# Relativistic Range-Separated Density Functional Theory

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- Strong correlation.
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Are relativistic effects only minor corrections?

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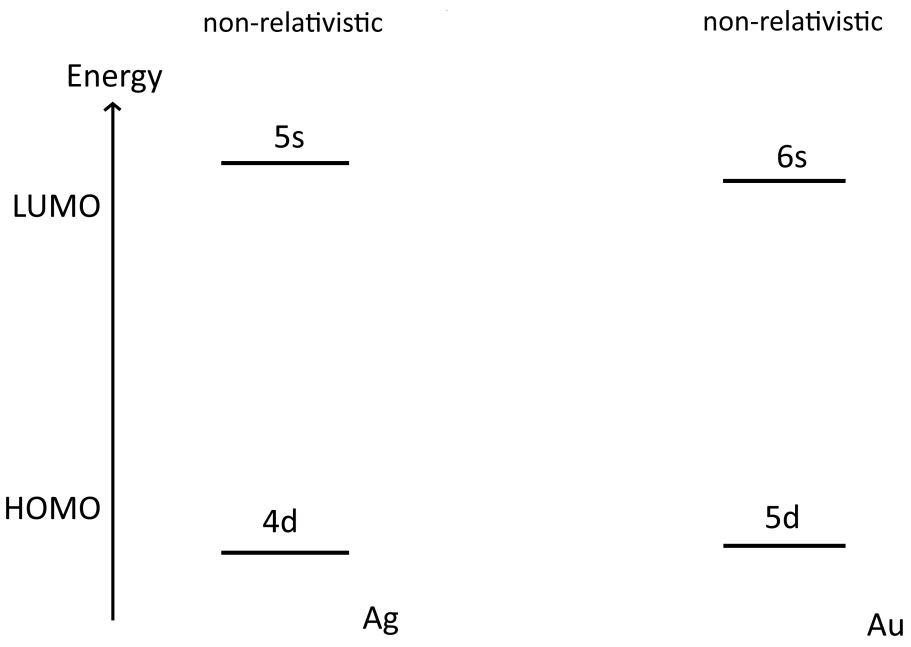
Usual exemple n°1: the color of gold

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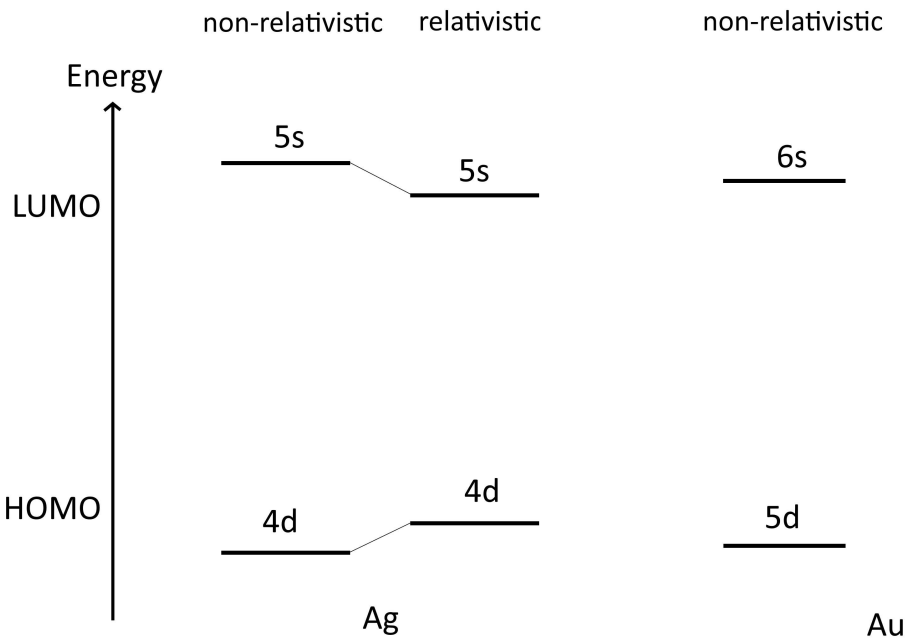


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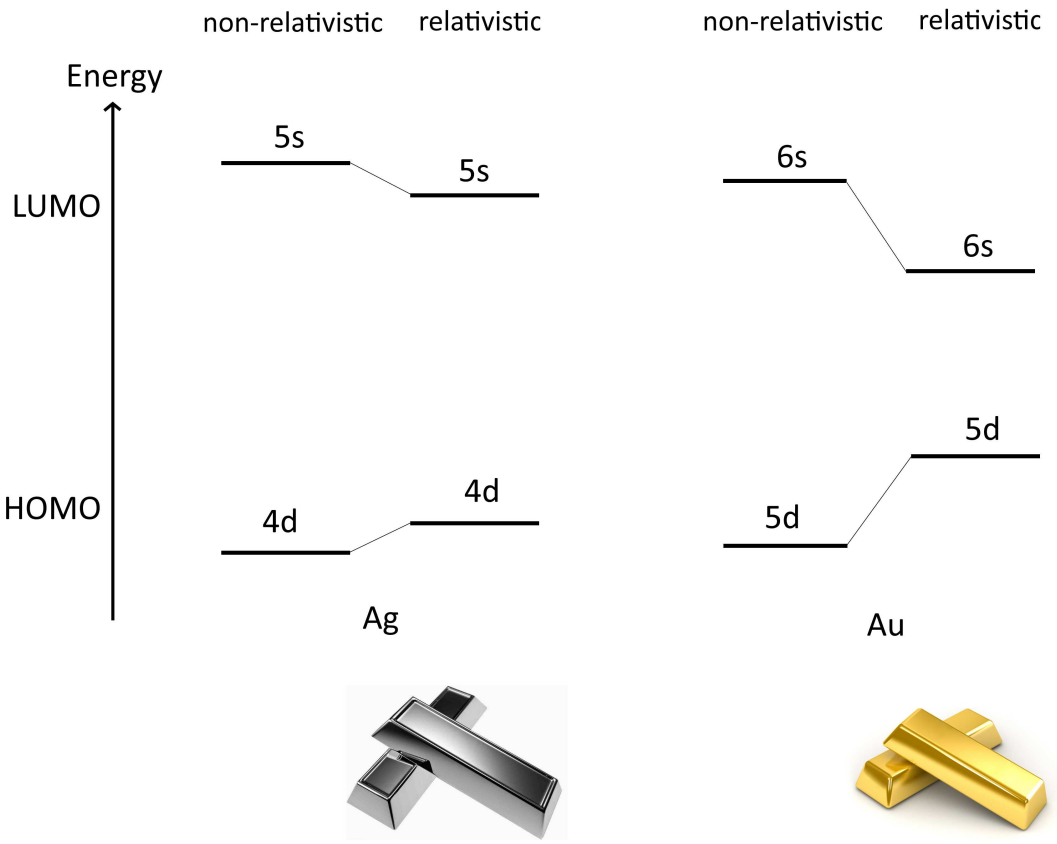


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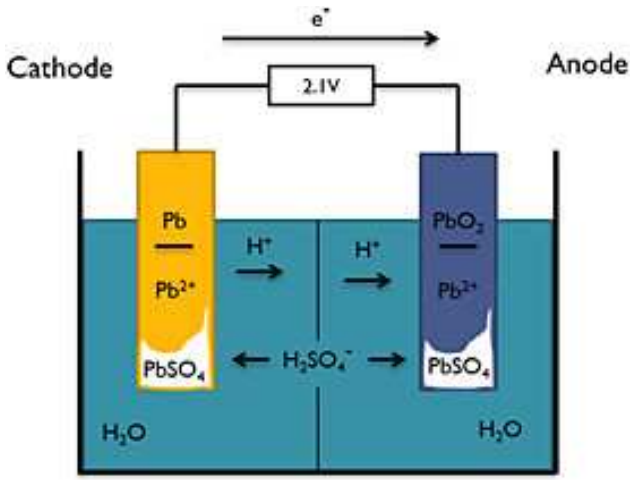


$$Pb(s) + PbO_2(s) + 2\ H_2SO_4(aq) = 2\ PbSO_4(s) + 2\ H_2O(l)$$

experiment: +2.11 V
non-relativistic calculation: +0.39 V

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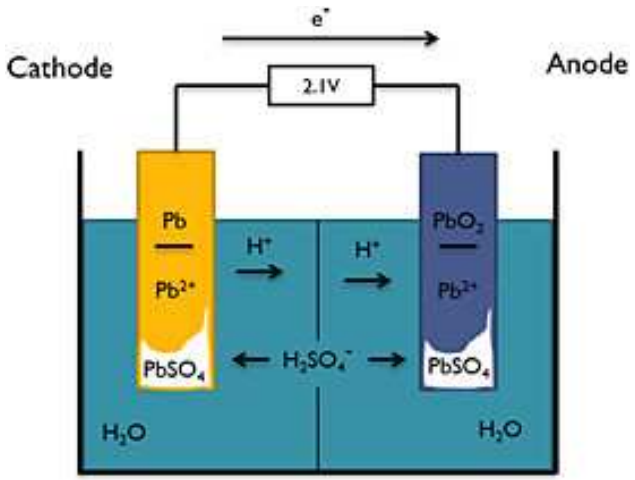


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relativistic calculation: +2.13 V

R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö, and P. Zaleski-Ejgierd,"Relativity and the Lead-Acid Battery", Phys. Rev. Lett. 106 (2011) 018301

# How to bother with relativity?

- Four-component formalism
  - Quantum Electrodynamics (QED)

$$\mathcal{L}_{QED} = \mathcal{L}_{mat} + \mathcal{L}_{rad} + \mathcal{L}_{int}$$

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This formalism is overly complicated.

"QED is the fundamental theory of chemistry describing perfectly well all phenomena that do not play any role for chemistry."

M. Reiher, A. Wolf, "Relativistic Quantum Chemistry: The fundamental Theory of Molecular Science", WILEY-VCH (2009)

# How to bother with relativity?

- Four-component formalism
  - Quantum Electrodynamics (QED)
  - Dirac equation

Non-interacting Dirac Hamiltonian in second quantization (from $\mathcal{L}_{mat}$) :

$$\hat{H}^{\mathrm{D}} = \int \mathrm{d}\mathbf{r}\, \hat{\psi}^{\dagger}(\mathbf{r}) \left[ c\, (\boldsymbol{\alpha} \cdot \mathbf{p}) + \boldsymbol{\beta}\, mc^2 + v_{\mathrm{ne}}(\mathbf{r}) \mathbf{I}_4 \right] \hat{\psi}(\mathbf{r}),$$

where

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0}_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0}_2 \end{pmatrix} \text{ and } \boldsymbol{\beta} = \begin{pmatrix} \mathbf{I}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{I}_2 \end{pmatrix}$$

and

$$\hat{\psi}(\mathbf{r}) = \sum_p \psi_p(\mathbf{r})\, \hat{a}_p \text{ and } \hat{\psi}^{\dagger}(\mathbf{r}) = \sum_p \psi_p^{\dagger}(\mathbf{r})\, \hat{a}_p^{\dagger}.$$

# How to bother with relativity?

- Four-component formalism
  - Quantum Electrodynamics (QED)
  - Dirac equation
    - Coulomb, Coulomb-Gaunt and Coulomb-Breit

Relativistic electron-electron interaction potential (from $\mathcal{L}_{int}$):

$$\hat{W}_{ee} = \frac{1}{2}\iint \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\, \hat{\psi}^\dagger(\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r}_2)\mathbf{w}_{ee}(\mathbf{r}_{12})\hat{\psi}(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_1),$$

with, in Coulomb gauge:

$$\begin{aligned}
\mathbf{w}_{ee}^{Coulomb} &= \frac{(\mathbf{I}_4)_1\,(\mathbf{I}_4)_2}{r_{12}}, \\
\mathbf{w}_{ee}^{Coulomb-Gaunt} &= \frac{(\mathbf{I}_4)_1\,(\mathbf{I}_4)_2}{r_{12}} - \frac{1}{c^2}\frac{c\boldsymbol{\alpha}_1.c\boldsymbol{\alpha}_2}{r_{12}}, \\
\mathbf{w}_{ee}^{Coulomb-Breit} &= \frac{(\mathbf{I}_4)_1\,(\mathbf{I}_4)_2}{r_{12}} - \frac{1}{c^2}\frac{1}{2}\left(\frac{c\boldsymbol{\alpha}_1.c\boldsymbol{\alpha}_2}{r_{12}} + \frac{(c\boldsymbol{\alpha}_1.\mathbf{r}_{12})(c\boldsymbol{\alpha}_2.\mathbf{r}_{12})}{r_{12}^3}\right)
\end{aligned}$$

# How to bother with relativity?

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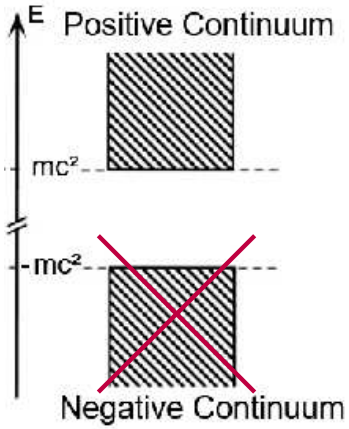
    - No-pair approximation

No-pair approximation to describe only electrons:




Minmax principle with the projector $P_+$ on the positive energy space:

$$E = \min_{\Psi} \left[ \max_{P_+} \langle \Psi | P_+ \left( \hat{H}^{\mathrm{D}} + \hat{W}_{ee} \right) P_+ | \Psi \rangle \right].$$

# How to bother with relativity?

- Four-component formalism
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Decoupling the negative-energy states to describe only electrons.

# How to bother with relativity?

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- Two-component formalism
- One-component formalism

Schrödinger formalism with a relativistic effective core potential.

# How to bother with relativity?

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# Relativistic Wave Function Theory

- Wave-function as linear combinations of Slater determinants as linear combinations of gaussian atomic orbitals $\chi$:

$$\chi(\mathbf{r}) = (x - x_0)^{n_x}(y - y_0)^{n_y}(z - z_0)^{n_z} e^{-\alpha\left((x-x_0)^2+(y-y_0)^2+(z-z_0)^2\right)},$$

  description of the electron-electron cusp requires to very large basis-sets.

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  description of the electron-electron cusp requires to very large basis-sets.

- Relativistic spinors expressed as Large component and Small component:

$$\Psi(\mathbf{r}) = \begin{pmatrix} \Psi^{Large}(\mathbf{r}) \\ \Psi^{Small}(\mathbf{r}) \end{pmatrix},$$

  kinetic balance requires one basis set for each component.

# Relativistic Wave Function Theory

$$E = \min_{\Psi} \left[ \max_{P_+} \langle \Psi | P_+ \left( \hat{H}^{\mathrm{D}} + \hat{W}_{ee} \right) P_+ | \Psi \rangle \right].$$

# Range-separated Relativistic Density Functional Theory

$$E = \min_{\Psi} \left[ \max_{P_+} \left\{ \langle \Psi | P_+ \left( \hat{H}^{\mathrm{D}} + \hat{W}_{ee}^{\mathrm{lr},\mu} \right) P_+ | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n_\Psi, \mathbf{j}_\Psi] \right\} \right],$$

# Range-separated Relativistic Density Functional Theory

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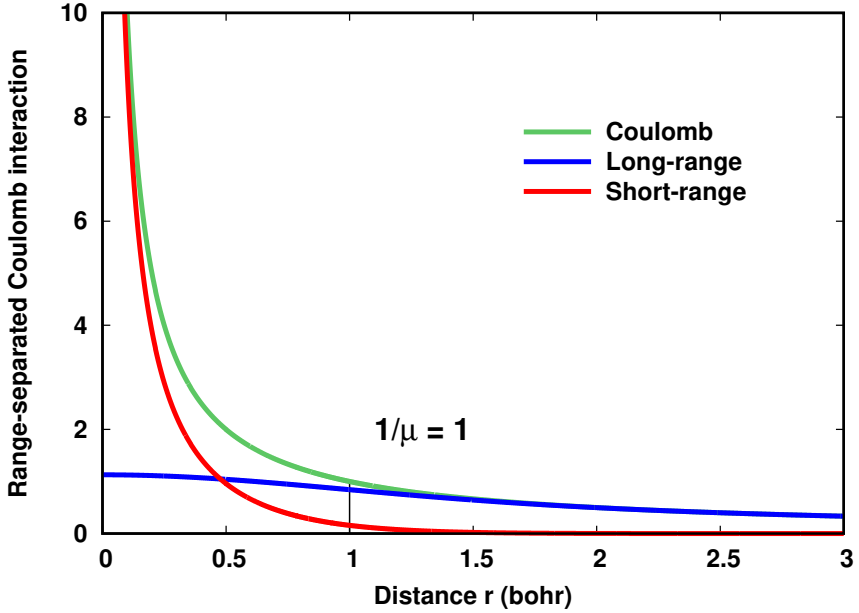


$$\frac{1}{r} = \frac{erf(\mu r)}{r} + \frac{1 - erf(\mu r)}{r}$$

where $\mu$ is the range-separation parameter, lr stands for long-range and sr stands for short-range.

# RS-RDFT: Local Density Approximation

For closed-shell systems $\mathbf{j} = 0$, the Hartree-exchange-correlation functional is:

$$E_{\mathrm{Hxc}}^{\mathrm{sr},\mu}[n] = E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] + E_{\mathrm{x}}^{\mathrm{sr},\mu}[n] + E_{\mathrm{c}}^{\mathrm{sr},\mu}[n],$$

where we define the Hartre functional:

$$E_{\mathrm{H}}^{\mathrm{sr},\mu}[n] = \frac{1}{2}\iint n(\mathbf{r}_1)n(\mathbf{r}_2)\frac{1 - erf\left(\mu|\mathbf{r}_1 - \mathbf{r}_2|\right)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2$$

and the exchange functional:

$$E_{\mathrm{x}}^{\mathrm{sr},\mu}[n] = \langle \mathbf{\Phi}|\hat{W}_{\mathrm{ee}}^{\mathrm{sr},\mu}|\mathbf{\Phi}\rangle - E_{\mathrm{H}}^{\mathrm{sr},\mu}[n].$$

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We are interested in:

$$E_{\mathrm{x}}^{\mathrm{RLDA,sr},\mu}[n] = \int n(\mathbf{r})\ \epsilon_{\mathrm{x}}^{\mathrm{RHEG,sr},\mu}\big(n(\mathbf{r})\big)d\mathbf{r},$$

where RHEG stands for relativistic homogeneous electron gas.

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# Relativistic Homogeneous Electron Gas

- $N$ electrons in a box of volume $V$ so that $n = N/V$ is kept constant in the thermodynamic limit $N \to \infty$ and $V \to \infty$.
- Fermi wave-vector $k_{\mathrm{F}} = (3\pi^2 n)^{1/3}$.
- Non-interacting electron gas described by spinors solutions of the non-interacting Dirac equation:

$$\left(c(\boldsymbol{\alpha}.\hat{\mathbf{p}}) + \beta mc^2\right) \psi_{\mathbf{k},\sigma}(\mathbf{r}) = E_k \; \psi_{\mathbf{k},\sigma}(\mathbf{r})$$

# Relativistic Homogeneous Electron Gas

The non-interacting four-component spinors are described as plane-waves:

$$\psi_{\mathbf{k},\sigma}(\mathbf{r}) = \begin{pmatrix} \varphi_{\mathbf{k},\sigma}(\mathbf{r}) \\ \chi_{\mathbf{k},\sigma}(\mathbf{r}) \end{pmatrix}$$

$$\varphi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{V}}\sqrt{\frac{E_k + mc^2}{2E_k}}e^{-i\mathbf{k}.\mathbf{r}}\varphi_\sigma, \qquad \chi_{\mathbf{k},\sigma}(\mathbf{r}) = \frac{c(\boldsymbol{\sigma}.\mathbf{k})}{E_k + mc^2}\varphi_{\mathbf{k},\sigma}(\mathbf{r})$$

where

- $\varphi_\sigma$ so that $\varphi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\varphi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$,
- $E_k = +\sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$

# Dirac-Coulomb-Breit Hamiltonian

$$\hat{H}^{\mathrm{DCB}} = \sum_{i}^{N} c(\boldsymbol{\alpha}_i.\hat{\mathbf{p}}_i) + \boldsymbol{\beta}_i mc^2 + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$- \sum_{i<j}^{N} \left( \frac{\boldsymbol{\alpha}_i.\boldsymbol{\alpha}_j}{2|\mathbf{r}_i - \mathbf{r}_j|} + \frac{(\boldsymbol{\alpha}_i.(\mathbf{r}_i - \mathbf{r}_j))(\boldsymbol{\alpha}_j.(\mathbf{r}_i - \mathbf{r}_j))}{2|\mathbf{r}_i - \mathbf{r}_j|^3} \right)$$

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# Exchange energy per particle of the HEG

For the non-relativistic exchange energy per particle we have:

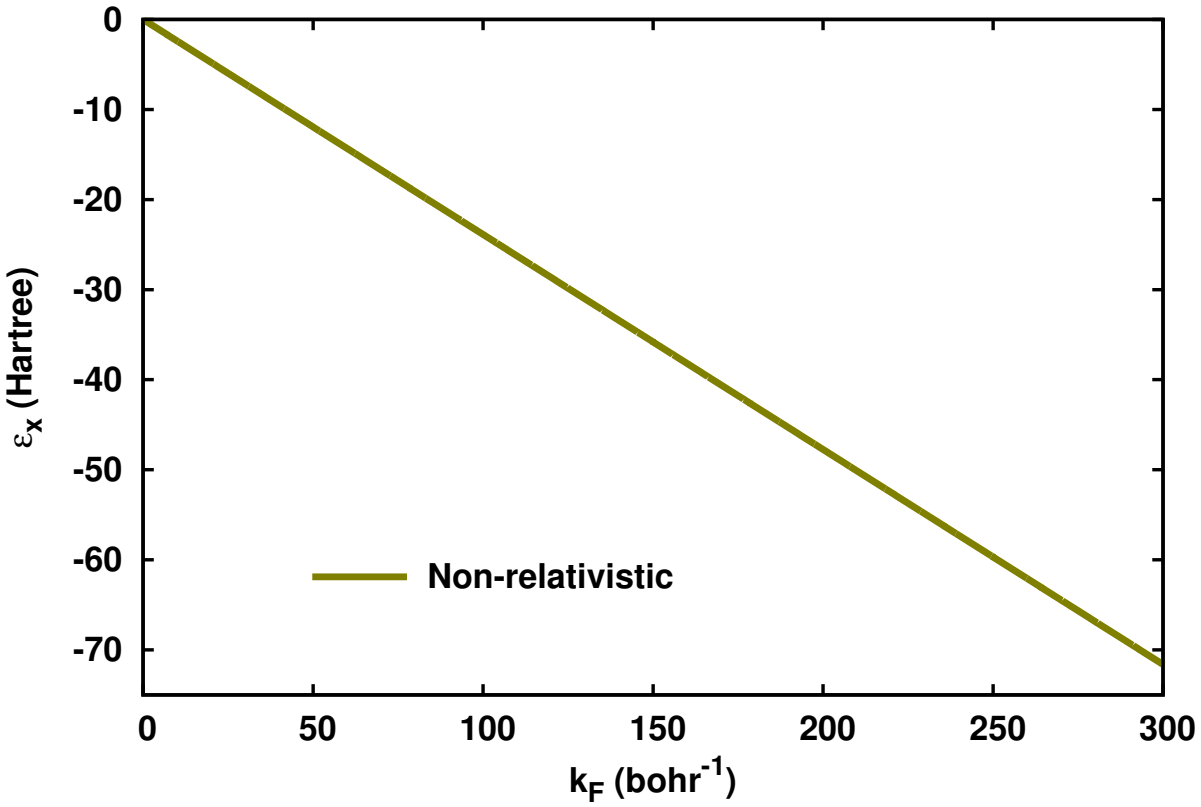
$$
\begin{aligned}
\epsilon_{\mathrm{x}}^{\mathrm{NR}} &= -\frac{V^2}{2N(2\pi)^6} \iint\limits_{V_{k_{\mathrm{F}}}} \iint\limits_{V} \frac{e^{-i(\mathbf{k}_1-\mathbf{k}_2).(\mathbf{r}_1-\mathbf{r}_2)}}{V^2} \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{r}_1 d\mathbf{r}_2 \\
&= -\frac{1}{2n(2\pi)^6} \iint\limits_{V_{k_{\mathrm{F}}}} \frac{4\pi}{|\mathbf{k}_1-\mathbf{k}_2|^2} d\mathbf{k}_1 d\mathbf{k}_2 \\
&= -\frac{3\ k_{\mathrm{F}}}{4\pi}.
\end{aligned}
$$

This is very classic textbook knowledge.

P. A. M. Dirac, "note on exchange phenomena in the Thomas atom", Mathematical Proceedings of the Cambridge Philosophical Society, 1930.

# Exchange energy per particle of the HEG

$$\epsilon_x^{NR} = -\frac{3\ k_F}{4\pi}$$



# Exchange energy per particle of the RHEG

For the relativistic Coulomb-Breit exchange energy per particle we have:

$$\epsilon_{\mathrm{x}}^{\mathrm{CB}} = -\frac{V^2}{2N(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \iint_{V} \frac{e^{-i(\mathbf{k}_1-\mathbf{k}_2).(\mathbf{r}_1-\mathbf{r}_2)}}{V^2} \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \frac{4\pi}{|\mathbf{k}_1-\mathbf{k}_2|^2} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2$$

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$$= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_F}} \frac{4\pi}{|\mathbf{k}_1-\mathbf{k}_2|^2} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2$$

$$= -\frac{3\ k_F}{4\pi} \left( \frac{11}{6} + \frac{7}{3}\tilde{c}^2 - \frac{1}{3}\left(1 + 8\tilde{c}^2 + 7\tilde{c}^4\right) \ln\left(1 + \frac{1}{\tilde{c}^2}\right) + \frac{2}{3}\sqrt{1+\tilde{c}^2}\ \mathrm{arcsinh}\left(\frac{1}{\tilde{c}}\right) - \frac{5}{2}\left[\sqrt{1+\tilde{c}^2} - \tilde{c}^2 \mathrm{arcsinh}\left(\frac{1}{\tilde{c}}\right)\right]^2 \right).$$

where we use $\tilde{c} = \frac{mc}{k_F}$ in atomic units.

This is slightly less classic textbook knowledge.

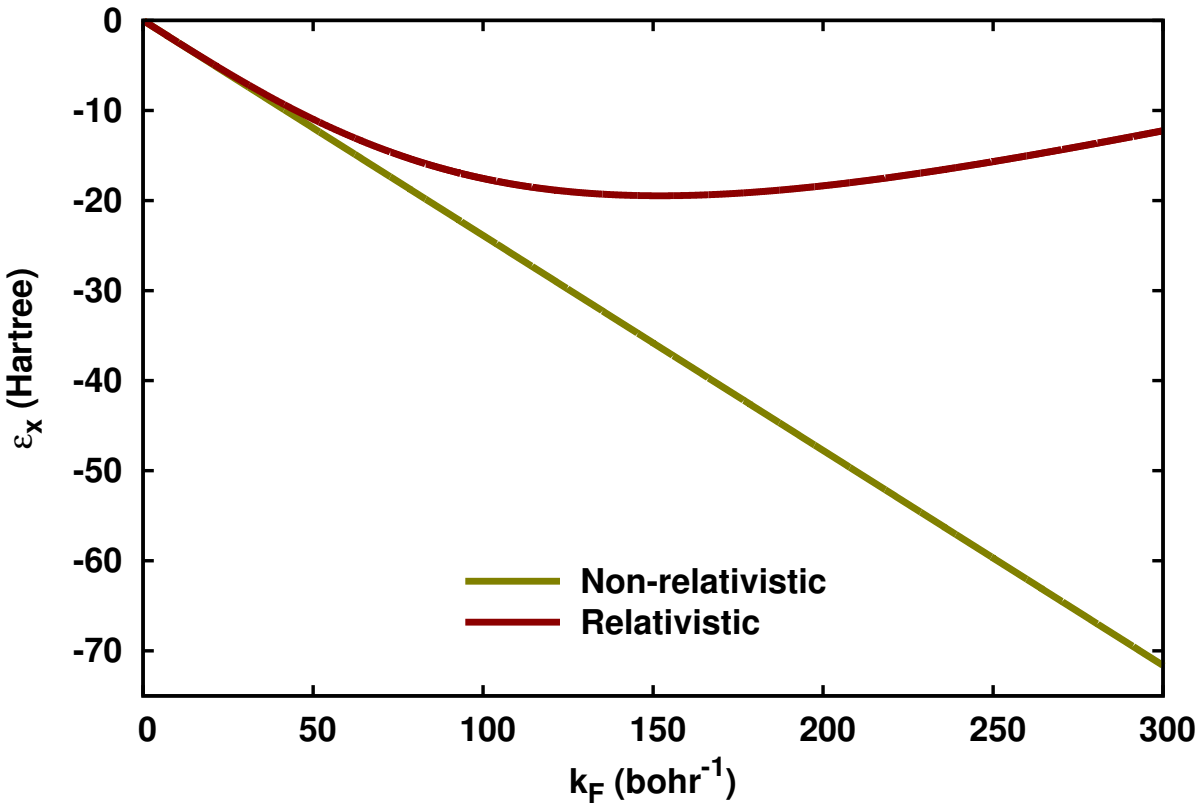
A. H. McDonald and S. H. Vosko, "A relativistic density functional formalism", Journal of Physics C: Solide State Physics,1979.

M. V. Ramana and A. K. Rajagopal, "Effects of correlation and Breit and transverse interactions in the relativistic local-density theory for atoms", Physical Review A, 1982.

# Exchange energy per particle of the RHEG

$$\epsilon_x^{CB} = -\frac{3\ k_F}{4\pi}\left(\frac{11}{6}+\frac{7}{3}\tilde{c}^2-\frac{1}{3}\left(1+8\tilde{c}^2+7\tilde{c}^4\right)\ln\left(1+\frac{1}{\tilde{c}^2}\right)+\frac{2}{3}\sqrt{1+\tilde{c}^2}\,\text{arcsinh}\left(\frac{1}{\tilde{c}}\right)-\frac{5}{2}\left[\sqrt{1+\tilde{c}^2}-\tilde{c}^2\text{arcsinh}\left(\frac{1}{\tilde{c}}\right)\right]^2\right)$$

,




where $\tilde{c} = \frac{mc}{k_F}$.

# Exchange pair distribution function of the RHEG

We express the exchange energy:

$$\epsilon_{\mathrm{x}}^{\mathrm{CB}} = \frac{1}{2}\int_V n\, g_{\mathrm{x}}^{\mathrm{CB}}(r)\frac{1}{r}d\mathbf{r}$$

using the exchange pair distribution:

$$g_{\mathrm{x}}^{\mathrm{CB}}(r) = -\frac{9}{4}\frac{1}{k_{\mathrm{F}}^2 r^2}\left\{-j_1(k_{\mathrm{F}}r)^2 + 3(1-\lambda)A_\lambda(k_{\mathrm{F}}r)^2 + \lambda B_\lambda(k_{\mathrm{F}}r)^2\right\},$$

where

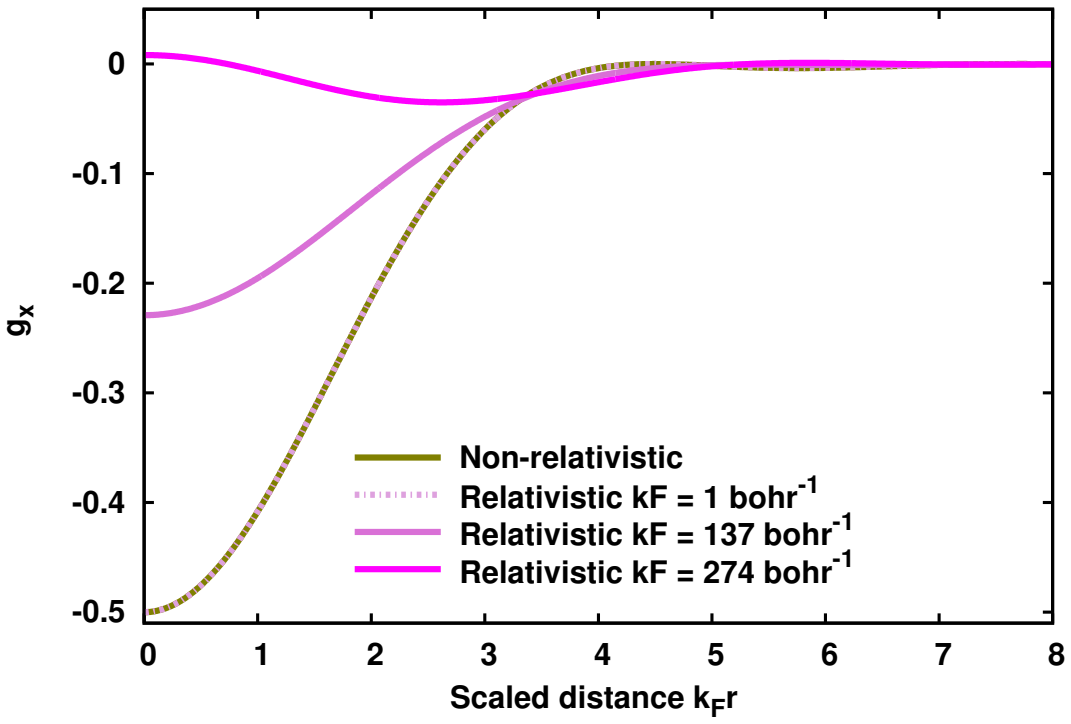
- $\lambda = \dfrac{k_{\mathrm{F}}^2}{k_{\mathrm{F}}^2 + m^2c^2}$
- $A_\lambda(k_{\mathrm{F}}r) = \sum_{k=0}^{\infty}\left[\dfrac{(2k+1)!!}{(2k+1)}\right] j_{k+1}(k_{\mathrm{F}}r)\lambda^k \dfrac{1}{k_{\mathrm{F}}^k r^k}$
- $B_\lambda(k_{\mathrm{F}}r) = \sum_{k=0}^{\infty}\left[\dfrac{(2k+1)!!}{(2k+1)}\right] j_{k+2}(k_{\mathrm{F}}r)\lambda^k \dfrac{1}{k_{\mathrm{F}}^k r^k}$

The Coulomb part of this equation had been published in 1979.

A. H. McDonald and S. H. Vosko, "A relativistic density functional formalism", Journal of Physics C: Solide State Physics,1979.

# Effective exchange pair distribution function of the RHEG

We have defined an effective relativistic exchange Fermi hole.




The on-top exchange pair distribution function appears very much affected by relativistic effects.

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# Short-range Coulomb-Breit interaction potential

$$\hat{W}_{ee}^{\mathrm{CB,sr},\mu} = \sum_{i<j}^{N} \frac{1 - erf(\mu r)}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i<j}^{N} \frac{1 - erf(\mu r)}{|\mathbf{r}_i - \mathbf{r}_j|} \left( \boldsymbol{\alpha}_i . \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i . (\mathbf{r}_i - \mathbf{r}_j))(\boldsymbol{\alpha}_j . (\mathbf{r}_i - \mathbf{r}_j))}{2|\mathbf{r}_i - \mathbf{r}_j|^2} \right)$$

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# Expression of the short-range exchange energy per particle

For the short-range Coulomb-Breit exchange energy per particle we have:

$$\epsilon_{\mathrm{x}}^{\mathrm{CB,sr},\mu} = -\frac{V^2}{2N(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \iint_{V} \frac{e^{-i(\mathbf{k}_1-\mathbf{k}_2).(\mathbf{r}_1-\mathbf{r}_2)}}{V^2} \frac{1-\mathrm{erf}(\mu|\mathbf{r}_1-\mathbf{r}_2|)}{|\mathbf{r}_1-\mathbf{r}_2|} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \frac{4\pi\left(1-e^{-\frac{|\mathbf{k}_1-\mathbf{k}_2|^2}{4\mu^2}}\right)}{|\mathbf{k}_1-\mathbf{k}_2|^2} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2$$

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$$= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \frac{4\pi\left(1-e^{-\frac{|\mathbf{k}_1-\mathbf{k}_2|^2}{4\mu^2}}\right)}{|\mathbf{k}_1-\mathbf{k}_2|^2} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2$$

$$= \frac{3k_{\mathrm{F}}}{4\pi} \int_{\tilde{k}_1=0}^{1} \int_{\tilde{k}_2=0}^{1} \tilde{k}_1\tilde{k}_2 \Bigg( \frac{1}{\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}} \left[ \tilde{k}_1\tilde{k}_2 + \left( e^{-(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}})^2} - e^{-(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}})^2} \right) \tilde{\mu}^2 \right]$$

$$+ \frac{6\tilde{c}^2+\tilde{k}_1^2+\tilde{k}_2^2-2\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}}{4\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}} \left[ \mathrm{Ei}\left(-(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}})^2\right) - \mathrm{Ei}\left(-(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}})^2\right) \right.$$

$$\left. + \ln\left((\tilde{k}_1-\tilde{k}_2)^2\right) - \ln\left((\tilde{k}_1+\tilde{k}_2)^2\right) \right] \Bigg) d\tilde{k}_1 d\tilde{k}_2,$$

where $\tilde{k}_\lambda = \frac{k_\lambda}{k_{\mathrm{F}}}$, $\tilde{\mu} = \frac{\mu}{k_{\mathrm{F}}}$ and Ei is the exponential integral function.

# Expression of the short-range exchange energy per particle

For the short-range Coulomb-Breit exchange energy per particle we have:

$$\epsilon_{\mathrm{x}}^{\mathrm{CB,sr},\mu} = -\frac{V^2}{2N(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \iint_{V} \frac{e^{-i(\mathbf{k}_1-\mathbf{k}_2).(\mathbf{r}_1-\mathbf{r}_2)}}{V^2} \frac{1-\mathrm{erf}(\mu|\mathbf{r}_1-\mathbf{r}_2|)}{|\mathbf{r}_1-\mathbf{r}_2|} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{r}_1 d\mathbf{r}_2$$

$$= -\frac{1}{2n(2\pi)^6} \iint_{V_{k_{\mathrm{F}}}} \frac{4\pi\left(1-e^{-\frac{|\mathbf{k}_1-\mathbf{k}_2|^2}{4\mu^2}}\right)}{|\mathbf{k}_1-\mathbf{k}_2|^2} \left( \frac{-E_{k_1}E_{k_2} + \mathbf{k}_1.\mathbf{k}_2 c^2 + 3m^2c^4}{E_{k_1}E_{k_2}} \right) d\mathbf{k}_1 d\mathbf{k}_2$$

$$= \frac{3k_{\mathrm{F}}}{4\pi} \int_{\tilde{k}_1=0}^{1} \int_{\tilde{k}_2=0}^{1} \tilde{k}_1\tilde{k}_2 \left( \frac{1}{\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}} \left[ \tilde{k}_1\tilde{k}_2 + \left( e^{-(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}})^2} - e^{-(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}})^2} \right) \tilde{\mu}^2 \right] \right.$$

$$+ \frac{6\tilde{c}^2+\tilde{k}_1^2+\tilde{k}_2^2-2\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}}{4\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}} \left[ \mathrm{Ei}\left(-(\frac{\tilde{k}_1+\tilde{k}_2}{2\tilde{\mu}})^2\right) - \mathrm{Ei}\left(-(\frac{\tilde{k}_1-\tilde{k}_2}{2\tilde{\mu}})^2\right) \right.$$

$$\left.\left. + \ln\left((\tilde{k}_1-\tilde{k}_2)^2\right) - \ln\left((\tilde{k}_1+\tilde{k}_2)^2\right) \right] \right) d\tilde{k}_1 d\tilde{k}_2,$$

where $\tilde{k}_\lambda = \frac{k_\lambda}{k_{\mathrm{F}}}$, $\tilde{\mu} = \frac{\mu}{k_{\mathrm{F}}}$ and Ei is the exponential integral function.

# Taylor expansion for large values of $\tilde{c}$

Two steps:

- Taylor expansion of the integrand for large values of $\tilde{c}$.

$$\frac{1}{\sqrt{\tilde{c}^2+\tilde{k}_1^2}\sqrt{\tilde{c}^2+\tilde{k}_2^2}} = \frac{1}{16\pi\tilde{c}^2} - \frac{\tilde{k}_1^2+\tilde{k}_2^2}{32\pi\tilde{c}^4} + \mathrm{o}\Big(\frac{1}{\tilde{c}^6}\Big)$$

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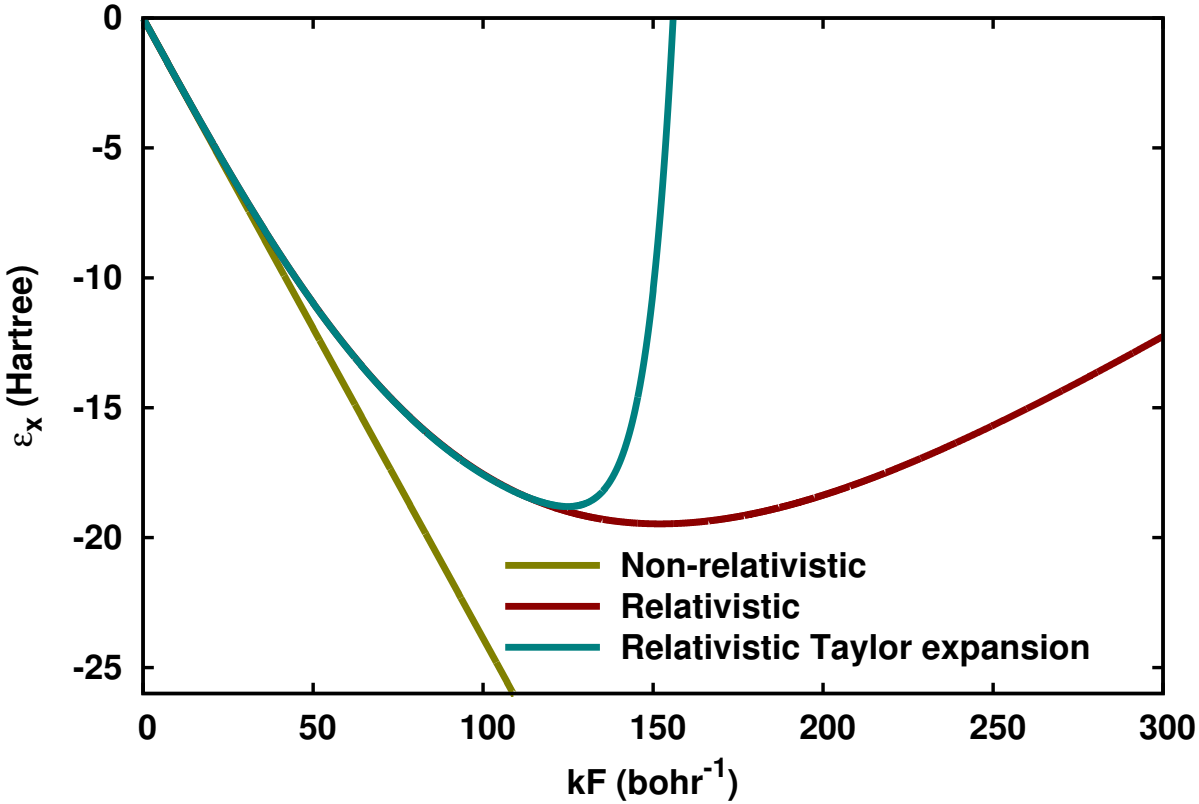
- Analytical integration of the general term of the Taylor expansion.

$$\epsilon_{\mathrm{x}}^{\mathrm{CB,sr},\mu} = \frac{k_{\mathrm{F}}}{4\pi}\left[-3+2\tilde{\mu}^2\left(-3+2\tilde{\mu}^2-\left(-2+\tilde{\mu}^2\right)e^{-\frac{1}{\tilde{\mu}^2}}\right)+4\sqrt{\pi}\tilde{\mu}\ \mathrm{erf}\left(\frac{1}{\tilde{\mu}}\right)\right]$$
$$+\frac{k_{\mathrm{F}}}{10\pi\tilde{c}^2}\left[6\tilde{\mu}^2\left(-1-2\tilde{\mu}^2+3\tilde{\mu}^4\right)e^{-\frac{1}{\tilde{\mu}^2}}-\left(-5-15\tilde{\mu}^2-30\tilde{\mu}^4+18\tilde{\mu}^6+3\sqrt{\pi}\tilde{\mu}\left(2+5\tilde{\mu}^2\right)\ \mathrm{erf}\left(\frac{1}{\tilde{\mu}}\right)\right)\right]+\mathrm{O}\left(\frac{1}{\tilde{c}^4}\right)$$

# Taylor expansion for large values of $\tilde{c}$

$$\epsilon_x^{\mathrm{CB,sr},\mu} = \sum_{i=0}^{M} \frac{A_{2i}(\tilde{\mu})}{\tilde{c}^{2i}} + \mathrm{O}\left(\frac{1}{\tilde{c}^{2M+2}}\right)$$

For $\mu = 0$ we have a divergent expression at $k_F = c$.

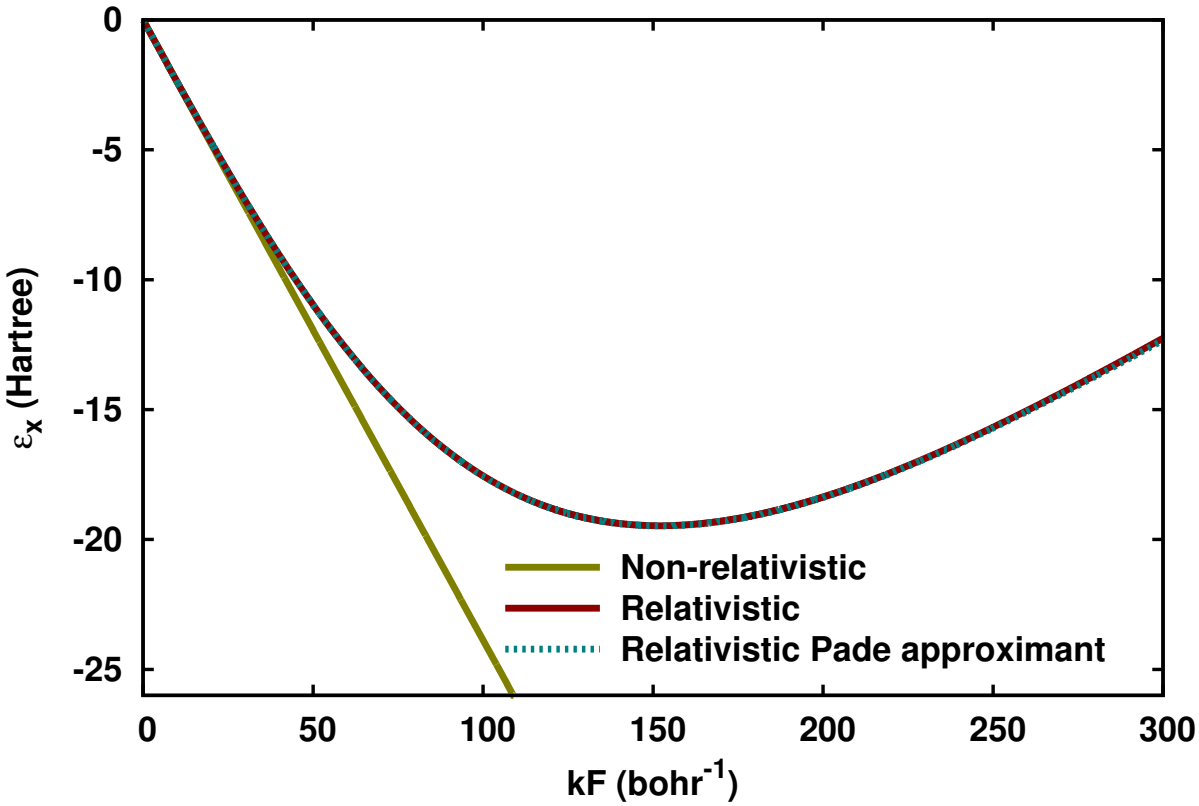



This figure was obtained with the $18^{th}$ order of the Taylor expansion.

# Padé approximant for large values of $\tilde{c}$

$$\epsilon_x^{\mathrm{CB,sr},\mu} \approx \frac{\sum_{i=0}^{M} \frac{B_{2i}(\tilde{\mu})}{\tilde{c}^{2i}}}{\sum_{j=0}^{M} \frac{C_{2j}(\tilde{\mu})}{\tilde{c}^{2j}}}$$

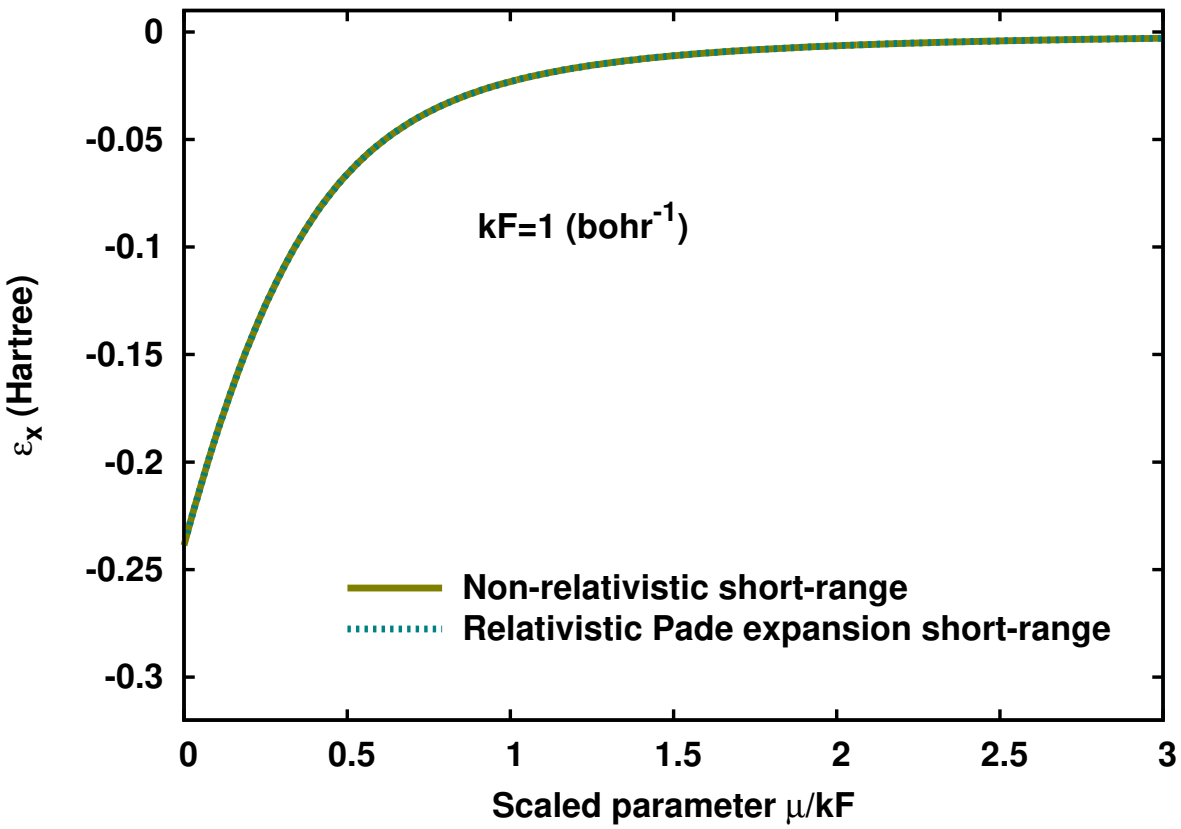
For $\mu = 0$ we have removed the divergency.




This figure was obtained with the $6^{th}$ order of the Padé approximant.

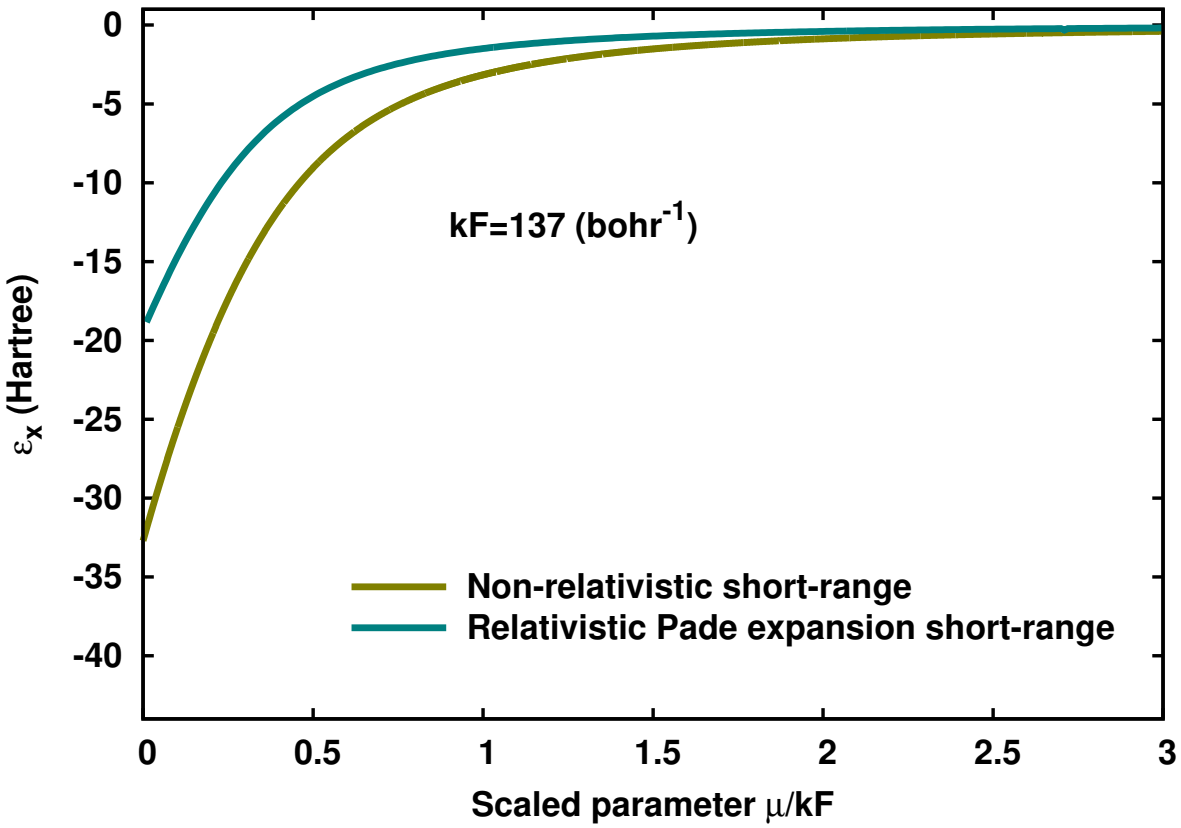
# Short-range exchange energy per particle of the RHEG

$$\epsilon_x^{\mathrm{NR,sr},\mu} = \frac{k_F}{4\pi}\left[-3 + 2\frac{\mu^2}{k_F^2}\left(-3 + 2\frac{\mu^2}{k_F^2} - \left(-2 + \frac{\mu^2}{k_F^2}\right)e^{-\frac{k_F^2}{\mu^2}}\right) + 4\sqrt{\pi}\frac{\mu}{k_F}\,\mathrm{erf}\left(\frac{k_F}{\mu}\right)\right]$$

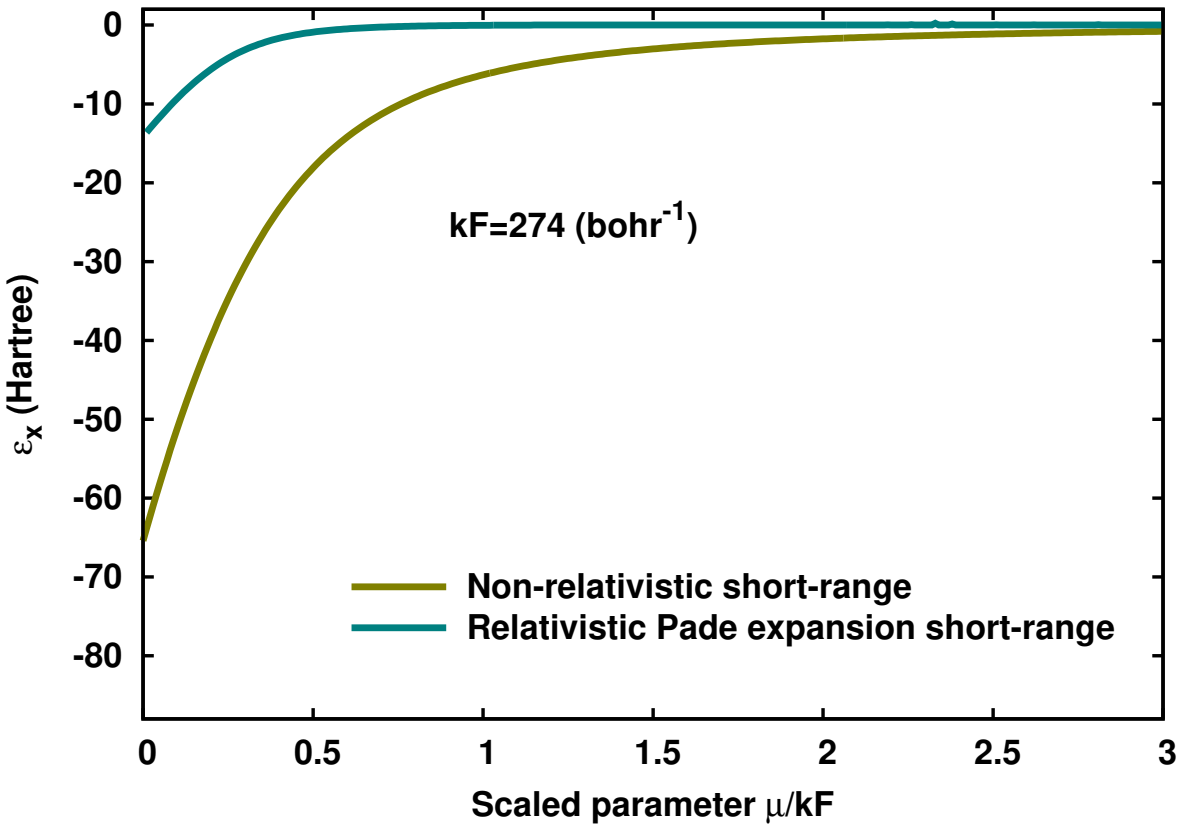



A. Savin, "Beyond the Kohn-Sham Determinant", World Scientific, 1996

# Short-range exchange energy per particle of the RHEG



# Short-range exchange energy per particle of the RHEG



# Conclusion

## Take-home message

- Relativity decreases the exchange energy in absolute value within high electronic density regions.
- Construction of a systematic approximant of a relativistic short-range local-density approximation exchange functional.

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# Conclusion

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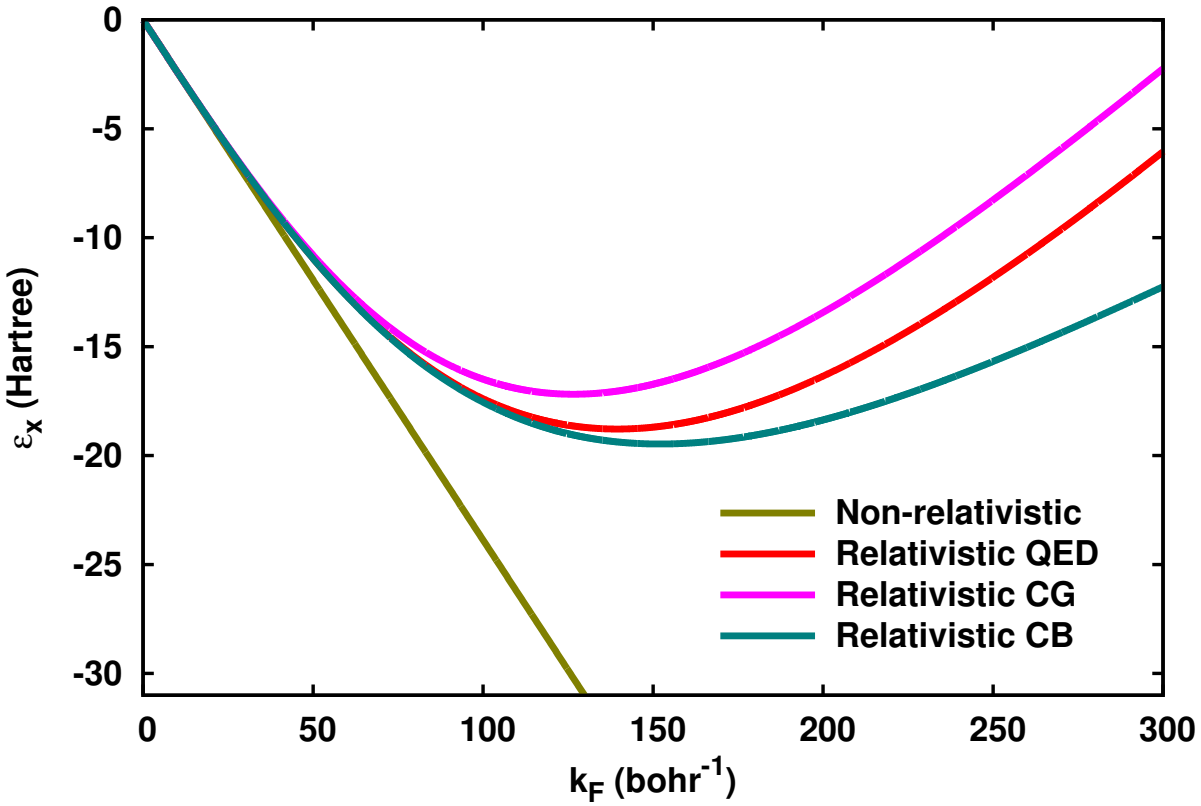
## Perspectives

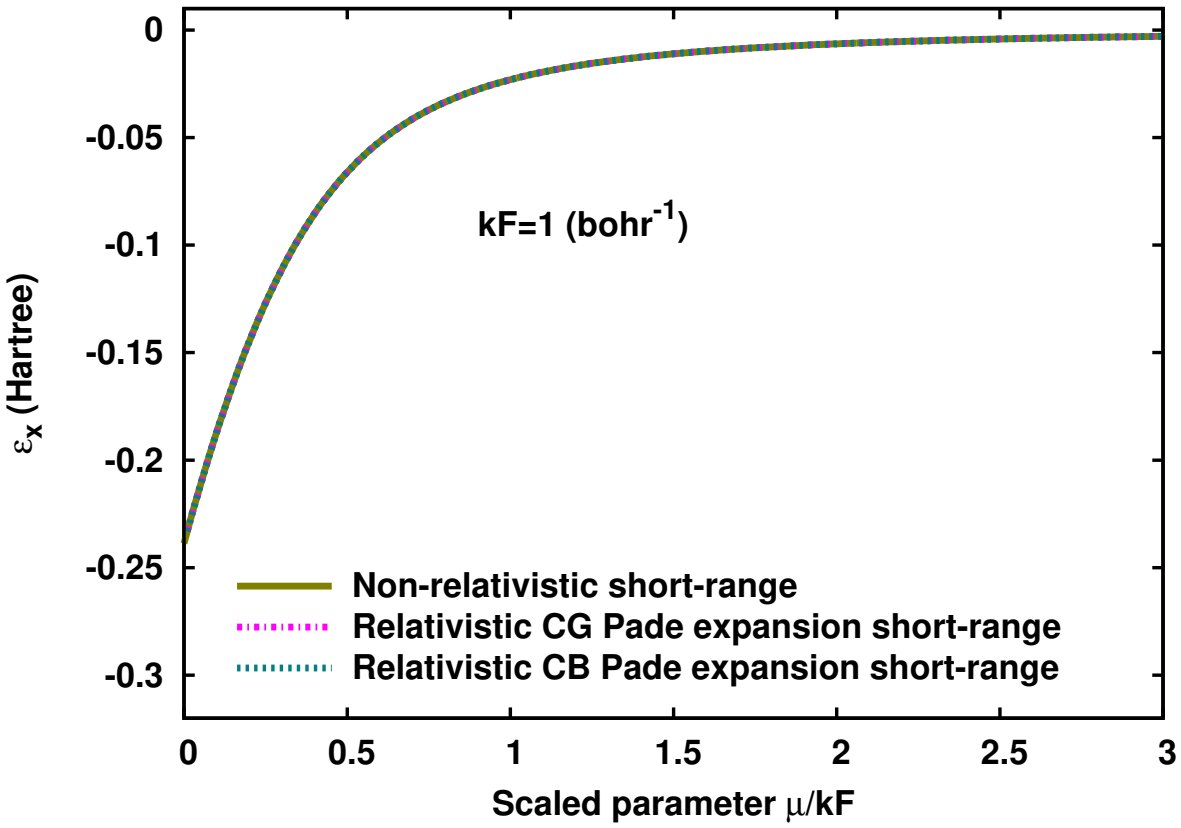
- Implementation of a four-component range-separated scheme in order to test our functional on real systems.
- Extension to a relativistic short-range correlation functional.

# Comparison between QED, Coulomb-Gaunt and Coulomb-Breit full-range exchange energies per particle




A. K. Rajagopal, "Inhomogeneous relativistic electron gas", J. Phys. C : Solid State Physics, 1978.

# Comparison between Coulomb-Gaunt and Coulomb-Breit short-range exchange energies per particle



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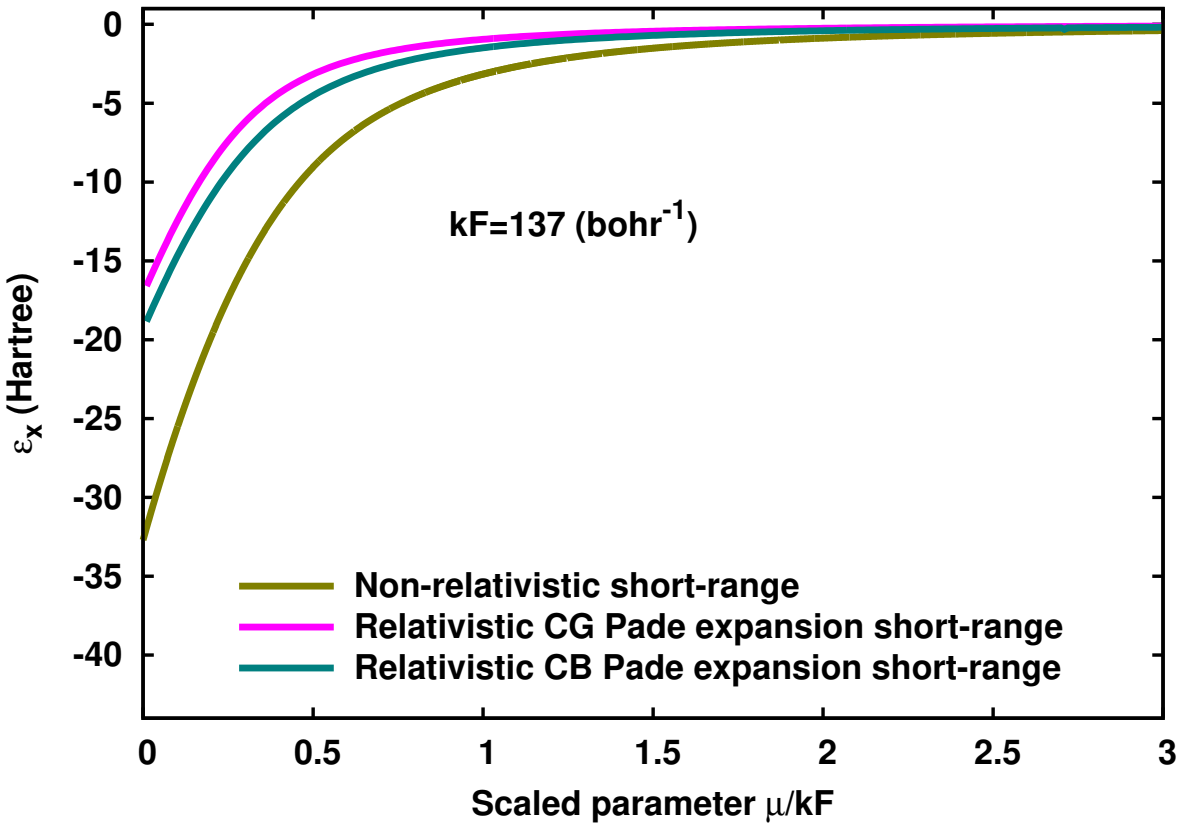

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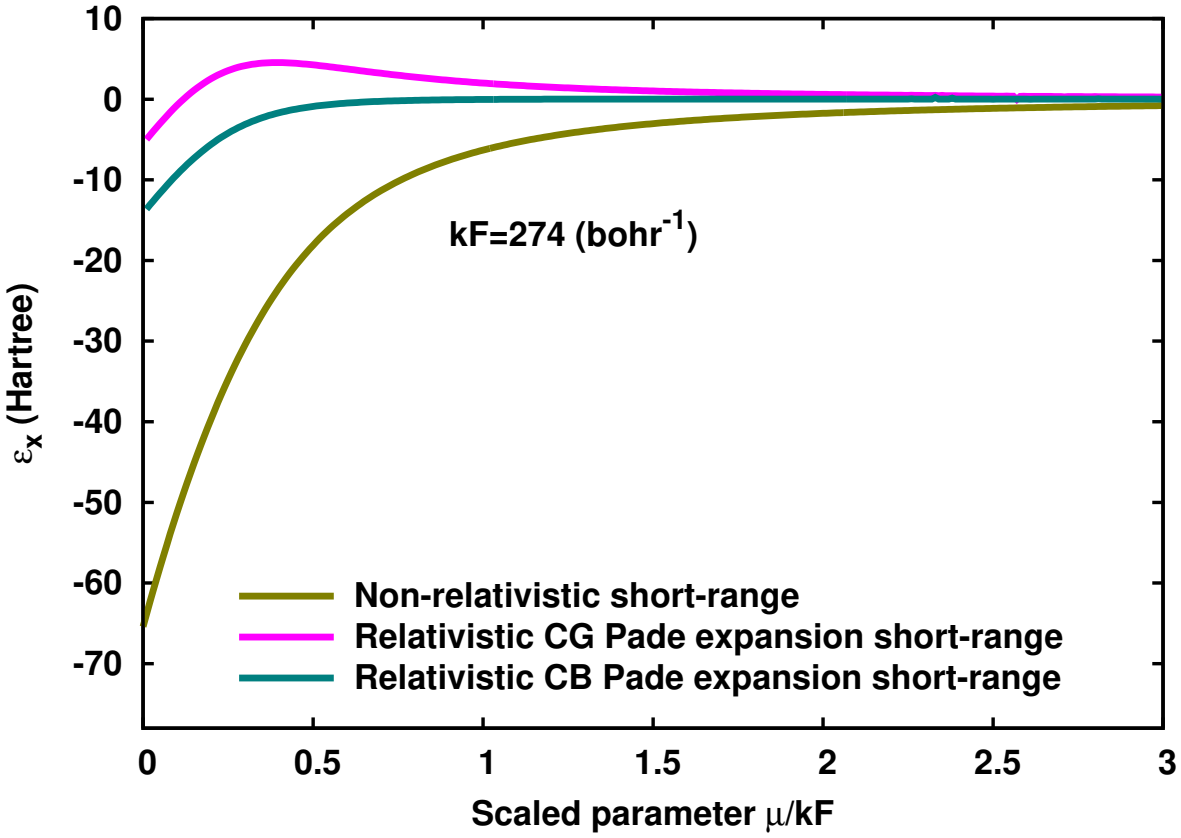

Thank you for your attention.