

## Relativistic exchange-correlation energy functional: Gauge dependence of the no-pair correlation energy

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We analyze the gauge dependence of the relativistic electron gas correlation energy  $E_c$  resulting from the no-pair approximation. In particular, we evaluate the relativistic no-pair Lindhard function as the basic ingredient of the random-phase approximation (RPA) for  $E_c$ . The resulting gauge-dependent no-pair RPA is compared with a gauge-invariant counterpart. The implications for relativistic density functionals are examined by applying the local-density approximation based on each of these forms of  $E_c$  to atoms. It is found that the gauge dependence of  $E_c$  is irrelevant on the overall level of accuracy obtained with present density functionals. [S1050-2947(98)07207-2]

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### I. INTRODUCTION AND SUMMARY OF RESULTS

The extension of nonrelativistic many-body methods to the relativistic domain leads to the question how to deal with the negative-energy continuum states. Sucher [1] has pointed out in the context of the relativistic Hartree-Fock (RHF) approximation that these states must be projected out in order to obtain variationally stable bound-state solutions, thereby defining the *no-(virtual)-pair* approximation. It is well known that this projection leads to gauge-dependent results for the exchange-correlation (xc) energy if the complete relativistic electron-electron interaction is taken into account. While for conventional many-body methods this gauge dependence has recently been analyzed in great detail for heliumlike ions [2–5], it has to date not been addressed in the framework of relativistic density-functional theory (DFT) [6,7]. However, the more refined DFT methods, like the generalized gradient approximation (GGA) [8–10] and the optimized potential method (OPM) [11,12], are now approaching quantum chemical accuracy [13–15]. For applications to high- $Z$  atoms these techniques have recently been extended to include relativistic corrections [16–18], so that the question arises to what extent the resulting xc energies depend on the gauge chosen for the electron-electron interaction, i.e., the photon propagator.

In addition to the no-pair approximation there exists a second possible source of gauge dependence: Transition matrix elements or Feynman diagrams may become gauge dependent if they are evaluated with single-particle orbitals that experience a nonlocal potential (as, e.g., in the RHF scheme). However, due to the multiplicative nature of the DFT single-particle potential this second source of gauge dependence is not present in DFT calculations, as discussed in detail elsewhere [19] (note that gauge-invariant transition matrix elements can also be obtained with RHF orbitals if a suitable resummation of the perturbation series is used [20–

22]). In particular, it has been shown for the relativistic exchange energy  $E_x$  that, in contrast to the RHF scheme [2], the exact DFT treatment of the no-pair exchange via the relativistic OPM ensures gauge invariance even if the full transverse interaction is used self-consistently [19]. On the other hand, explicit approximations for the relativistic DFT correlation energy  $E_c$  are not gauge invariant when the no-pair approximation is used in their derivation [19]. As an analysis of the importance of gauge effects for  $E_c$  we here discuss the no-pair approximation for the relativistic local-density approximation (RLDA) [16,23–25]. The RLDA plays a central role as it is the most simple approximation for  $E_c$  and serves as basis for the construction of more accurate density functionals such as relativistic GGAs [18]. It is thus well suited for this study.

In the RLDA the local xc energy density of the inhomogeneous system of interest is approximated by the xc energy density  $e_{xc}^{\text{RHEG}}$  of a relativistic homogeneous electron gas (RHEG) with given local density. Our discussion thus starts with a brief review of the random-phase approximation (RPA) for  $e_{xc}^{\text{RHEG}}$ , which gives the main contribution to  $e_{xc}^{\text{RHEG}}$  in the high-density limit relevant for the present purpose. In particular, we contrast the usual no-pair approximation with the gauge-invariant *no-sea* approximation. While in the former the negative-energy continuum states are projected out completely, only the vacuum QED limit of each individual fermion loop in a given energy diagram is omitted in the no-sea approximation [25,26,7]. Until today, in the context of the RLDA, the no-sea approximation has been used exclusively. On the other hand, the no-pair approximation represents the standard in conventional quantum chemical methods [27–30]. Any previous comparison of RLDA and quantum chemical results (as in [16]) has ignored this difference. This study of the no-pair RLDA therefore also provides an estimate for the accompanying uncertainty.

The basic ingredient of the RPA is the noninteracting current-current response function  $\chi_0^{\mu\nu}$ , i.e., the relativistic Lindhard function [31–33]. We thus evaluate  $\chi_0^{\mu\nu}$  within the no-pair approximation and use the result to calculate the no-pair RPA for  $e_c^{\text{RHEG}}$  (in Sec. II). The differences between the no-sea and the no-pair results for  $e_c^{\text{RHEG}}$  are discussed in Sec. III. It is shown that these differences are comparatively small in the density range relevant for atoms (see Sec. III A). The importance of higher-order retardation effects is studied by a comparison of results obtained with the full transverse interaction and those found with its weakly relativistic limit, the Breit approximation. The differences again turn out to be rather small in the interesting density range. In Sec. III B the consequences for electronic structure calculations for atoms are discussed. Here the neon isoelectronic series serves as a basis, as it is the most systematic set of atomic systems beyond heliumlike or lithiumlike ions for which reference data are available [28]. While the absolute size of the gauge effects is shown to increase with  $Z$ , the percentage deviation is largest for light atoms, indicating that the gauge dependence is already present in the lowest-order weakly relativistic correction (compare [2]). On the other hand, the differences between the various gauges are marginal compared with the overall error of the RLDA with respect to relativistic second-order many-body perturbation theory (RMBPT2) [28].

This demonstrates that the failure of the RLDA to accurately reproduce the relativistic contribution to atomic  $E_c$  does not originate from the different treatment of negative-energy states and photon retardation effects in the no-sea RLDA and the RMBPT2 reference data, thus supporting the conclusions in [16]. To complete the analysis of [16] the role of the so-called second-order exchange graphs, which have only been included on the nonrelativistic level in this study, remains to be investigated. Unfortunately, the complete density dependence of these contributions to the RHEG is not known. From the high-density limit [34], however, the second-order exchange graphs are expected to give roughly 40% of the RPA. These contributions should thus not affect the principal conclusions drawn on basis of the RPA.

In view of the overall accuracy of the RLDA for atoms the results presented here should only be understood as an order of magnitude estimate of the gauge dependence inherent in more accurate many-body schemes, both in the quantum chemical framework and in DFT. Nevertheless, this estimate suggests that the error introduced by the no-pair approximation is smaller than the differences between the various many-body techniques, e.g., between RMBPT2 and the relativistic coupled-cluster approach [29]. In particular, the accuracy of the more refined DFT approximations for  $E_c$  (as GGAs [9,10]) has not yet reached the level on which a gauge dependence would be relevant.

## II. THEORY

The starting point of our discussion is the representation of the xc energy density  $e_{xc}$  of the RHEG via a coupling constant integral [7,25,31,33] ( $\hbar = c = 1$ )

$$e_{xc}^{\text{RHEG}} = \frac{i}{2} \int_0^1 ds \int \frac{d^4q}{(2\pi)^4} D_{\mu\nu}^0(q) [\chi_s^{\mu\nu}(q) - \chi_{v,s}^{\mu\nu}(q)]. \quad (1)$$

Here  $\chi_s^{\mu\nu}$  represents the time-ordered current-current response function of the RHEG [35]. The subscript  $s$  indicates that the coupling constant  $e^2$  is scaled by  $s$ .  $\chi_{v,s}^{\mu\nu}$  is the vacuum QED limit of  $\chi_s^{\mu\nu}$ . Finally,  $D_{\mu\nu}^0$  denotes the free photon propagator of QED, for which various gauges are in use. In the covariant gauge one has [36]

$$D_{\mu\nu}^0(q) = D(q^2) \left( g_{\mu\nu} - \frac{\lambda - 1}{\lambda} \frac{q_\mu q_\nu}{q^2} \right), \quad (2)$$

with

$$D(q^2) = \frac{-4\pi e^2}{q^2 + i\epsilon}, \quad (3)$$

where the gauge parameter  $\lambda$  represents an additional degree of freedom. In practice, however, only the two choices  $\lambda = 1$  [Feynman gauge (FG)] and  $\lambda = \infty$  [Landau gauge, (LG)] are relevant. Alternatively, in the Coulomb gauge (CG) the photon propagator reads

$$D_{\mu\nu}^{0,\text{CG}}(q) = \begin{pmatrix} D(-q^2) & 0 \\ 0 & D(q^2) \left( g_{ij} + \frac{q_i q_j}{q^2} \right) \end{pmatrix}. \quad (4)$$

Often the weakly relativistic limit of Eq. (4), the Coulomb-Breit (CGB) interaction [37], is utilized,

$$D_{\mu\nu}^{0,\text{CGB}}(q) = D(-q^2) \begin{pmatrix} 1 & 0 \\ 0 & g_{ij} + \frac{q_i q_j}{q^2} \end{pmatrix}, \quad (5)$$

which includes transverse (retardation and magnetic) effects to lowest order in  $1/c$ .

To date, the response function of the RHEG has only been evaluated in the RPA [25,31], defined by the Dyson equation

$$\chi_{\text{RPA}}^{\mu\nu}(q) = \chi_0^{\mu\nu}(q) + \chi_0^{\mu\rho}(q) D_{\rho\kappa}^0(q) \chi_{\text{RPA}}^{\kappa\nu}(q), \quad (6)$$

where  $\chi_0^{\mu\nu}$  represents the noninteracting limit of  $\chi^{\mu\nu}$ , i.e., the relativistic Lindhard function,

$$\chi_0^{\mu\nu}(q) = -i \int \frac{d^4p}{(2\pi)^4} \text{tr} \{ \gamma^\mu G^0(p) \gamma^\nu G^0(p+q) \}. \quad (7)$$

Here  $G^0$  is the electron propagator of the noninteracting RHEG, which may be decomposed in two different ways,

$$G^0(p) = G_V^0(p) + G_D^0(p) \quad (8)$$

$$= G_+^0(p) + G_-^0(p), \quad (9)$$

$$G_V^0(p) = \frac{\not{p} + m}{p^2 - m^2 + i\epsilon}, \quad (10)$$

$$G_D^0(p) = 2\pi i \delta(p^0 - E_p) \frac{\not{p} + m}{2E_p} \Theta(k_F - |p|), \quad (11)$$

$$G_+^0(p) = \frac{\not{p}_+ + m}{2E_p} \left[ \frac{\Theta(|\mathbf{p}| - k_F)}{p^0 - E_p + i\epsilon} + \frac{\Theta(k_F - |\mathbf{p}|)}{p^0 - E_p - i\epsilon} \right], \quad (12)$$

$$G_-^0(p) = \frac{\not{p}_- + m}{2E_p} \frac{-1}{p^0 + E_p - i\epsilon}, \quad (13)$$

where  $E_p = (\mathbf{p}^2 + m^2)^{1/2}$ ,  $p_\pm^\mu = (\pm E_p, \mathbf{p}^i)$ , and  $k_F = (3\pi^2 n)^{1/3}$ ,  $n$  being the density of the RHEG. In Eq. (8) the vacuum QED propagator  $G_V^0$  has been extracted from  $G^0$ , leaving a remainder  $G_D^0$ , in which the occupied gas states are isolated. On the other hand, in Eq. (9) the contributions of the positive- ( $G_+^0$ ) and negative- ( $G_-^0$ ) energy states have been separated. In the nonrelativistic limit  $G_+^0$  approaches the standard nonrelativistic electron gas propagator.

These two different decompositions of  $G^0$  form the basis for the no-pair and no-sea approximations. In the former all negative-energy states are projected out [1]. On the propagator level this corresponds to replacing  $G^0$  by  $G_+^0$ , so that the noninteracting response function reduces to

$$\chi_{0,\text{np}}^{\mu\nu}(q) = -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \{ \gamma^\mu G_+^0(p) \gamma^\nu G_+^0(p+q) \}. \quad (14)$$

Evaluating Eq. (14) one finds for the tensor structure of  $\chi_{0,\text{np}}^{\mu\nu}$ ,

$$\chi_{0,\text{np}}^{\mu\nu} = P_L^{\mu\nu} \chi_{\text{np}}^L - P_T^{\mu\nu} \chi_{\text{np}}^T + \bar{P}_T^{\mu\nu} \bar{\chi}_{\text{np}}^T, \quad (15)$$

where

$$P_L^{\mu\nu} = \frac{-1}{q^2 q^2} \begin{pmatrix} \mathbf{q}^4 & \mathbf{q}^2 q^0 q^i \\ \mathbf{q}^2 q^0 q^j & (q^0)^2 q^i q^j \end{pmatrix}, \quad (16)$$

$$P_T^{\mu\nu} = \frac{1}{q^2} \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{q}^2 g^{ij} + q^i q^j \end{pmatrix}, \quad (17)$$

$$\bar{P}_T^{\mu\nu} = \frac{1}{q^2} \begin{pmatrix} 0 & 0 \\ 0 & q^i q^j \end{pmatrix}. \quad (18)$$

The explicit forms for  $\chi_{\text{np}}^{L,T}$  and  $\bar{\chi}_{\text{np}}^T$  are listed in the Appendix.

The no-sea approximation [25,26], on the other hand, is defined as

$$\chi_{0,\text{ns}}^{\mu\nu} = \chi_0^{\mu\nu} - \chi_{0,V}^{\mu\nu}, \quad (19)$$

which is easily evaluated using the decomposition (8). In contrast to Eq. (15),  $\chi_{0,\text{ns}}^{\mu\nu}$  has only two independent tensorial components

$$\chi_{0,\text{ns}}^{\mu\nu} = P_L^{\mu\nu} \chi_{\text{ns}}^L - P_T^{\mu\nu} \chi_{\text{ns}}^T. \quad (20)$$

$\chi_{\text{ns}}^{L,T}$  has often been reported in the literature [25,32,33,38,39].

It is well known that the no-pair approximation quite generally leads to gauge dependent correlation energies, which is reflected by the nontransversality of  $\chi_{0,\text{np}}^{\mu\nu}$  [40],

$$q_\mu \chi_{0,\text{np}}^{\mu 0}(q) = 0, \quad q_\mu \chi_{0,\text{np}}^{\mu j}(q) = -q^j \bar{\chi}_{\text{np}}^T(q). \quad (21)$$

The no-sea approximation, on the other hand, is gauge invariant as both  $\chi_0^{\mu\nu}$  and  $\chi_{0,V}^{\mu\nu}$  satisfy the transversality relation  $q_\mu \chi^{\mu\nu} = 0$ . For the RPA this can be verified immediately [41] using Eqs. (16), (17), and (20).

For any gauge of the photon propagator and tensor structure of the Lindhard function the full response function (6) can be written in terms of the tensors (16)–(18). For example, in the covariant gauge one obtains

$$\begin{aligned} \chi_{\text{RPA}}^{\mu\nu}(q) = F(q) & \left[ \chi_{\text{np}}^L(q) [1 - D(q^2) \Lambda(q, \lambda) \bar{\chi}_{\text{np}}^T(q)] P_L^{\mu\nu} \right. \\ & + \bar{\chi}_{\text{np}}^T(q) \left( 1 + D(q^2) \frac{\mathbf{q}^2}{q^2} \chi_{\text{np}}^L(q) \right) \bar{P}_T^{\mu\nu} \\ & \left. - D(q^2) \frac{\mathbf{q}^2}{q^2} \chi_{\text{np}}^L(q) \bar{\chi}_{\text{np}}^T(q) g^{0\mu} g^{0\nu} \right] \\ & - \frac{\chi_{\text{np}}^T(q)}{1 + D(q^2) \chi_{\text{np}}^T(q)} P_T^{\mu\nu}, \end{aligned} \quad (22)$$

with

$$\begin{aligned} F(q) = & \left\{ 1 - D(q^2) \left[ \chi_{\text{np}}^L(q) - \bar{\chi}_{\text{np}}^T(q) [1 - \Lambda(q, \lambda)] \right. \right. \\ & \left. \left. - D(q^2) \chi_{\text{np}}^L(q) \bar{\chi}_{\text{np}}^T(q) \left( \Lambda(q, \lambda) + \frac{\mathbf{q}^2}{q^2} \right) \right] \right\}^{-1} \end{aligned}$$

and  $\Lambda(q, \lambda) = (\mathbf{q}^2/q^2)(1 - \lambda)/\lambda$ . As  $D_{\mu\nu} \chi_{\text{RPA}}^{\mu\nu}$  is even in  $q^0$  and analytic for  $\text{Re}(q^0) \geq 0$  and  $\text{Im}(q^0) \geq 0$ , the  $q^0$  integration along the real axis in Eq. (1) can be deformed to a contour along the imaginary axis. The replacement  $q^0 \rightarrow i\omega$  leads to purely real  $\chi_{\text{ns,np}}^{L,T}$ , which can be obtained by insertion of  $q_W = (i\omega, \mathbf{q})$  into the real part of the forms given in the Appendix [this is abbreviated by  $\chi(q_W)$  in all subsequent formulas]. The coupling constant integration can then be performed analytically. After subtraction of the exchange contribution this leads to

$$\begin{aligned} e_{\text{c,np}}^{\text{RPA}}(n, \lambda) = & 2 \int_0^\infty d\omega \int_0^\infty \frac{\mathbf{q}^2 dq}{(2\pi)^3} (-\ln |F(q_W)| \\ & + 2 \ln |1 + D(q_W^2) \chi_{\text{np}}^T(q_W)| \\ & + D(q_W^2) \{ \chi_{\text{np}}^L(q_W) - \bar{\chi}_{\text{np}}^T(q_W) [1 - \Lambda(q_W, \lambda)] \\ & - 2 \chi_{\text{np}}^T(q_W) \}) \end{aligned} \quad (23)$$

in the covariant gauge, while for the CG one finds

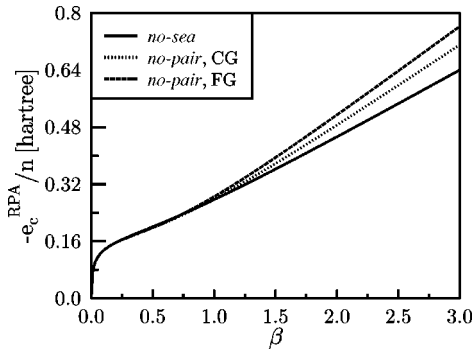


FIG. 1. RPA correlation energy per particle for the no-sea and no-pair approximations.

$$e_{c,np}^{\text{RPA}}(n) = 2 \int_0^\infty d\omega \int_0^\infty \frac{q^2 dq}{(2\pi)^3} \{ \ln|1 - D(q_W^2)\chi_{np}^L(q_W)| + 2 \ln|1 + D(q_W^2)\chi_{np}^T(q_W)| + D(q_W^2)[\chi_{np}^L(q_W) - 2\chi_{np}^T(q_W)] \}. \quad (24)$$

The CGB approximation for  $e_{c,np}^{\text{RPA}}$  is obtained from Eq. (24) by substituting  $(-q_W^2/q^2)\chi_{np}^T$  for  $\chi_{np}^T$ . The corresponding no-sea result  $e_{c,ns}^{\text{RPA}}$  [7,16,25,42] is given by Eq. (24) with  $\chi_{np}^{L,T}$  replaced by  $\chi_{ns}^{L,T}$ . The integrations in Eqs. (23) and (24) have to be performed numerically [for this purpose we have used polar coordinates  $z^2 = \omega^2 + q^2$ ,  $\phi = \arctan(|q|/\omega)$ ].

### III. RESULTS

#### A. Gauge dependence of $e_{c,np}^{\text{RPA}}$

The no-sea RPA represents a gauge-invariant approximation for the RHEG correlation energy, in which the density-dependent part of  $\chi_0^{\mu\nu}$  is fully taken into account. It therefore can serve as a comparative standard with respect to which the gauge dependence of no-pair results can be measured. The correlation energy per particle  $e_c^{\text{RHEG}}/n$  in the FG and CG is plotted together with the corresponding no-sea data in Fig. 1 as a function of the dimensionless density variable  $\beta$ ,

$$\beta = k_F/mc = (3\pi^2 n)^{1/3}/mc. \quad (25)$$

While in the nonrelativistic limit  $\beta \rightarrow 0$  the gauge dependence of  $e_c^{\text{RHEG}}$  vanishes, the differences between the gauges increase linearly in the high-density regime (as to be expected from a dimensional analysis; compare Appendix B of [7]).

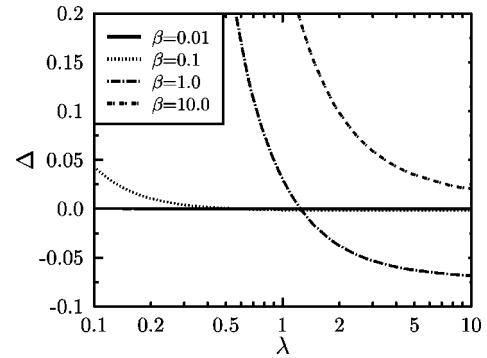


FIG. 2. Relative deviation  $\Delta$  [Eq. (26)] of no-pair correlation energies with respect to no-sea values as a function of the gauge parameter  $\lambda$  [Eq. (2)].

A direct estimate of the importance of the negative-energy continuum is obtained from the relative deviation  $\Delta$  of no-pair from no-sea results,

$$\Delta = \frac{e_{c,np}^{\text{RPA}} - e_{c,ns}^{\text{RPA}}}{e_{c,ns}^{\text{RPA}}}. \quad (26)$$

For the covariant gauge  $\Delta$  is plotted as a function of the gauge parameter  $\lambda$  for different values of  $\beta$  [Eq. (25)] in Fig. 2. While  $\beta \approx 1$  corresponds to inner-shell densities of very heavy elements,  $\beta \approx 0.01$  is a typical value for the valence regime. As all the functions involved in Eq. (23) are strictly monotonic, the overall gauge dependence of  $e_{c,np}^{\text{RPA}}(n, \lambda)$  is governed by the factor  $(1-\lambda)/\lambda$ , which fixes the relative weight of the two components of the photon propagator (2). In fact, the nontransversality of  $\chi_{0,np}^{\mu\nu}$ , [Eq. (21)] is irrelevant in the product  $D_{\mu\nu}^0 \chi_{0,np}^{\nu\rho}$ , which determines the RPA energy via Eqs. (1) and (6) when  $\lambda = 1$ . Accordingly, Fig. 2 shows that in the range of atomic densities  $\Delta$  is smallest in the vicinity of  $\lambda = 1$ , i.e., for the FG. On the other hand, while the gauge dependence of  $e_{c,np}^{\text{RPA}}$  is of the order of a few percent for  $\lambda > 1$ , it increases drastically for  $\lambda < 1$ . This is easily understood by noting that for  $\lambda \geq 1$   $e_{c,np}^{\text{RPA}}$  is essentially linear in  $(1-\lambda)/\lambda$ , as  $(1-\lambda)/\lambda \chi_{np}^T$  represents only a small contribution to the total  $D_{\mu\nu}^0 \chi_{0,np}^{\nu\rho}$  in this regime, so that an expansion of  $e_{c,np}^{\text{RPA}}(n, \lambda)$  with respect to this term is legitimate. In any case, for ultrarelativistic values of  $\beta$  the deviation between the no-pair and the no-sea approximation becomes arbitrarily large, reflecting the growing importance of virtual electron-positron pair creation.

Some CG results for  $\Delta$  are given in Table I. The overall

TABLE I. Relative deviation  $\Delta$  [Eq. (26)] for CG, CGB, FG, and LG [37] for different values of  $\beta$  [Eq. (25)].

$\beta$	$\Delta$			
	CGB	CG	FG	LG
0.01	$3.6 \times 10^{-7}$	$1.4 \times 10^{-5}$	$7.1 \times 10^{-6}$	$7.1 \times 10^{-6}$
0.1	$-9.0 \times 10^{-4}$	$-9.1 \times 10^{-4}$	$-1.2 \times 10^{-3}$	$-1.9 \times 10^{-3}$
0.5	$-1.1 \times 10^{-2}$	$-1.3 \times 10^{-2}$	$-1.2 \times 10^{-2}$	$-4.5 \times 10^{-2}$
1.0	$1.8 \times 10^{-2}$	$7.1 \times 10^{-3}$	$3.0 \times 10^{-2}$	$-7.2 \times 10^{-2}$
10.0	$2.2 \times 10^{-1}$	$1.7 \times 10^{-1}$	$2.7 \times 10^{-1}$	$1.1 \times 10^{-2}$

TABLE II. Relative deviation  $\delta$  [Eq. (27)] for CG, FG, and LG [37] for different values of  $\beta$  [Eq. (25)].

$\beta$	$\delta$		
	CG	FG	LG
0.1	$-4.3 \times 10^{-1}$	$-5.7 \times 10^{-1}$	$-9.1 \times 10^{-1}$
0.5	$-1.5 \times 10^{-1}$	$-1.4 \times 10^{-1}$	$-5.0 \times 10^{-1}$
1.0	$2.7 \times 10^{-2}$	$1.2 \times 10^{-1}$	$-2.8 \times 10^{-1}$
10.0	$1.9 \times 10^{-1}$	$3.1 \times 10^{-1}$	$1.3 \times 10^{-2}$

density dependence of  $\Delta$  in the CG is similar to that observed in the FG. While the CG  $\Delta$  is smaller than the FG result for  $\beta \geq 1$ , neither of the two gauges gives a  $\Delta$  that is consistently smaller than that of the other in the atomic density range. In addition,  $\Delta$  has no definite sign, so that it is not clear at this stage which of the two gauges will lead to smaller gauge errors in atomic RLDA calculations (see Sec. III B). In contrast, gauge effects are more pronounced in the LG. Moreover, the error of the Breit approximation (CGB) with respect to the full transverse interaction (CG) is of the same order as the deviations between the different gauges. An analogous observation has been made by Lindgren *et al.* [5], analyzing two-electron systems.

The no-pair approximation for  $\chi_0^{\mu\nu}$  does not approach the correct weakly relativistic limit, which is given by a combination of the nonrelativistic paramagnetic current-current and spin-spin response functions [43]: This can be verified directly by taking the weakly relativistic limit of Eq. (15), in which the  $\bar{\chi}_{np}^T$  contribution does not vanish. The consequences of this deficiency can be seen in Table II: While the resulting large deviation of  $e_{c,np}^{\text{RPA}}$  in  $\Delta$  for small  $\beta$  is masked by the very small absolute size of the relativistic correction, the problem becomes obvious as soon as the difference between no-pair and no-sea energies is normalized with respect to the relativistic correction  $e_{c,ns}^{\text{RPA}} - e_{c,NR}^{\text{RPA}}$  rather than the total correlation energy

$$\delta = \frac{e_{c,np}^{\text{RPA}} - e_{c,ns}^{\text{RPA}}}{e_{c,ns}^{\text{RPA}} - e_{c,NR}^{\text{RPA}}} \quad (27)$$

TABLE III. Relativistic correlation energy ( $E_c^R$ ) for the Ne isoelectronic series: Comparison of no-pair RLDA values for FG, CG, and CGB [37] with no-sea RLDA and RMBPT2 results [28]. The total  $E_c^R$  is decomposed into the nonrelativistic correlation energy  $E_c^{\text{NR}}$  and the relativistic correction  $E_c^R - E_c^{\text{NR}}$  (all energies are in mhartree).

Ne isoelectronic series	Method approximation gauge	$-E_c^{\text{NR}}$		$E_c^{\text{NR}} - E_c^R$				
		MBPT2	LDA	RMBPT2 no-pair CGB	RLDA			
					no-pair CGB	no-pair CG	no-pair FG	no-sea
Ne		383.2	746.4	2.1	0.5	0.5	0.4	0.7
Ca <sup>10+</sup>		394.5	1009.0	10.6	4.2	4.2	3.8	5.6
Zn <sup>20+</sup>		403.9	1144	26	14	14	13	17
Zr <sup>30+</sup>		408.6	1236	49	31	30	30	36
Sn <sup>40+</sup>		411.5	1307	80	57	56	56	64
Yb <sup>60+</sup>		414.8	1413	172	148	144	149	152
Hg <sup>70+</sup>		415.8	1454	237	218	211	222	217
Th <sup>80+</sup>		416.6	1491	322	312	301	320	301
Fm <sup>90+</sup>		417.2	1524	436	441	425	455	413

This agrees with a corresponding observation [2] in the context of atomic RHF calculations.

### B. No-pair RLDA results for atoms

In this section we discuss the gauge dependence of atomic correlation energies resulting from the no-pair RPA for the RLDA. In the RLDA [23–25] the xc energy density of the inhomogeneous system of interest is approximated by the xc energy density of the RHEG, evaluated with the local density  $n(\mathbf{r})$ ,

$$E_{xc}^{\text{RLDA}}[n] = \int d^3r e_{xc}^{\text{RHEG}}(n(\mathbf{r})). \quad (28)$$

The no-pair RPA for the RLDA is defined by insertion of either Eqs. (23) or (24), depending on the gauge chosen. Alternatively, use of  $e_{c,ns}^{\text{RPA}}$  yields the no-sea RPA for the RLDA, which again serves as a comparative standard. In order to obtain a correlation functional that is more complete than the RPA for low (nonrelativistic) densities the various forms for the RPA are combined with an accurate parametrization of the nonrelativistic LDA [16],

$$E_c^{\text{RLDA}}[n] = E_c^{\text{RPA-RLDA}}[n] - E_c^{\text{RPA-LDA}}[n] + E_c^{\text{LDA}}[n]$$

(in our calculations we have used the parametrization of [44] for  $E_c^{\text{LDA}}[n]$ ). For the present purpose the corresponding atomic correlation energies have been evaluated perturbatively by insertion of exact exchange-only densities, obtained via the relativistic OPM [16,19], which provides the most accurate DFT densities available to date. As the correlation potential  $v_c$  represents only a small contribution to the total effective Kohn-Sham potential, the neglect of  $v_c$  does not have a significant impact on the resulting  $E_c$ .

Results for the neon isoelectronic series, which allow the extraction of the  $Z$  dependence of relativistic corrections most easily, as well as results for some neutral atoms are listed in Tables III and IV. The RLDA values are compared with relativistic second-order many-body perturbation theory data [28], calculated on the basis of the Dirac-Coulomb-Breit Hamiltonian (i.e., the CGB interaction). The total  $E_c^{\text{RLDA}}$  is-

TABLE IV. Relativistic correlation energy ( $E_c^R$ ) for neutral atoms: Comparison of no-pair RLDA values for FG, CG, and CGB [37] with no-sea RLDA and RMBPT2 results [28]. The total  $E_c^R$  is decomposed into the nonrelativistic correlation energy  $E_c^{NR}$  and the relativistic correction  $E_c^R - E_c^{NR}$  (all energies are in mhartree).

Atom	Method approximation gauge	$-E_c^{NR}$		$E_c^{NR} - E_c^R$				
		MBPT2	LDA	RMBPT2 no-pair CGB	RLDA			
					no-pair CGB	no-pair CG	no-pair FG	no-sea
Xe		2921	5199	146	92	90	90	103
Hg		5086	8356	486	301	293	303	310
Rn		5392	9026	548	385	374	387	393

split into the corresponding nonrelativistic energy, obtained by insertion of the nonrelativistic  $x$ -only OPM density  $n^{NR}$  into  $E_c^{LDA}[n]$  and the relativistic correction

$$\Delta E_c = E_c^{RLDA}[n^R] - E_c^{LDA}[n^{NR}]. \quad (29)$$

$\Delta E_c$  has been calculated for both the FG and CG. In addition, for the CG the results obtained with the Breit approximation (CGB) are also given, allowing a direct comparison with the RMBPT2 data.

As is well known, the nonrelativistic LDA results, which are here given as a measure of the absolute size of the gauge dependence of the no-pair energies, overestimate atomic  $E_c$  drastically. Compared with the total error of the nonrelativistic LDA, the differences between its various relativistic forms are rather small: While for low  $Z$  the no-pair approximation clearly underestimates the no-sea  $\Delta E_c$ , the percentage deviation being roughly 40% for Ne, the relation is reversed for high  $Z$ , with the error reducing to about 10%. This tendency is somewhat more pronounced in the FG than in the CG, as expected from Tables I and II. Furthermore, the Breit approximation accurately reproduces the results obtained with the full transverse interaction: It overestimates the full transverse results by only 1–3 %, the error increasing slowly with  $Z$ . Nevertheless, for heavy elements this error is as large as the differences between the various gauges.

Compared with the  $\Delta E_c$  found with RMBPT2, the corresponding RLDA results for the Ne isoelectronic series deviate by about a factor 2–4 for low  $Z$ , but seem to become more accurate with increasing  $Z$ . However, the agreement for heavy neonlike ions has to be regarded as fortuitous, as it is not found for neutral atoms (see Table IV): For example, for neutral Hg the no-pair CGB RLDA yields  $\Delta E_c = -301$  mhartree, compared with the RMBPT2 value of  $\Delta E_c = -486$  mhartree [28]. Tables III and IV should thus only be understood as an indication of the size of gauge effects in finite many-electron systems. Nevertheless, these gauge effects are smaller than the differences observed between standard many-body methods: For Xe CGB RMBPT2 gives a  $\Delta E_c$  of 146 mhartree [28], which may be compared with the CGB coupled-cluster value of 103 mhartree [29], whereas Table IV suggests that the gauge dependence of this  $\Delta E_c$  is of the order of 10 mhartree. On the other hand, the  $E_c$  obtained with the two most widely used GGAs for  $E_c[n]$ , from Lee, Yang, and Parr [9] (2749 mhartree) and Perdew [10] (3145

mhartree), differ by 396 mhartree, which is more than an order of magnitude larger than the gauge uncertainty.

The importance of gauge effects for the physically more relevant energy differences depends on the type of process investigated: While for the ionization of inner-shell electrons or inner-shell transitions in highly charged ions the gauge errors resulting from the no-pair approximation are roughly as large as for total energies, they are much smaller for the ionization potential (IP) of valence electrons. As in the latter process the core density, for which relativity and thus gauge effects are important, remains essentially unchanged, the gauge error in the neutral atom is more or less identical to that in the corresponding ion. In fact, the IPs obtained with the various versions of the RPA discussed here differ only on the  $\mu$ hartree level. An analogous statement applies to radiative corrections, i.e., the creation of virtual electron-positron pairs in the field of the nucleus: While for elements such as nobelium the absolute size of the resulting energy shifts is larger than the total correlation energy (compare, e.g., [4,5]), both their direct and indirect (via the rearrangement of  $K$ - and  $L$ -shell electrons) impacts on the valence electrons are rather small. Thus radiative corrections must be included for all those processes in which  $K$ - and  $L$ -shell electrons are involved, but can be safely neglected in the standard density-functional applications to quantum chemical and condensed matter problems.

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#### APPENDIX: INDEPENDENT COMPONENTS OF THE NO-PAIR LINDHARD FUNCTION

After evaluating the frequency integration in Eq. (14) the  $q$  integration can be done directly in spherical coordinates. For the calculation we have proceeded as outlined in the Appendix of Ref. [38], after suitably rearranging the terms in the integrands. The division into a real and an imaginary part is achieved using the Dirac identity

$$\frac{1}{\omega \pm i\epsilon} = \mathcal{P}\left(\frac{1}{\omega}\right) \mp i\pi\delta(\omega)$$

( $\mathcal{P}$  symbolizes the Cauchy principal value). One finally obtains for the three independent components of  $\chi_{0,np}^{\mu\nu}$ ,

$$\begin{aligned}
\chi_{\text{np}}^L(q) = & \frac{q^2}{8\pi^2|q|^3} \left\{ \frac{(E_F^+)^3 - (E_F^-)^3}{9} + \frac{8}{3} E_F k_F |q| + \left( \frac{7}{3} E_F^2 + \frac{q_0^2}{3} - q^2 + \frac{4m^2 q^2}{3q^2} \right) (E_F^+ - E_F^-) \right. \\
& + \left( \frac{4}{3} E_F^3 + q^2 E_F \right) \ln \left| \frac{(E_F^+ - E_F)^2 - q_0^2}{(E_F^- - E_F)^2 - q_0^2} \right| + \left( 2E_F^2 - \frac{q^2}{2} + \frac{q_0^2}{6} \right) q_0 \ln \left| \frac{(E_F^+ - E_F - q_0)(E_F^- - E_F + q_0)}{(E_F^- - E_F - q_0)(E_F^+ - E_F + q_0)} \right| \\
& + \frac{q^2}{3} \left( 1 + \frac{2m^2}{q^2} \right) a \ln \left| \frac{(E_F^+ + E_F - a)(E_F^- + E_F + a)}{(E_F^- + E_F - a)(E_F^+ + E_F + a)} \right| - \frac{|q|^3}{3} \ln \left| \frac{(E_F^+ + E_F - |q|)(E_F^- + E_F + |q|)}{(E_F^- + E_F - |q|)(E_F^+ + E_F + |q|)} \right| \\
& - i \frac{\pi}{6} \Theta(|E_F^- - E_F| < |q_0| < E_F^+ - E_F) [-(2E_F + |q_0|)^3 + a^3 + 3q^2(2E_F + |q_0| - a)] \\
& \left. + i \frac{\pi}{3} \Theta(2k_F - |q|) \Theta(|q_0| < E_F - E_F^-) |q_0| [12E_F^2 + q_0^2 - 3q^2] \right\}, \tag{A1}
\end{aligned}$$

$$\begin{aligned}
\chi_{\text{np}}^T(q) = & \frac{q^2}{16\pi^2|q|^3} \left\{ \frac{2[(E_F^+)^5 - (E_F^-)^5]}{5q^2} + \left( \frac{1}{3} - \frac{2E_F^2 + 3q^2}{q^2} \right) \frac{(E_F^+)^3 - (E_F^-)^3}{3} + 4 \left( \frac{2}{3} + \frac{q^2}{q^2} \right) E_F k_F |q| + \left( \frac{7}{3} E_F^2 - \frac{q^2}{q^2} E_F^2 + \frac{q_0^2}{3} \right. \right. \\
& \left. \left. + \frac{16m^2 q^2}{3q^2} + \frac{q^2 q_0^2}{q^2} \right) (E_F^+ - E_F^-) + \left( \frac{4}{3} E_F^2 + q_0^2 + q^2 + \frac{4m^2 q^2}{q^2} \right) E_F \ln \left| \frac{(E_F^+ - E_F)^2 - q_0^2}{(E_F^- - E_F)^2 - q_0^2} \right| + \left( 2E_F^2 + \frac{q_0^2}{6} + \frac{q^2}{2} + \frac{2m^2 q^2}{q^2} \right) \right. \\
& \times q_0 \ln \left| \frac{(E_F^+ - E_F - q_0)(E_F^- - E_F + q_0)}{(E_F^- - E_F - q_0)(E_F^+ - E_F + q_0)} \right| - \frac{2q^2}{3} \left( 1 + \frac{2m^2}{q^2} \right) a \ln \left| \frac{(E_F^+ + E_F - a)(E_F^- + E_F + a)}{(E_F^- + E_F - a)(E_F^+ + E_F + a)} \right| \\
& \left. + \frac{2|q|^3}{3} \ln \left| \frac{(E_F^+ + E_F - |q|)(E_F^- + E_F + |q|)}{(E_F^- + E_F - |q|)(E_F^+ + E_F + |q|)} \right| + i \frac{\pi}{6} \Theta(|E_F^- - E_F| < |q_0| < E_F^+ - E_F) \right. \\
& \times \left[ (2E_F + |q_0|)^3 - a^3 + 3q^2 \left( 1 + \frac{4m^2}{q^2} \right) (2E_F + |q_0| - a) \right] + i \frac{\pi}{3} \Theta(2k_F - |q|) \Theta(|q_0| < E_F - E_F^-) \\
& \left. \times |q_0| \left[ 12E_F^2 + q_0^2 + 3q^2 \left( 1 + \frac{4m^2}{q^2} \right) \right] \right\}, \tag{A2}
\end{aligned}$$

and

$$\bar{\chi}_{\text{np}}^T(q) = \frac{1}{6\pi^2|q|^3} \left\{ \frac{(E_F^+)^5 - (E_F^-)^5}{5} - k_F |q| [(E_F^+)^3 + (E_F^-)^3] \right\}, \tag{A3}$$

where

$$E_F = \sqrt{k_F^2 + m^2}, \quad E_F^\pm = \sqrt{(k_F \pm |q|)^2 + m^2}, \quad a = |q| \sqrt{1 - \frac{4m^2}{q^2}}, \tag{A4}$$

and

$$\Theta(a < b) = \Theta(b - a), \quad \Theta(a < b < c) = \Theta(a < b) \Theta(b < c). \tag{A5}$$

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