

Abstract

Range-separated density-functional theory allows one to rigorously combine a (semi)local density-functional approximation for the short-range part of the electron-electron interaction with explicit many-body methods for the long-range part of the electron-electron interaction (see, e.g., Ref. [1]).

This theory has been designed first with non-relativistic formalism, but may be extended so as to encompass relativistic effects as it was recently done by Kullie and Saue [2] through the use of the Dirac-Coulomb Hamiltonian, but using a non-relativistic short-range functional. The goal of this work is to study short-range relativistic effects in order to design such a relativistic short-range exchange-correlation functional to describe more accurately heavy atoms.

Four-Component Relativistic Range-Separated Density-Functional Theory

We consider here a multideterminantal extension of the Kohn-Sham scheme with range separation in four-component formalism, with only the Coulombic interaction. Here the minimisation is realised in the space spanned by the positive energy electronic states, an approximation which is also called the no-pair approximation.

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{H}_0 + \hat{W}_{ee}^{lr} | \Psi \rangle + E_{Hxc}^{sr}[n_{\Psi}] \right\}$$

- $\hat{H}_0 = c(\alpha \cdot \hat{\mathbf{p}}) + \beta m c^2 + \hat{V}_{ne}$: **One-electron Dirac Hamiltonian**

$$\text{with } \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \sigma = \begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix} \text{ and } \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$$

- $\hat{W}_{ee}^{lr} = \sum_{k < l} I_{4,k} \otimes I_{4,l} w_{ee}^{lr}(r_{kl})$: **Two-electron long-range Coulombic interaction**

$$\text{with } w_{ee}^{lr}(r) = \frac{\text{erf}(\mu r)}{r} \text{ and } w_{ee}^{sr}(r) = \frac{1 - \text{erf}(\mu r)}{r}$$

- $E_{Hxc}^{sr}[n]$: **Short-range Hxc density functional**

- Parameter μ controls the range of separation.

If $\mu = 0$ there is no long-range interaction and the wavefunction Ψ reduces to the relativistic Kohn-Sham determinant Φ .

If $\mu \rightarrow \infty$ there is no short-range interaction and the density functional becomes null.

Short-Range Hxc density functional

One may decompose the short-range Hxc density functional:

$$E_{Hxc}^{sr}[n] = E_H^{sr}[n] + E_x^{sr}[n] + E_c^{sr}[n]$$

With the Hartree term

$$E_H^{sr}[n] = \frac{1}{2} \iint n(\mathbf{r}_1)n(\mathbf{r}_2)w_{ee}^{sr}(r_{12})d\mathbf{r}_1d\mathbf{r}_2$$

and the exchange term

$$E_x^{sr}[n] = \langle \Phi | \hat{W}_{ee}^{sr} | \Phi \rangle - E_H^{sr}[n]$$

Expression in terms of Pair Density

One may express the exchange term through the use of the exchange pair density $n_{2,x}$:

$$E_x^{sr} = \frac{1}{2} \iint n_{2,x}(\mathbf{r}_1, \mathbf{r}_2)w_{ee}^{sr}(r_{12})d\mathbf{r}_1d\mathbf{r}_2$$

We may express $n_{2,x}(\mathbf{r}_1, \mathbf{r}_2)$ in terms of the Fermi hole $n_x(\mathbf{r}_1, \mathbf{r}_2)$ or in terms of the pair distribution function $g_x(\mathbf{r}_1, \mathbf{r}_2)$:

$$n_{2,x}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n_x(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g_x(\mathbf{r}_1, \mathbf{r}_2)$$

We may also express $n_{2,x}(\mathbf{r}_1, \mathbf{r}_2)$ with the four-spinor $\psi_i(\mathbf{r}) = \begin{pmatrix} \varphi_i(\mathbf{r}) \\ \chi_i(\mathbf{r}) \end{pmatrix}$, φ_i being the large component and χ_i the small component

$$n_{2,x}(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{i,j}^{\text{Occupied}} \psi_i^\dagger(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_j^\dagger(\mathbf{r}_2)\psi_i(\mathbf{r}_2)$$

or in term of (4x4) one-electron density matrix

$$\begin{aligned} n_{2,x}(\mathbf{r}_1, \mathbf{r}_2) &= - \sum_{i,j}^{\text{Occupied}} \text{Tr}[\psi_i(\mathbf{r}_2)\psi_j^\dagger(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_i^\dagger(\mathbf{r}_2)] \\ &= -\text{Tr}[\gamma(\mathbf{r}_1, \mathbf{r}_2)\gamma(\mathbf{r}_2, \mathbf{r}_1)] \end{aligned}$$

One can make a large μ expansion in terms of the exchange on-top pair density

$$E_x^{sr} = \frac{\pi}{2\mu^2} \int n_{2,x}(\mathbf{r}, \mathbf{r})d\mathbf{r} + O\left(\frac{1}{\mu^4}\right)$$

Note that contrary to the non-relativistic case the exchange term in the large μ expansion is not directly related to the square of the local spin density

$$n_{2,x}(\mathbf{r}, \mathbf{r}) = -\text{Tr}[\gamma(\mathbf{r}, \mathbf{r})^2] \neq - \sum_{\sigma} n_{\sigma}(\mathbf{r})^2$$

Local Density Approximation

Despite the previous conclusion, we must look at the LDA[3] for exchange energies, if only to construct more advanced functionals later on. We may then look at calculations on the Relativistic Homogeneous Electron Gas (or RHEG).

$$E_x^{sr,LDA} = \int n(\mathbf{r})\epsilon_x^{sr,unif}(n(\mathbf{r}))d\mathbf{r}$$

$$\epsilon_x^{sr,unif}(n) = -\frac{1}{2} \int_V n g_x^{unif}(r_{12}, n)w_{ee}^{sr}(r_{12})d\mathbf{r}_{12}$$

g_x^{unif} can be calculated analytically [4,5] and expressed through $k_F = (3\pi^2 n)^{1/3}$ the Fermi wavevector of the RHEG and j_k the Spherical Bessel Function of the k^{th} order

$$g_x^{unif}(r_{12}, n) = -\frac{9}{4k_F^2 r_{12}^2} \left\{ j_1(k_F r_{12})^2 + (1 - \lambda)A(k_F r_{12})^2 + \lambda B(k_F r_{12})^2 \right\}$$

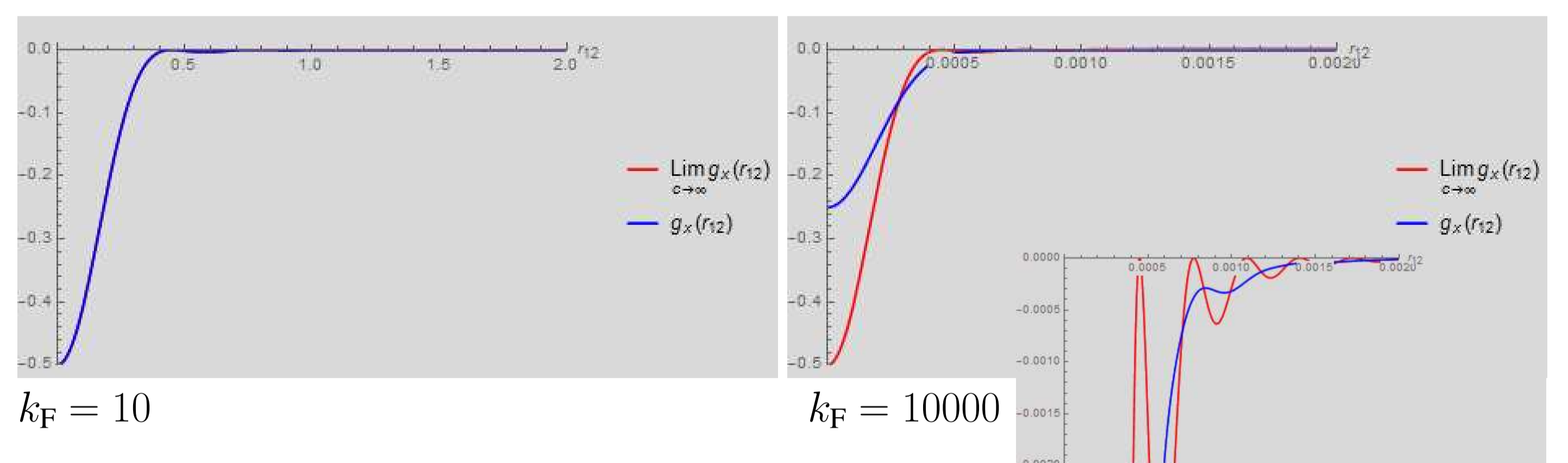
with

- $\lambda = \frac{k_F^2}{k_F^2 + m^2 c^2}$
- $A(k_F r_{12}) = \sum_{k=0}^{\infty} \left[\frac{(2k+1)!!}{(2k+1)} \right] j_{k+1}(k_F r_{12}) \lambda^k \frac{1}{k_F^k r_{12}^k}$
- $B(k_F r_{12}) = \sum_{k=0}^{\infty} \left[\frac{(2k+1)!!}{(2k+1)} \right] j_{k+2}(k_F r_{12}) \lambda^k \frac{1}{k_F^k r_{12}^k}$

The non-relativistic limit may be found as

$$\lim_{c \rightarrow +\infty} g_x^{unif}(r_{12}, n) = -\frac{9}{2k_F^2 r_{12}^2} j_1(k_F r_{12})^2$$

One may represent the pair distribution functions, for low and high densities.

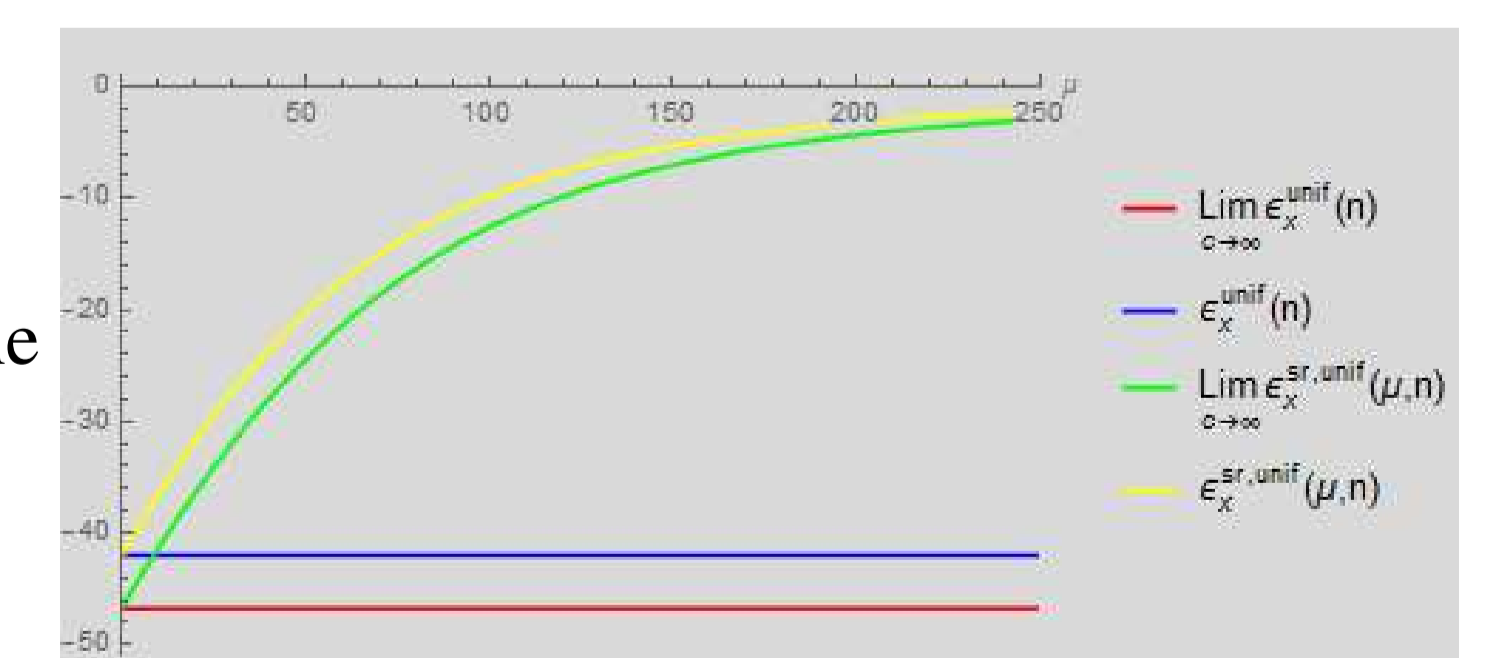


We observe that the hole is unchanged at low density, while it gets broader and shallower at very high density. The Friedel oscillations are also modified at very high density.

One may then calculate the short-range exchange energy per particle of the RHEG, knowing that the relativistic range-separated calculations have no analytical solutions and must be done through numerical integration.

We may do the calculation using $k_F = 196$, a value related to the electronic density of the 1S Slater orbital of uranium through

$$k_F = \left(3\pi^2 \frac{Z^3}{\sqrt{\pi}} \right)^{1/3}$$



Conclusion

From the previous calculation we may observe substantial variation in short-range exchange energy per particle for heavy atoms, up to 12% for small values of μ .

As for future work, the Breit interaction shall be taken in account and correlation calculations using full Breit-Dirac Hamiltonian shall be realised.

References

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