very useful in practice. However, having in mind electronic structure calculations for atoms, molecules and solids with heavy constituents, two simplifications offer themselves:

- (i) If no external magnetic fields are present the four current version of RDFT (presented so far) can be reduced to a density-only variant: The complete proof of the existence theorem can be gone through using just the ground state density $j^0 = n$ as basic RDFT-variable [19], leading to the statement that E_{tot} for such systems can be written as a unique functional of n only,

$$E_{tot}[j^\mu] \xrightarrow{B \rightarrow 0} \tilde{E}_{tot}[n] .$$

This does not imply that the spatial components $\mathbf{j}(\mathbf{r})$ of the ground state four current vanish, but rather that they have to be interpreted as functionals of the density, $\mathbf{j}([n]; \mathbf{r})$. Correspondingly, the functional $\tilde{E}_{tot}[n]$ is not identical with $E_{tot}[j^0 = n, \mathbf{j} = \mathbf{0}]$, indicated by $\tilde{\cdot}$. For brevity, however, the $\tilde{\cdot}$ will be dropped from now on, as the density-only variant of RDFT will be used exclusively in the following.

- (ii) In addition, the selfconsistent treatment of vacuum corrections is not necessary in standard applications of RDFT: These contributions only lead to shifts in

[§]Note that in the relativistic Hartree term (last term of Eq.(11)) the retarded electron-electron interaction via the photon propagator of QED reduces to the static Coulomb interaction due to the time-independence of \mathbf{j} (compare [16]).

absolute ground state energies, but do not affect the physically relevant quantities like ionization potentials or dissociation energies. One can thus safely neglect j_V^μ , $T_{s,V}$ and the vacuum contributions to E_{xc} , at least on the selfconsistent level, thus enormously reducing the complexity of the KS-equations (3-10).

The subsequent discussion will be based on these two simplifications. The resulting electrostatic, no-sea KS-equations read

$$\left\{ -i\alpha \cdot \nabla + \beta m + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right\} \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (12)$$

where the Hartree and xc-potentials are now given by

$$v_H(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_H^T[n]}{\delta n(\mathbf{r})} \quad ; \quad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (13)$$

$$E_H^T = -\frac{e^2}{2} \int d^3r \int d^3r' \frac{\mathbf{j}(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (14)$$

$$n(\mathbf{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\mathbf{r}) \varphi_k(\mathbf{r}) \quad ; \quad \mathbf{j}(\mathbf{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\mathbf{r}) \alpha \varphi_k(\mathbf{r}) . \quad (15)$$

Note that the KS-current (15) of density-only RDFT in general is no longer identical with the exact current, leading to a corresponding redefinition of the transverse Hartree energy E_H^T .

In a final step one can isolate the two sources for relativistic corrections, i.e. the relativistic kinematics of the electrons and the photons, by decomposing the electron-electron interaction into a longitudinal (Coulomb) and a transverse (Breit + ...) component,

$$D_{\mu\nu}^0(x-y) = g_{\mu 0} g_{\nu 0} \delta(x^0 - y^0) \frac{e^2}{|\mathbf{x} - \mathbf{y}|} + D_{\mu\nu}^T(x-y) . \quad (16)$$

Here $D_{\mu\nu}^0$ represents the free photon propagator of QED, which mediates the electron-electron interaction, and $D_{\mu\nu}^T$ is its transverse part. Complete neglect of $D_{\mu\nu}^T$ leads to the longitudinal limit of RDFT, in which only the electrons are dealt with on the relativistic level. This limit of RDFT corresponds to the (no-pair) Dirac-Coulomb Hamiltonian in standard quantum chemistry. All photon retardation effects are contained in $D_{\mu\nu}^T$, whose inclusion leads to the RDFT equivalent of the Dirac-Coulomb-Breit (DCB) Hamiltonian (ignoring the fact that $D_{\mu\nu}^T$ agrees with the Breit interaction only to lowest order in $1/c^2$).

RELATIVISTIC OPTIMIZED-POTENTIAL-METHOD

In analogy to the nonrelativistic case [26, 27, 28] the exchange-only energy of RDFT is defined via the relativistic Fock term [29, 30, 31], using the KS-spinors [19, 16],

$$E_x[n] = -\frac{e^2}{2} \int d^3r \int d^3r' \sum_{-m < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\cos(\omega_{kl} |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \bar{\varphi}_k(\mathbf{r}) \gamma_\mu \varphi_l(\mathbf{r}) \bar{\varphi}_l(\mathbf{r}') \gamma^\mu \varphi_k(\mathbf{r}') , \quad (17)$$

where $\omega_{kl} = |\epsilon_k - \epsilon_l|$ and the φ_k have to be interpreted as functionals of n . In (17) we have used Feynman gauge for $D_{\mu\nu}^0$. The correlation energy is then simply given by

$$E_c[n] = E_{xc}[n] - E_x[n] , \quad (18)$$

with E_{xc} as in (11), taking into account the redefinition of \mathbf{j} , Eq.(15). In the longitudinal limit (17) reduces to the more familiar form [24, 19]

$$E_x^L[n] = -\frac{\epsilon^2}{2} \int d^3r \int d^3r' \sum_{-m < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\varphi_k^\dagger(\mathbf{r}) \varphi_l(\mathbf{r}) \varphi_l^\dagger(\mathbf{r}') \varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (19)$$

The difference between E_x and E_x^L is the transverse exchange energy, $E_x^T = E_x - E_x^L$.

The x-only potential corresponding to either (17) or (19) can not be evaluated by directly taking the functional derivative (13). To calculate this potential one uses the fact that there is a one-to-one correspondence between the ground state density and the total KS-potential v^{KS} . Consequently the minimization of $E_{tot}[n]$ with respect to $n(\mathbf{r})$ is equivalent to

$$\frac{\delta E_{tot}[n]}{\delta v^{KS}(\mathbf{r})} = 0 \quad (20)$$

together with a simultaneous solution of the KS-equations (12-15) (in order to establish the functional dependence between v^{KS} and n). Eq.(20) leads to the ROPM integral equation for the x-only potential v_x ,

$$\int d^3r' K(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') = Q(\mathbf{r}) \quad (21)$$

with

$$K(\mathbf{r}, \mathbf{r}') = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') + c.c. \quad (22)$$

$$Q(\mathbf{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \int d^3r' \varphi_k^\dagger(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \frac{\delta E_x[n]}{\delta \varphi_k^\dagger(\mathbf{r}')} + c.c. \quad (23)$$

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{l \neq k} \frac{\varphi_l(\mathbf{r}) \varphi_l^\dagger(\mathbf{r}')}{\epsilon_l - \epsilon_k}, \quad (24)$$

which has to be solved selfconsistently together with the KS-equations. Some remarks are appropriate:

- The ROPM integral equation determines v_x only up to a global constant, which, for finite systems, is fixed via $v_x(\mathbf{r}) \xrightarrow{|\mathbf{r}| \rightarrow \infty} 0$, in analogy to the nonrelativistic case.
- The ROPM allows to include the transverse exchange selfconsistently without introducing a gauge dependence. In contrast to the transverse RHF-potential the local, non-orbital-dependent x-only potential (21) does not produce gauge dependent spinors [25]. Thus all gauges for the photon propagator give the same exchange energy and potential, justifying the particular choice of Feynman gauge in (17).
- The ROPM procedure is by no means restricted to x-only functionals, as is obvious from the general form of its ingredients K and Q . It can also be used to deal with orbital-dependent correlation energy functionals, as e.g. the Colle-Salvetti functional [32, 33].
- As the current \mathbf{j} is a trivial functional of the φ_k , the previous statement particularly applies to \mathbf{j} -dependent functionals like E_H^T , thus establishing a transition from the four current to the density-only variant of (R)DFT.

Table 1. Longitudinal x-only ground state energies: Selfconsistent ROPM, RHF, RLDA and RGGA results for neutral atoms with closed subshells (in *hartree* [34]).

Atom	$-E_{tot}^L$	$E_{tot}^L - E_{tot}^{L,ROPM}$		
	ROPM	RHF	RLDA	RPW91
He	2.862	0.000	0.138	0.006
Be	14.575	-0.001	0.350	0.018
Ne	128.690	-0.002	1.062	-0.024
Mg	199.932	-0.003	1.376	-0.001
Ar	528.678	-0.005	2.341	0.041
Ca	679.704	-0.006	2.656	0.026
Zn	1794.598	-0.014	4.140	-0.262
Kr	2788.848	-0.013	5.565	-0.021
Sr	3178.067	-0.013	5.996	-0.008
Pd	5044.384	-0.016	7.707	-0.067
Cd	5593.299	-0.020	8.213	-0.033
Xe	7446.876	-0.019	9.800	0.085
Ba	8135.625	-0.019	10.289	0.059
Yb	14067.621	-0.048	13.272	-0.893
Hg	19648.826	-0.039	17.204	-0.250
Rn	23601.969	-0.035	19.677	0.004
Ra	25028.027	-0.034	20.460	-0.006

While the (R)OPM definition of exchange within (R)DFT has a number of conceptual advantages [35], its legitimacy finally relies on its success in practice. In Table 1 we list the x-only ground state energies E_{tot}^L obtained from selfconsistent ROPM calculations utilizing only the longitudinal Fock energy (19) for neutral atoms with closed subshells. Also given is the difference between these energies and the corresponding RHF values [36]. These differences explicitly demonstrate the somewhat more restricted variational freedom of the ROPM as compared to the RHF scheme with its nonlocal exchange potential. The absolute magnitude of the differences, however, is marginal. The ROPM thus explicitly demonstrates the ability of local (i.e. multiplicative) xc-potentials to capture the complete physics (at least on the x-only level).

Table 2 gives the corresponding comparison including the transverse exchange. However, while the ROPM data have been obtained from a selfconsistent calculation with transverse contributions, the RHF energies result from perturbatively adding the transverse exchange energies to the longitudinal RHF ground state energy. As a consequence the RHF energies are somewhat lower than the ROPM values for low Z where E_x^T is rather irrelevant. For heavy atoms, on the other hand, the variational treatment of E_x^T leads to a lowering of the energy which dominates over the energy differences resulting from the reduced variational freedom of the ROPM. From comparing selfconsistent and perturbative ROPM energies one extracts a selfconsistency effect of roughly $1eV$, which is also the size of many higher order QED contributions [37]. On the level of accuracy one tries to achieve in the spectroscopy of high- Z ions a selfconsistent treatment of the transverse exchange thus seems useful.

The numerical solution of the ROPM integral equation is rather involved, so that for applications to complex systems more efficient, but still accurate approximations are required. On the level of orbital-dependent potentials the KLI-approximation [38] can be extended to the relativistic domain [39]. On the other hand, the density functionals

Table 2. Total relativistic x-only ground state energies: Selfconsistent ROPM, RLDA and (R)GGA results for neutral atoms with closed subshells in comparison with perturbative RHF data (in *hartree* [34]).

Atom	$-E_{tot}^{L+T}$	$E_{tot}^{L+T} - E_{tot}^{L+T,ROPM}$			
	ROPM	RHF (p)	RLDA	RPW91	PW91
He	2.862	0.000	0.138	0.006	0.006
Be	14.575	-0.001	0.351	0.018	0.017
Ne	128.674	-0.002	1.080	-0.024	-0.043
Mg	199.900	-0.003	1.408	-0.001	-0.037
Ar	528.546	-0.005	2.458	0.041	-0.111
Ca	679.513	-0.006	2.818	0.026	-0.195
Zn	1793.840	-0.014	4.702	-0.263	-1.146
Kr	2787.429	-0.012	6.543	-0.022	-1.683
Sr	3176.359	-0.011	7.149	-0.010	-2.014
Pd	5041.098	-0.013	9.765	-0.069	-3.953
Cd	5589.496	-0.016	10.556	-0.035	-4.537
Xe	7441.173	-0.011	13.161	0.083	-6.705
Ba	8129.161	-0.009	14.051	0.058	-7.652
Yb	14053.750	-0.021	20.888	-0.894	-17.660
Hg	19626.705	0.008	29.161	-0.257	-27.253
Rn	23573.354	0.029	35.207	-0.009	-35.145
Ra	24996.946	0.038	37.395	-0.022	-38.267

most often used at present are GGAs, whose relativistic extension will be discussed in the following Section.

RELATIVISTIC GENERALIZED GRADIENT APPROXIMATION

The starting point for the derivation of RGGAs is the RLDA [14, 15, 19],

$$E_{xc}^{RLDA}[n] = \int d^3r e_{xc}^{RHEG}(n) = \int d^3r e_{xc}^{HEG}(n) \Phi_{xc,0}(\beta) . \quad (25)$$

In (25) the xc-energy density e_{xc}^{RHEG} of the relativistic homogeneous electron gas (HEG) has been decomposed into a product of its nonrelativistic limit e_{xc}^{HEG} and a relativistic correction factor $\Phi_{xc,0}$, whose density dependence is most conveniently written in terms of

$$\beta = \frac{(3\pi^2 n)^{1/3}}{m} . \quad (26)$$

In the case of the x-only RLDA $\Phi_{xc,0}$ e.g. reads

$$\Phi_{x,0}(\beta) = 1 - \frac{3}{2} \left[\frac{\sqrt{1+\beta^2}}{\beta} - \frac{\text{Arsh}(\beta)}{\beta^2} \right] \stackrel{\beta \ll 1}{\approx} 1 - \frac{2}{3}\beta^2 + \dots , \quad (27)$$

which can be further decomposed into a longitudinal and a transverse part using (16) (for details see [18, 16]).

The RLDA forms the basis for RGGAs, which take into account the inhomogeneity of the system via the most simple resummed form of the straightforward gradient

expansion (GEA). In the case of the x-only energy the 'general' form[¶] of the RGGA is

$$E_x^{RGGA}[n] = \int d^3r e_x^{HEG}(n) \left[\Phi_{x,0}(\beta) + g(\xi)\Phi_{x,2}(\beta) \right], \quad (28)$$

where $\xi = [\nabla n / (2(3\pi^2 n)^{1/3})]^2$ is the dimensionless characteristic density gradient and $g(\xi)$ represents a nonrelativistic gradient correction in the form of a GGA. The β -dependence of $\Phi_{x,2}$ can, in principle, be obtained from the weakly inhomogeneous limit, in which the RGGA should approach the relativistic GEA,

$$E_x^{RGGA}[n] \stackrel{\xi \ll 1}{\approx} E_x^{RGEA}[n] = \int d^3r e_x^{HEG}(n) \left[\Phi_{x,0}(\beta) + \frac{10}{81}\xi\Phi_{x,2}(\beta) + \dots \right]. \quad (29)$$

The ingredients of the RGEA, on the other hand, are determined by the long-wavelength expansion of the first order static irreducible current-current response function of the RHEG, $\Pi_{\mu\nu}^{(1)}(q^0 = 0, |\mathbf{q}|)$, which, however, is not available in the literature. Moreover, at present it is not clear whether the RGEA (29) exists at all, as a calculation of $\Phi_{x,2}$ using the Kirznits technique^{||} leads to an infrared divergent $\Phi_{x,2}$ [40]. While the Kirznits gradient expansion gives an incorrect (but finite) gradient coefficient for the nonrelativistic $E_x[n]$ [41] and thus does not allow a definitive conclusion concerning the RGEA, the form of the infrared divergence nevertheless indicates a logarithmic $|\mathbf{q}|$ -dependence of $\Pi_{00}^{(1)}$,

$$\Pi_{00}^{(1)}(q^0 = 0, |\mathbf{q}|) \stackrel{|\mathbf{q}| \ll 2k_F}{\approx} a + b \mathbf{q}^2 + c \mathbf{q}^2 \ln(|\mathbf{q}|/k_F) + \dots \quad (30)$$

Unfortunately, the complete \mathbf{q} -dependence of $\Pi_{00}^{(1)}$ is rather difficult to evaluate (compare [42, 43, 44, 45]), prohibiting an immediate verification of (30).

In this situation it seems legitimate to take a pragmatic point of view and construct a semiempirical RGGA [21], following the approach of Becke [8]. In the present context this means

- (i) choose a suitable $g(\xi)$ and keep it fixed in the following (both the B88 [8] and the PW91 [10] GGA have been considered, explicit results are given for the latter)
- (ii) make a sufficiently flexible ansatz for $\Phi_{x,2}(\beta)$, using the fact that due to time reversal invariance $\Phi_{x,2}$ must be an even function of β (here a [2/2]-Padé approximant has been used),

$$\Phi_{x,2}(\beta) = \frac{1 + a_1\beta^2 + a_2\beta^4}{1 + b_1\beta^2 + b_2\beta^4}. \quad (31)$$

Note that the ultrarelativistic limit of very large β is not relevant in practice as even for the heaviest atoms $\beta \leq 10$.

- (iii) fit the parameters in the ansatz to the exact relativistic correction

$$\Delta E_x = E_x^R - E_x^{NR} \quad (32)$$

in the x-only energies of closed subshell atoms, obtained from ROPM calculations (in the case of the PW91-GGA this leads to $a_1 = 2.2156$, $a_2 = 0.66967$, $b_1 = 1.3267$, $b_2 = 0.79420$ for the longitudinal part of the functional and $a_1 = 3.5122$, $a_2 = 0.62525$, $b_1 = 1.3313$, $b_2 = 0.10066$ for its transverse part — compare [25]).

[¶](28) is not the most general form of the RGGA, in that only one single relativistic correction factor is used for the complete gradient contribution, involving arbitrary powers of ξ . However, in the relativistic high-density regime $g(\xi)$ is usually dominated by the lowest order in ξ (apart from the physically irrelevant immediate vicinity of the nucleus).

^{||}The Kirznits commutator expansion is a real space version of the GEA which, in the case of $E_x[n]$, requires a regularization scheme in order to deal with the long range of the Coulomb interaction.

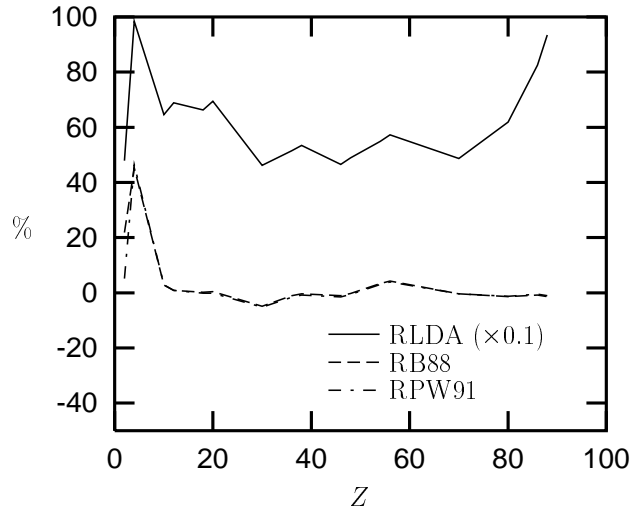


Figure 1. Relativistic contribution ΔE_x to the x-only energy: Percentage deviation of selfconsistent RLDA and RGGAs results from ROPM-data for neutral atoms.

The longitudinal and complete relativistic x-only ground state energies obtained with this RGGAs are listed in Tables 1,2 in comparison with the ROPM and RLDA values. In both cases the RGGAs reduce the error of the RLDA with respect to the ROPM standard by roughly two orders of magnitude. While the improvement is smaller for more subtle quantities than total ground state energies [21], it always remains substantial. Also given in Table 2 are the x-only energies obtained with the nonrelativistic PW91-GGA used in the relativistic KS-equations, demonstrating the necessity to introduce relativistic correction factors: In fact, in the relativistic regime of heavy atoms the nonrelativistic PW91-GGA overbinds as much as the RLDA underbinds.

The errors in the x-only ground state energies are directly related to the accuracy of the RGGAs exchange energies. In Fig.1 we plot the percentage deviation** of the RLDA and two RGGAs for the total relativistic correction ΔE_x , Eq.(32). As is obvious from Fig.1 the RGGAs reproduce ΔE_x as accurately as the total exchange energies, while the RLDA misrepresents ΔE_x by a factor of 5-10 (note the reduced scale for the RLDA). Fig.1 also demonstrates that the RGGAs concept is independent of its nonrelativistic basis, as the two GGAs considered give essentially identical values for ΔE_x .

The availability of the exact x-only potential via ROPM calculations allows to analyze the RGGAs also on a more microscopic level. In Fig.2 we show the percentage relativistic contribution to the longitudinal x-only potential,

$$\Delta v_x^L(r) = [v_x^L(r) - v_x^{NR}(r)]/v_x^{NR\text{OPM}}(r) , \quad (33)$$

for both the RLDA and the PW91-RGGAs in comparison with the OPM standard, using neutral Hg as a prototype for all atoms. A number of features are obvious from Fig.2:

- Δv_x^L reflects the contraction of *s*- and *p*-shells when going from a nonrelativistic to a relativistic treatment.
- Δv_x^L is of the order of 5-10% even for the outermost shells. This is the microscopic analogue of the shift of the 6*s*-eigenvalue from the nonrelativistic OPM value of -0.262 hartree to the ROPM result of -0.329 hartree .

**Neutral Mercury may serve as an example for the absolute size of ΔE_x : Its exact nonrelativistic E_x^{NR} is -345.24 hartree compared with a ΔE_x of $+2.61 \text{ hartree}$ [34]. Note, however, that the latter value results from a subtle cancellation of the relativistic contribution to E_x^L and E_x^T (for Hg $E_x^L - E_x^{NR} = -19.44 \text{ hartree}$ and $E_x^T = 22.05 \text{ hartree}$). As these two components have a different physical origin their size is more characteristic of the overall importance of relativistic corrections.

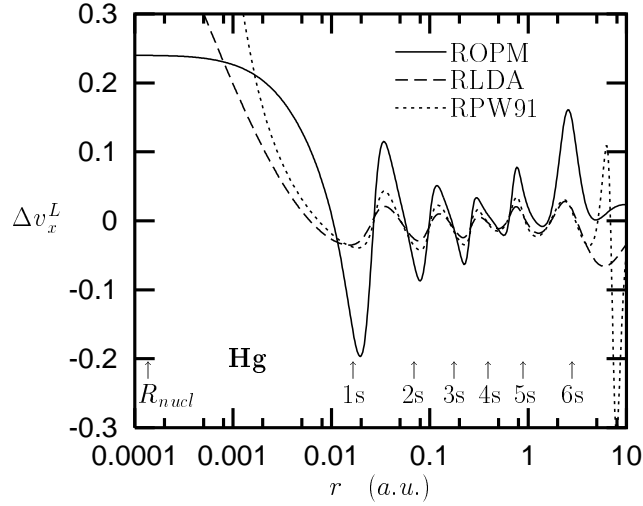


Figure 2. Relativistic contribution to the longitudinal x-only potential: Δv_x^L from selfconsistent ROPM, RLDA and RGGG calculations for neutral Hg.

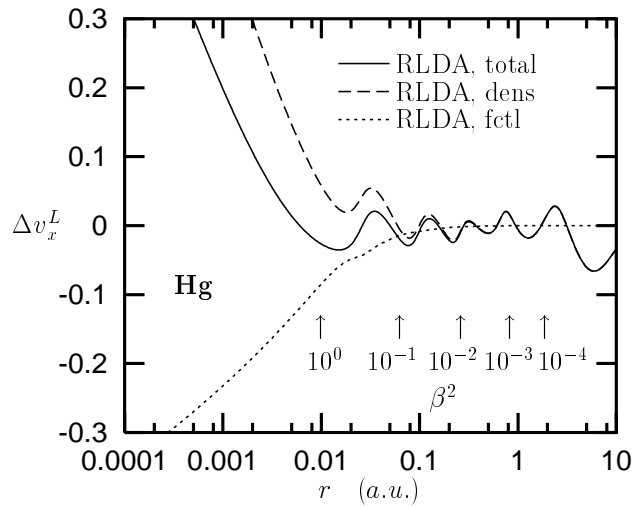


Figure 3. Decomposition of Δv_x^L into density (dens) and functional (fctl) contribution: RLDA-results for neutral Hg.

- Both approximate functionals are 'in phase' with the ROPM oscillations, but the amplitude of the RGGG oscillations is larger. However, the improvement that the RGGG offers for Δv_x^L is by far not as impressive as that for ΔE_x .
- The RLDA and the RGGG both deviate substantially from the ROPM for very small r . However, the immediate vicinity of the nucleus is physically irrelevant as both approximations give x-only potentials which in this regime are small compared with the nuclear potential.

In Fig.3 we have split Δv_x^L into the contribution resulting from the difference between the selfconsistent relativistic density n^R and its nonrelativistic counterpart n^{NR} for fixed (nonrelativistic) functional, $\Delta v_x^L(dens) = (v_x^{NR}[n^R] - v_x^{NR}[n^{NR}])/v_x^{NRROPM}$, and the contribution resulting from the relativistic modification of the functional for fixed density, $\Delta v_x^L(fctl) = (v_x^L[n^R] - v_x^{NR}[n^R])/v_x^{NRROPM}$. The latter quantity directly illustrates the r -regime in which the relativistic correction factors deviate from 1.

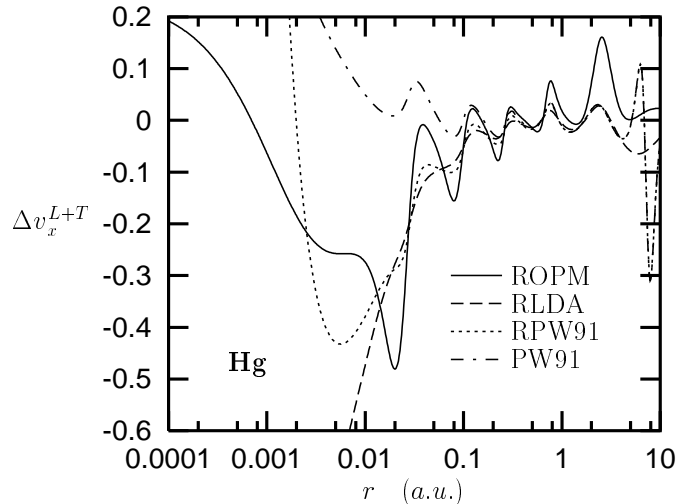


Figure 4. Complete relativistic contribution to the x-only potential: Δv_x^{L+T} from selfconsistent ROPM, RLDA, RGGA and GGA calculations for neutral Hg.

$\Delta v_x^L(dens)$, on the other hand, shows that the oscillatory structure in Δv_x^L is also present if a nonrelativistic xc-functional is used in the relativistic KS-equations, i.e. that the oscillations are completely due to the relativistic treatment of $T_s[n]$, which dominates the difference between n^R and n^{NR} .

Finally, Fig.4 displays the complete relativistic contribution to the x-only potential, $\Delta v_x^{L+T} = (v_x^L + v_x^T - v_x^{NR})/v_x^{NROPM}$. As is obvious from a comparison with Fig.2 v_x^T contributes substantially for the innermost shells. In fact, v_x^T and the relativistic contribution to v_x^L do not cancel to the extent observed for the x-only energy, with v_x^T dominating over $v_x^L - v_x^{NR}$. Moreover, while the RGGA roughly mimics the ROPM in the relevant regime, the nonrelativistic GGA fails completely. The same picture emerges from the corresponding eigenvalues listed in Table 3. However, more important than the eigenvalues of the innermost shells are those for the outermost orbitals. In this respect one finds that the relativistic corrections to $E_x[n]$ shift e.g. the $5p$ -eigenvalues of Hg by 12 *hartree* compared with 38 *hartree* resulting from the inclusion of the nonrelativistic correlation potential. Only the $5d$ - and $6s$ -orbitals remain unaffected. Moreover, in contrast to the correlation potential the relativistic corrections to $E_x[n]$ do not shift all eigenvalues into the same direction: While f -orbitals are stabilized, s -, p - and most d -eigenvalues become less attractive.

Given the semiempirical approach to the x-only RGGA and the involved structure of the relevant diagrammatic contributions to $\Pi_{\mu\nu}$, a first principles derivation of an RGGA for the correlation energy seems out of question. In fact, even the RLDA for $E_c[n]$ is not completely known: In contrast to the RPA diagrams [17], the second order exchange graphs, a contribution to E_c required for the relativistic regime [16], have not been evaluated beyond the ultrarelativistic limit [46]. In addition, some nonrelativistic GGAs for $E_c[n]$ [9] are not even based on the LDA. Fortunately, the relativistic corrections to E_c are quantitatively much smaller than their x-only counterparts [19], so that a more crude treatment might be sufficient. We have thus introduced only one overall correction factor for the complete correlation GGA,

$$E_c^{RGGA}[n] = \int d^3r e_c^{GGA}(n, (\nabla n)^2, \dots) \Phi_c(\beta) , \quad (34)$$

using a fixed nonrelativistic form for e_c^{GGA} (both the LYP [9] and the PW91 [10] GGA have been considered). The parameters of the [2/2]-Padé ansatz for $\Phi_c(\beta)$ (analogous

Table 3. Single particle energies ($-\epsilon_{nlj}$) for neutral Mercury from ROPM and RLDA calculations in comparison with PW91 results, based on its relativistic x-only (R-x) as well as its nonrelativistic x-only (NR-x) and xc (NR-(x+c)) form (in *hartree* [34]).

Level	OPM	LDA	PW91		
	R-x	R-x	R-x	NR-x	NR-(x+c)
1S1/2	3036.871	3027.914	3036.466	3050.287	3050.287
2S1/2	538.444	536.824	538.052	540.181	540.209
2P1/2	516.198	515.615	516.110	518.473	518.498
2P3/2	445.422	445.025	445.285	446.880	446.907
3S1/2	127.956	127.397	127.704	128.137	128.180
3P1/2	117.994	117.736	117.861	118.315	118.357
3P3/2	102.302	102.084	102.155	102.459	102.500
3D3/2	86.069	85.934	85.962	86.123	86.163
3D5/2	82.692	82.559	82.585	82.725	82.765
4S1/2	28.361	27.931	28.037	28.130	28.179
4P1/2	24.090	23.770	23.820	23.912	23.959
4P3/2	20.321	19.980	20.025	20.082	20.129
4D3/2	13.397	13.133	13.152	13.170	13.215
4D5/2	12.689	12.423	12.442	12.456	12.501
4F5/2	3.766	3.571	3.574	3.561	3.604
4F7/2	3.613	3.417	3.420	3.407	3.450
5S1/2	4.394	4.267	4.281	4.295	4.333
5P1/2	3.004	2.885	2.889	2.901	2.939
5P3/2	2.360	2.213	2.221	2.227	2.267
5D3/2	0.507	0.364	0.369	0.369	0.406
5D5/2	0.440	0.297	0.302	0.301	0.339
6S1/2	0.330	0.220	0.224	0.225	0.253

to (31)) have been fitted to the DCB second order perturbation theory (MBPT2) correlation energies for the Ne isoelectronic series [5], which seems to be the most systematic set of quantum chemical E_c available to date^{††} (Note that on the present level of sophistication the small difference between the exact RDFT correlation energy and the corresponding quantum chemical energy, originating from the KS treatment of the kinetic energy, is irrelevant). In addition, $\Phi_c(\beta)$ has been fitted to the relativistic correction to E_c ,

$$\Delta E_c = E_c^R - E_c^{NR} , \quad (35)$$

rather than the total E_c^R , in order to suppress errors in the individual values of E_c^R and E_c^{NR} as much as possible (for PW91 the resulting parameters are $a_1 = 1.9407$, $a_2 = 0.14435$, $b_1 = 0.28142$ and $b_2 = 0.004723$ — the longitudinal and the transverse part of the functional have not been fitted individually).

The success of this very simple approach can be seen from Fig.5, where ΔE_c is plotted for the Ne isoelectronic series^{††}. Again both RGGAs give very similar results for ΔE_c , in spite of their rather different nonrelativistic form. Compared with the RLDA the RGGAs improve the accuracy of ΔE_c by more than one order of magnitude. The situation is not as clear for the few quantum chemical results for ΔE_c , which have not been included in the fitting procedure. E.g. for neutral Xe the RGGGA gives a ΔE_c

^{††}Only selected systems have been considered within the framework of relativistic CI calculations (see e.g.[4]). For a fit of $\Phi_c(\beta)$, however, a series of E_c covering the complete Z -range is required.

^{‡‡}The nonrelativistic E_c^{NR} of -5.086 *hartree* (MBPT2) for neutral Mercury and the corresponding ΔE_c of -0.486 *hartree* may serve as an indication of the absolute size of the relativistic corrections.

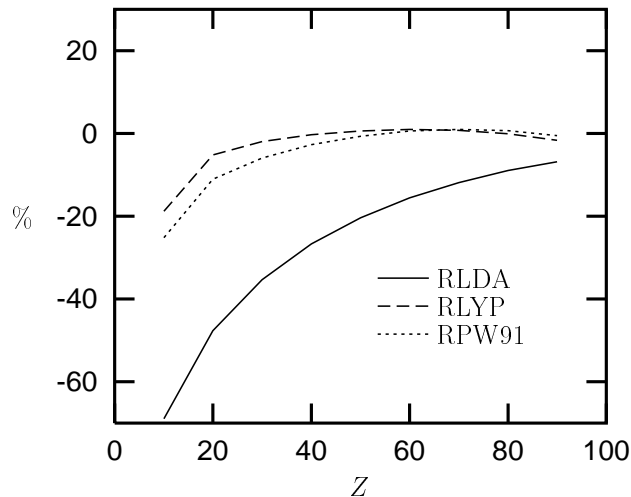


Figure 5. Relativistic correction ΔE_c to the correlation energy: Percentage deviation of self-consistent RLDA- and RGGA-results from MBPT2-data for Ne isoelectronic series.

of 145 *hartree*, compared with the RLDA result of 80 *hartree*, the DCB-MBPT2 energy of 146 *hartree* [5] and the DCB-Coupled-Cluster value of 103 *hartree* [47]. While the RGGA agrees very well with the quantum chemical E_c on the MBPT2 level, to which it has been fitted, the discrepancy between the MBPT2 and the Coupled-Cluster E_c is quite substantial, illustrating the uncertainty in the reference data used to construct Φ_c . Clearly, as soon as more accurate systematic data for ΔE_c become available, the fit should be adjusted.

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REFERENCES

1. *The Effects of Relativity in Atoms, Molecules and the Solid State*, ed. by S. Wilson, I. P. Grant and B. L. Gyorffy (Plenum, New York, 1991).
2. S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, *Phys. Rev. A* **37**, 3768 (1989).
3. E. Ilyabaev and U. Kaldor, *Chem. Phys. Lett.* **194**, 95 (1992).
4. E. Eliav, U. Kaldor, and Y. Ishikawa, *Phys. Rev. A* **49**, 1724 (1994).
5. Y. Ishikawa and K. Koc, *Phys. Rev. A* **50**, 4733 (1994).
6. U. Kaldor and B. A. Heß, *Chem. Phys. Lett.* **230**, 1 (1994).
7. A. Pizlo, G. Jansen, B. A. Heß, and W. von Niessen, *J. Chem. Phys.* **98**, 3945 (1993).
8. A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
9. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
10. J. P. Perdew, in *Electronic Structure of Solids 1991*, ed. by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
11. A. D. Becke, *J. Chem. Phys.* **96**, 2155 (1992).
12. B. G. Johnson, P. M. W. Gill, and J. A. Pople, *J. Chem. Phys.* **98**, 5612 (1993).
13. A. K. Rajagopal and J. Callaway, *Phys. Rev. B* **7**, 1912 (1973).
14. A. K. Rajagopal, *J. Phys. C* **11**, L943 (1978).
15. A. H. MacDonald and S. H. Vosko, *J. Phys. C* **12**, 2977 (1979).
16. E. Engel and R. M. Dreizler, in: *Density Functional Theory II*, ed. by R. F. Nalewajski, Topics in Current Chemistry, Vol. 181 (Springer, Berlin, 1996), p.1.
17. M. V. Ramana and A. K. Rajagopal, *Phys. Rev. A* **24**, 1689 (1981).
18. M. V. Ramana, A. K. Rajagopal, and W. R. Johnson, *Phys. Rev. A* **25**, 96 (1982).

19. E. Engel, S. Keller, A. Facco Bonetti, H. Müller, and R. M. Dreizler, Phys. Rev. A **52**, 2750 (1995).
20. S. Varga, W.-D. Sepp, B. Fricke, E. Engel and R. M. Dreizler, unpublished.
21. E. Engel, S. Keller, and R. M. Dreizler, Phys. Rev. A **53**, 1367 (1996).
22. R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).
23. J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
24. B. A. Shadwick, J. D. Talman, and M. R. Norman, Comp. Phys. Commun. **54**, 95 (1989).
25. E. Engel, S. Keller, and R. M. Dreizler, unpublished.
26. V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).
27. D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).
28. L. J. Sham, Phys. Rev. B **32**, 3876 (1985).
29. I. P. Grant, Proc. Roy. Soc. (London) **A262**, 555 (1961).
30. Y.-K. Kim, Phys. Rev. **154**, 17 (1967).
31. J. B. Mann and W. R. Johnson, Phys. Rev. A **4**, 41 (1971).
32. R. Colle and O. Salvetti, Theoret. Chim. Acta (Berl.) **37**, 329 (1975).
33. T. Grabo and E. K. U. Gross, Chem. Phys. Lett. **240**, 141 (1995).
34. In all our calculations the nuclei were represented by uniformly charged spheres with nuclear radii given by $R_{nuc} = 1.0793 A^{1/3} + 0.73587 fm$, A being the atomic mass (weighted by isotopic abundances) taken from Table III.7 of K. Hisaka, et al. (Particle Data Group), Phys. Rev. D **45**, Number 11, Part II (1992), unless explicitly stated otherwise. The speed of light had been set to $c = 137.0359895$.
35. M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
36. K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer, Comp. Phys. Commun. **55**, 425 (1989).
37. I. Lindgren, H. Persson, S. Salomonson, P. Sunnergren, to be pub. in "Proc. of the 15th Int. Conf. on Atomic Physics, Amsterdam, 5-9 August 1996" (World Scientific, Singapore).
38. J. B. Krieger, Y. Li and G. J. Iafrate, Phys. Lett. **146 A**, 256 (1990).
39. T. Kreibich, E. K. U. Gross, and E. Engel, unpublished.
40. E. Engel, diploma thesis (1983).
41. E. K. U. Gross and R. M. Dreizler, Z. Phys. A **302**, 103 (1981).
42. P. R. Antoniewicz and L. Kleinman, Phys. Rev. B **31**, 6779 (1985).
43. L. Kleinman and S. Lee, Phys. Rev. B **37**, 4634 (1988).
44. J. A. Chevary and S. H. Vosko, Phys. Rev. B **42**, 5320 (1990).
45. E. Engel and S. H. Vosko, Phys. Rev. B **42**, 4940 (1990); Phys. Rev. B **44**, 1446(E) (1991).
46. B. A. Freedman and L. D. McLerran, Phys. Rev. D **16**, 1130, 1147, 1169 (1977).
47. E. Eliav, U. Kaldor, and Y. Ishikawa, Int. J. Quantum Chem. **28S**, 205 (1994).