BEYOND KOHN-SHAM DFT: EXPLICITLY CORRELATED WAVE FUNCTIONS

Martin Panholzer

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JOHANNES KEPLER
UNIVERSITY LINZ

FWF
Der Wissenschaftsfonds.

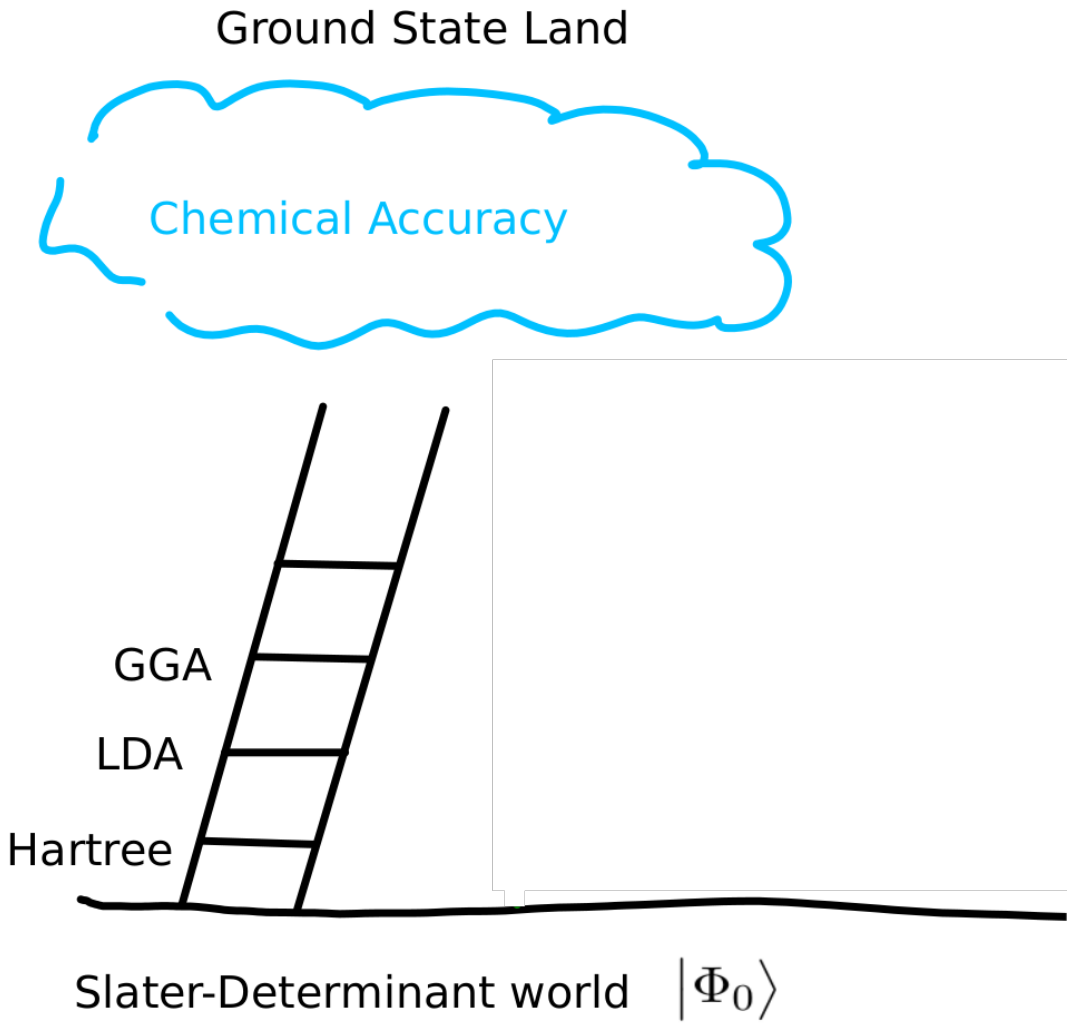
Motivation

1. The present status of DFT is a bit unsatisfactory:
   - There are a lot of different functionals for different situations
   - Newly developed functionals in DFT, designed to improve in the energy estimate, do not necessarily reduce the error in the density.[1]
   - No systematic error estimation

2. A precise, analytic description of the ground state allows to create accurate excitations.

[1] M. G. Medvedev et al., Science (New York, N.Y.) **355**, 49–52 (2017).

A strategy to extend KS-DFT



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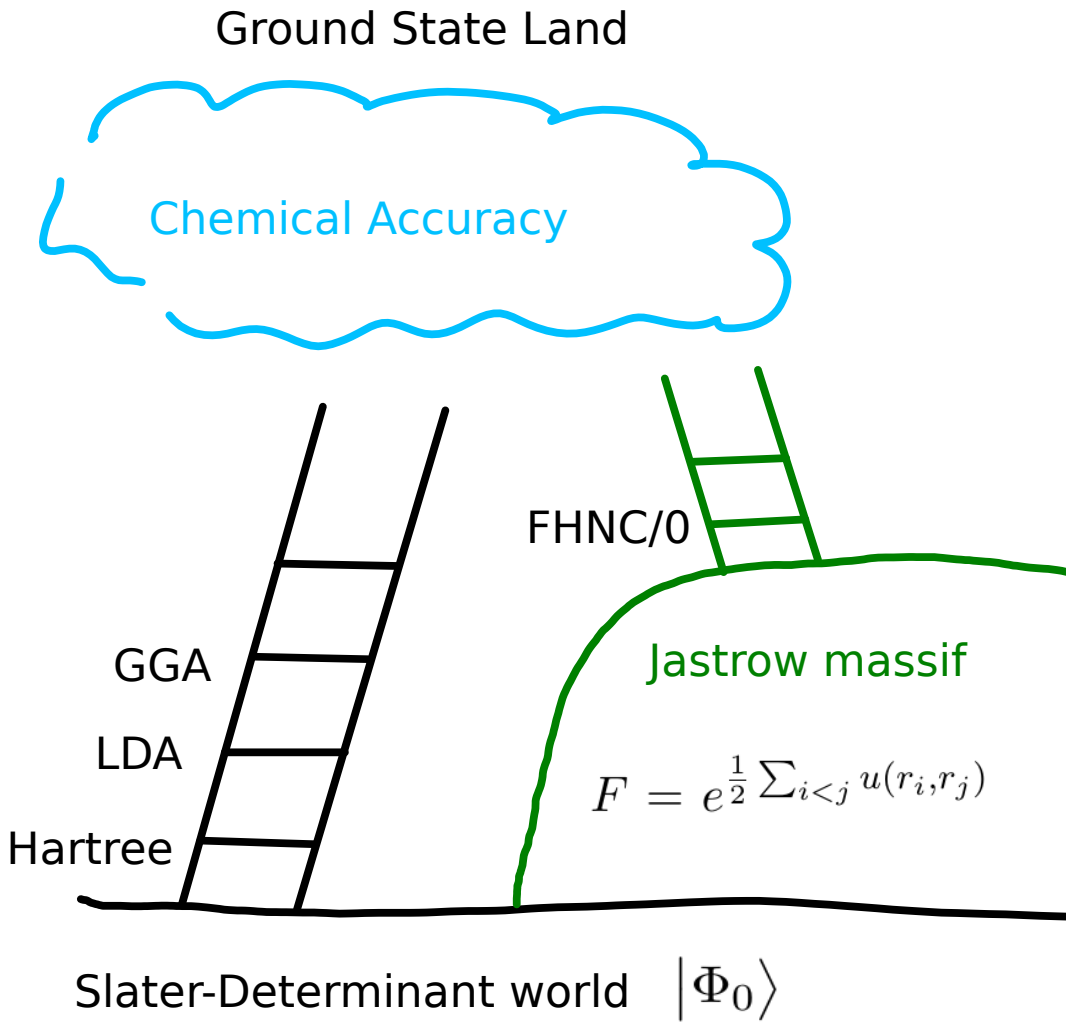


How good is the Jastrow ansatz

There are two points which are missing in order to describe the exact wave function:

- The nodes of the Slater-determinant are unchanged
- Three and higher particle correlations are absent

It depends on the investigated system whether they are critical or not.

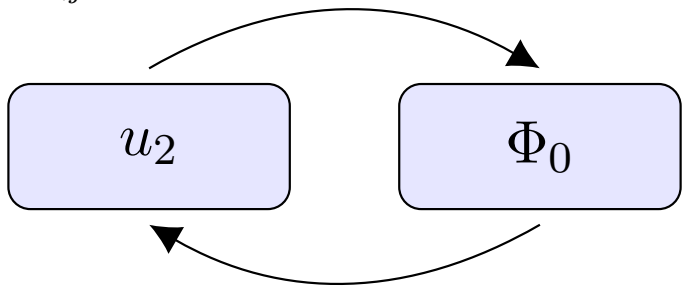
In practical implementations there are additional approximations made.

We should have control over them.

The general strategy

$$F \left|\Phi_0\right\rangle$$

with $F = e^{\sum_i u_1(r_i)} e^{\frac{1}{2}\sum_{i<j} u_2(r_i,r_j)}$



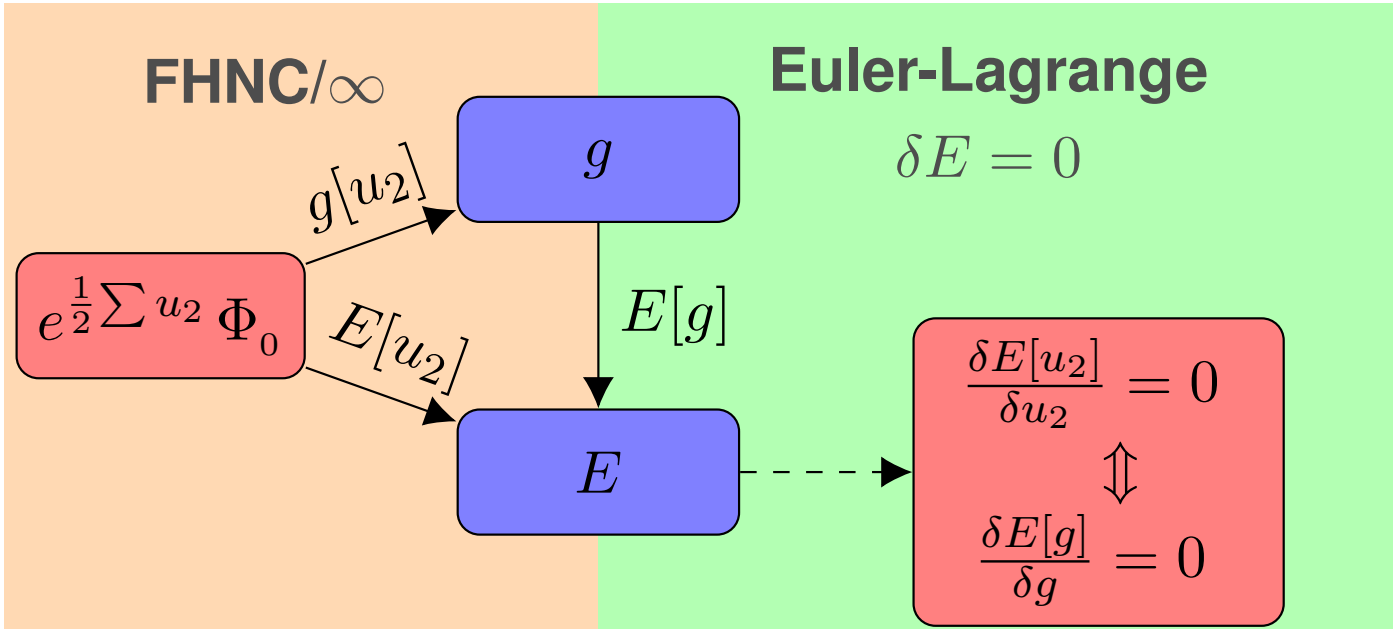
Optimization:

Dependent on: $\rho_F(r,r')$ $u_2, V_{\text{ext}}(r)$

Basic approx.: FHNC-0 Hartree and Hartree-Fock

What is FHNC?

a very brief outline



The FHNC eq. for homogeneous systems

Start with a particular approximation: ladder+[2]

$$\left[-\frac{\hbar^2}{m}\nabla^2 + v(r) + w_{\rm I}(r) + V_F(r) \right] \sqrt{g(r)} = 0 \ ,$$

with

$$\tilde{w}_{\rm I}(q) = -\frac{\hbar^2 q^2}{4m} \left[\frac{1}{S(q)} - \frac{1}{S_{\rm F}(q)} \right]^2 \left[2\frac{S(q)}{S_{\rm F}(q)} + 1 \right] \text{ and } V_F(r) = \frac{\hbar^2 \nabla^2 \sqrt{g_{\rm F}(r)}}{m\sqrt{g_{\rm F}(r)}}$$

an implementation of this and other approx. can be found on github: `github.com/mpanho/FHNC_3D`

For the generalization to periodic systems see ref.[3]

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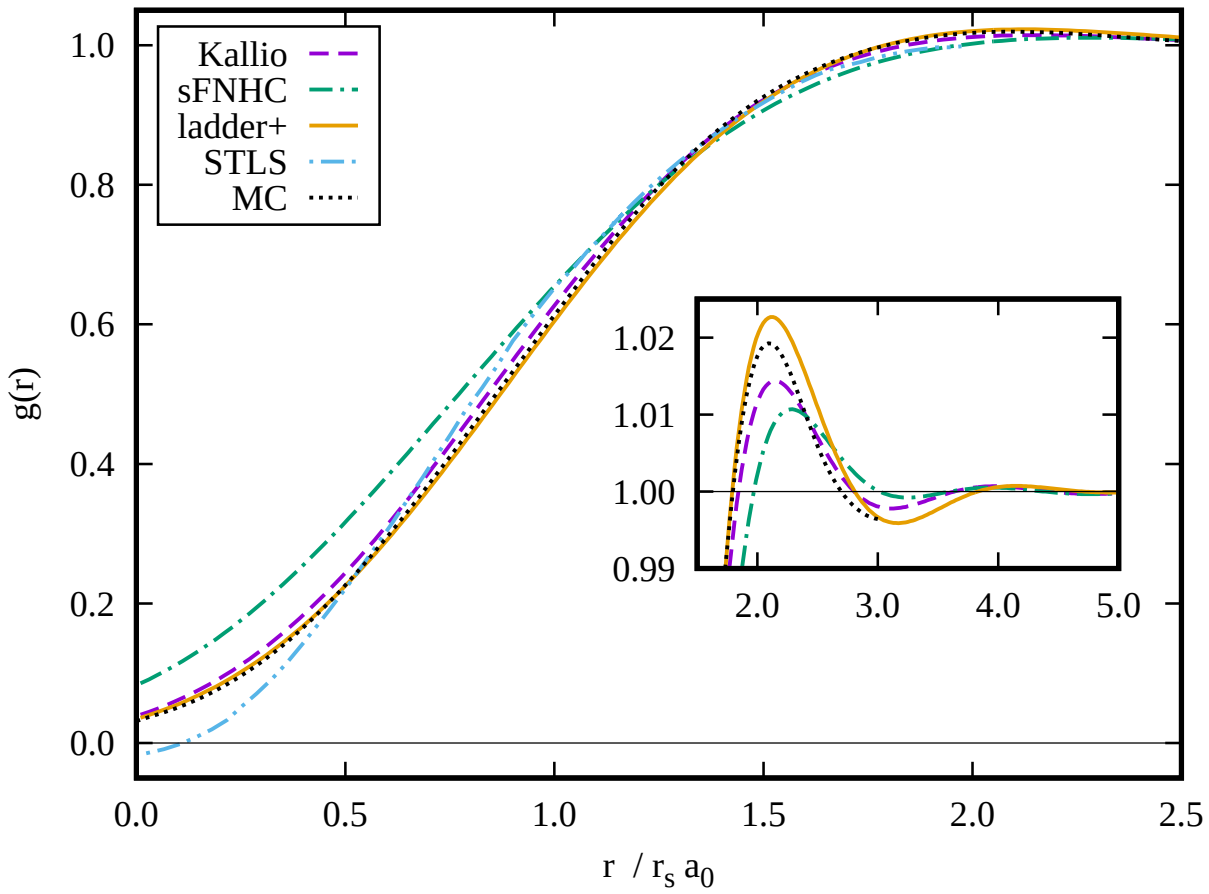
[2] M. Panholzer et al., Physical Review B **99**, 195156 (2019).

[3] M. Panholzer, Journal of Low Temperature Physics **187**, 639–645 (2017).

Pair distribution function 3D

$r_s = 5$



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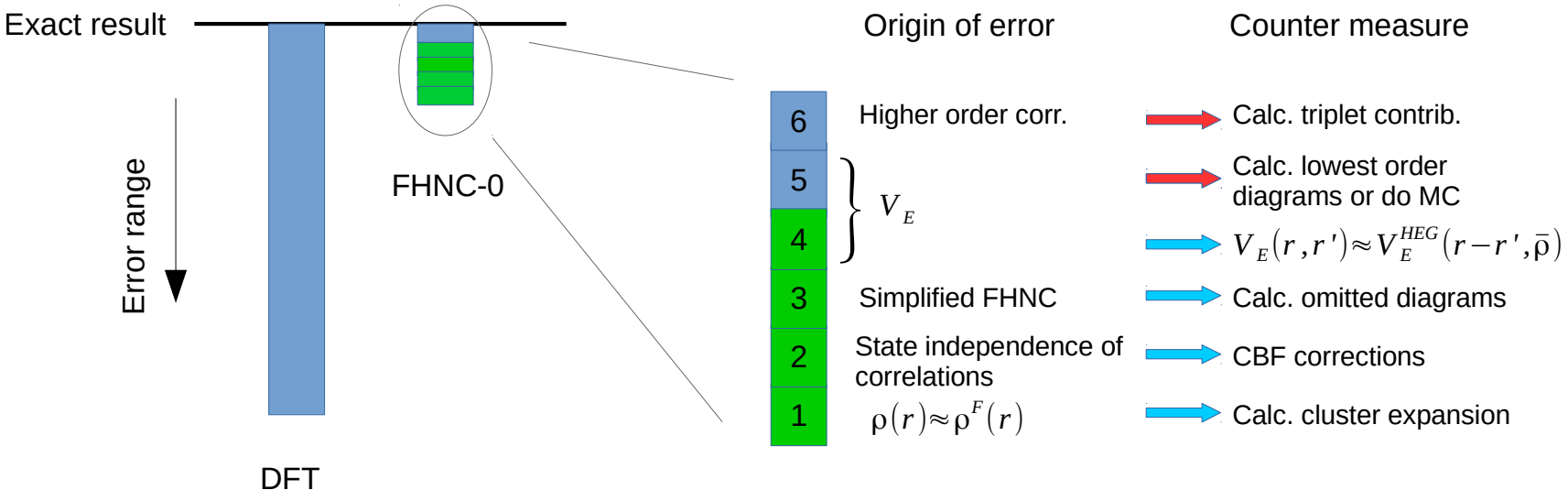
[4] A. Kallio and J. Piilo, Physical review letters **77**, 4237–4240 (1996), K. S. Singwi et al., Phys. Rev. **176**, 589–599 (1968), G. G. Spink et al., Physical Review B **88**, 085121 (2013).

Systematic improvement



Importing exact information

$$\left[-\frac{\hbar^2}{m}\nabla^2 + v(r) + w_{\mathrm{I}}(r) + V_F(r) \right] \sqrt{g(r)} = 0$$

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Importing exact information

$$\left[-\frac{\hbar^2}{m}\nabla^2 + v(r) + w_{\mathrm{I}}(r) + V_F(r) + V_R(r) \right] \sqrt{g(r)} = 0$$

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$V_R(r)$ contains all residual approximations.

It is calculated for all densities introducing $V_R^{r_s}(r)$, e.g. from MC results for the pair distribution function $g_{MC}^{r_s}(r)$

Do the analog of the “LDA” step

Importing to the real system:

MDA

$$V_R(r,r') \approx V_R^{\bar{r}_s}(r-r')$$

LDA-like

$$\begin{cases} V_R(r,r') \approx V_R^{r_s(r)}(r-r') \\ V_R(r,r') \approx V_R^{r_s(\frac{r+r'}{2})}(r-r') \\ V_R(r,r') \approx \frac{1}{2}(V_R^{r_s(r)}(r-r') + V_R^{r_s(r')}(r-r')) \\ V_R(r,r') \approx V_R^{\frac{2r_s(r)r_s(r')}{r_s(r)+r_s(r')}}(r-r') \\ V_R(r,r') \approx V_R^{\frac{r_s(r)+r_s(r')}{2}}(r-r') \end{cases}$$

or use the connector approach[5]

[5] M. Vanzini et al., arxiv:1903.07930v1, 1–6 (2019).

Finding the orbitals[6]

So we have $\frac{\delta}{\delta u_2(r,r')} E[u_2] = 0$ ✓

What about the Φ_0?

The optimization wrt. to the orbitals ϕ_k leads to a generalized HF eq.:

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V_{ext}(r) + V_H(r)\right]\phi_k(r) - \frac{1}{\nu}\int dr' V_F(r,r')\rho_1^F(r,r')\phi_k(r') = e_k\phi_k(r)$$

... this reminds a bit on hybrid functionals.

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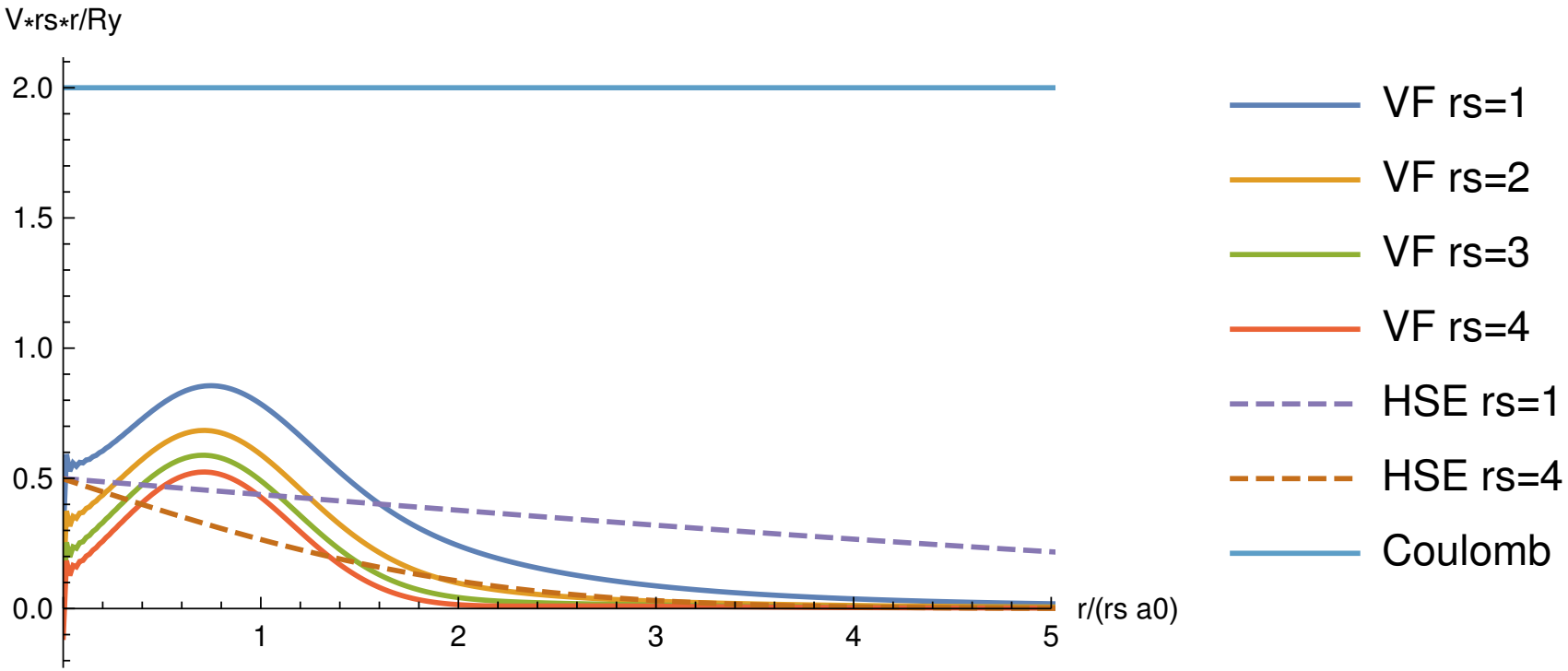
[6] E. Krotscheck, Physical Review B **31**, 4267–4278 (1985), E. Krotscheck et al., Physical Review B **32**, 5693–5712 (1985).

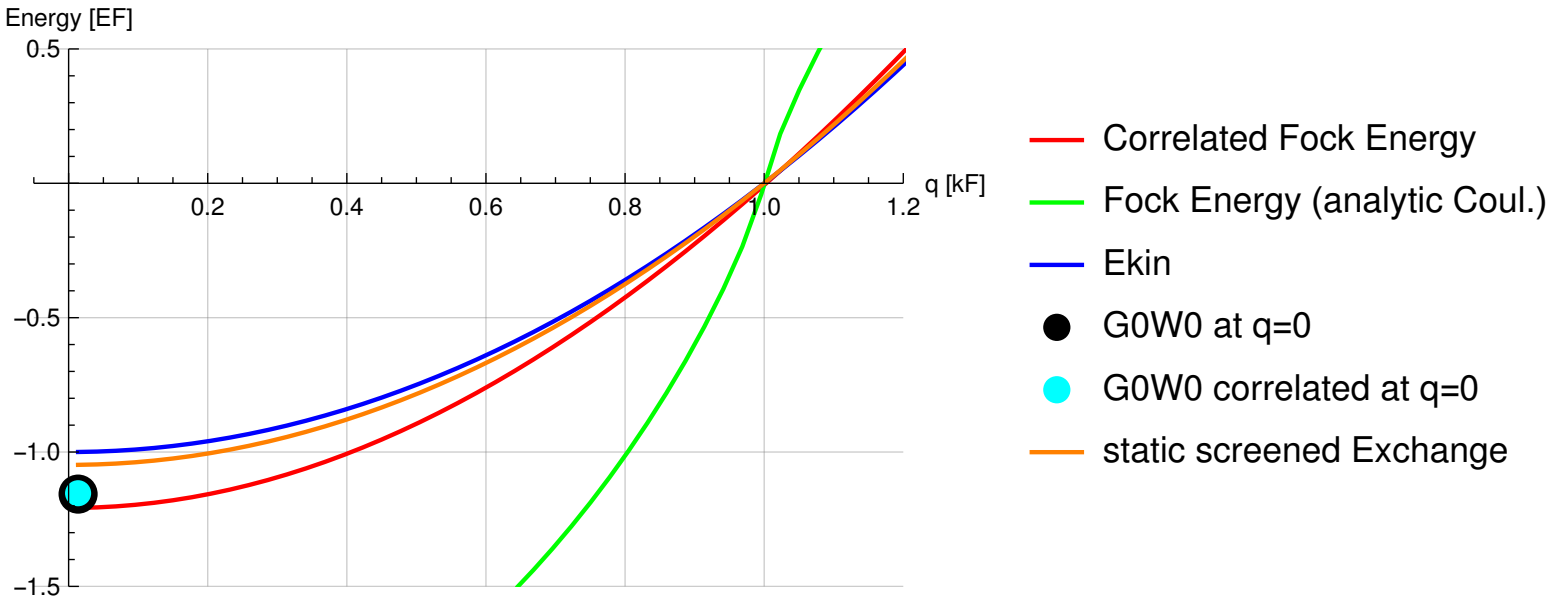
Comparison of V_F and the HSE06[7] potential



[7] J. Heyd et al., Journal of Chemical Physics **124**, 2005–2006 (2006).

Quasiparticle energy

Single particle energy at $r_s = 4$



Can we map this on a Kohn-Sham system:

Yes! The exchange correlation energy is given by[8]

$$E_{XC} = \int dr \int du \, \frac{v(u)}{2} n(r) n_{XC}(r, r+u)$$

with the coupling constant integrated exchange correlation hole

$$n_{XC} = \int_0^1 d\lambda \, n_{XC,\lambda}, \quad n_{XC,\lambda}(r, r') = \left[g_\lambda(r, r') - 1 \right] n(r')$$

$$V_{XC}(r) = \frac{\delta E_{XC}}{\delta n(r)}$$

not so easy for MC, but in FHNC we have an analytic formula.

[8] K. Burke et al., Journal of Chemical Physics **109**, 3760–3771 (1998).

What we gain and what we loose

- ✓ Simple treatment for the one body density
- ✓ Comparison with known results
- x Loss of quantitative band structure
- x Strictly speaking we have to do: $\Phi_{KS} \rightarrow \Phi_0$

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Results for the 1D model system

Interaction potential

Derived from the electron gas in a homogeneous trap

$$v(r) = \frac{e^2\sqrt{2}}{2b} \exp \frac{r^2}{4b^2} \operatorname{erfc} \frac{|\mathrm{r}|}{2\mathrm{b}}$$

$b = 0.1a_B$ determines the thickness of the harmonic trap.

Results I

A model for the orbitals:

Def: Single particle orbitals

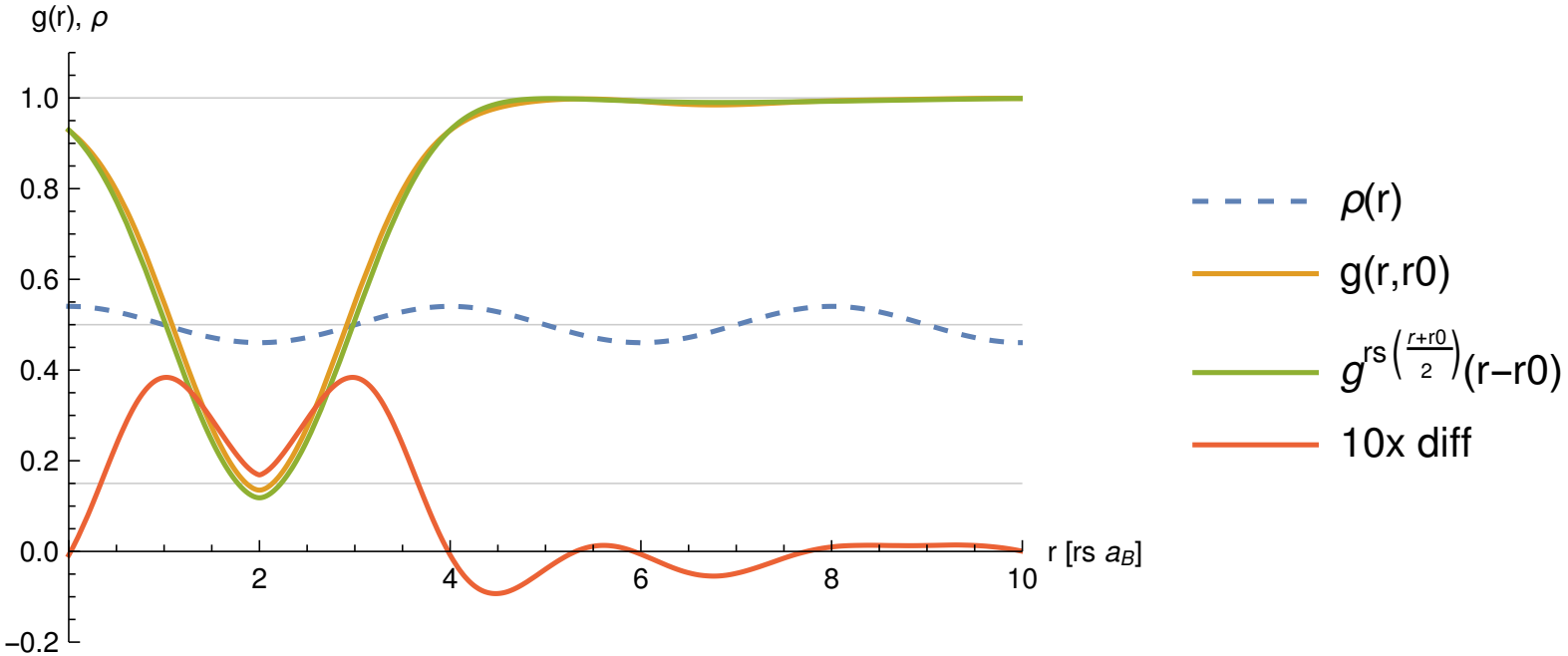
$$\sqrt{V_{\text{Crystal}}}\phi_k(r) = \sqrt{1-2\lambda^2}e^{ikr} + \lambda e^{i(k+G)r} + \lambda e^{i(k-G)r} \ . \quad (1)$$

$\Rightarrow$ sinusoidal modulated density, amplitude determined by λ.

$G = \frac{2\pi}{a}$ is the reciprocal lattice vector and

a the length of the unit cell.

Results[9]



[9] M. Panholzer, Journal of Low Temperature Physics **187**, 639–645 (2017), M. Panholzer et al., Physical Review Letters **120**, 166402 (2018).

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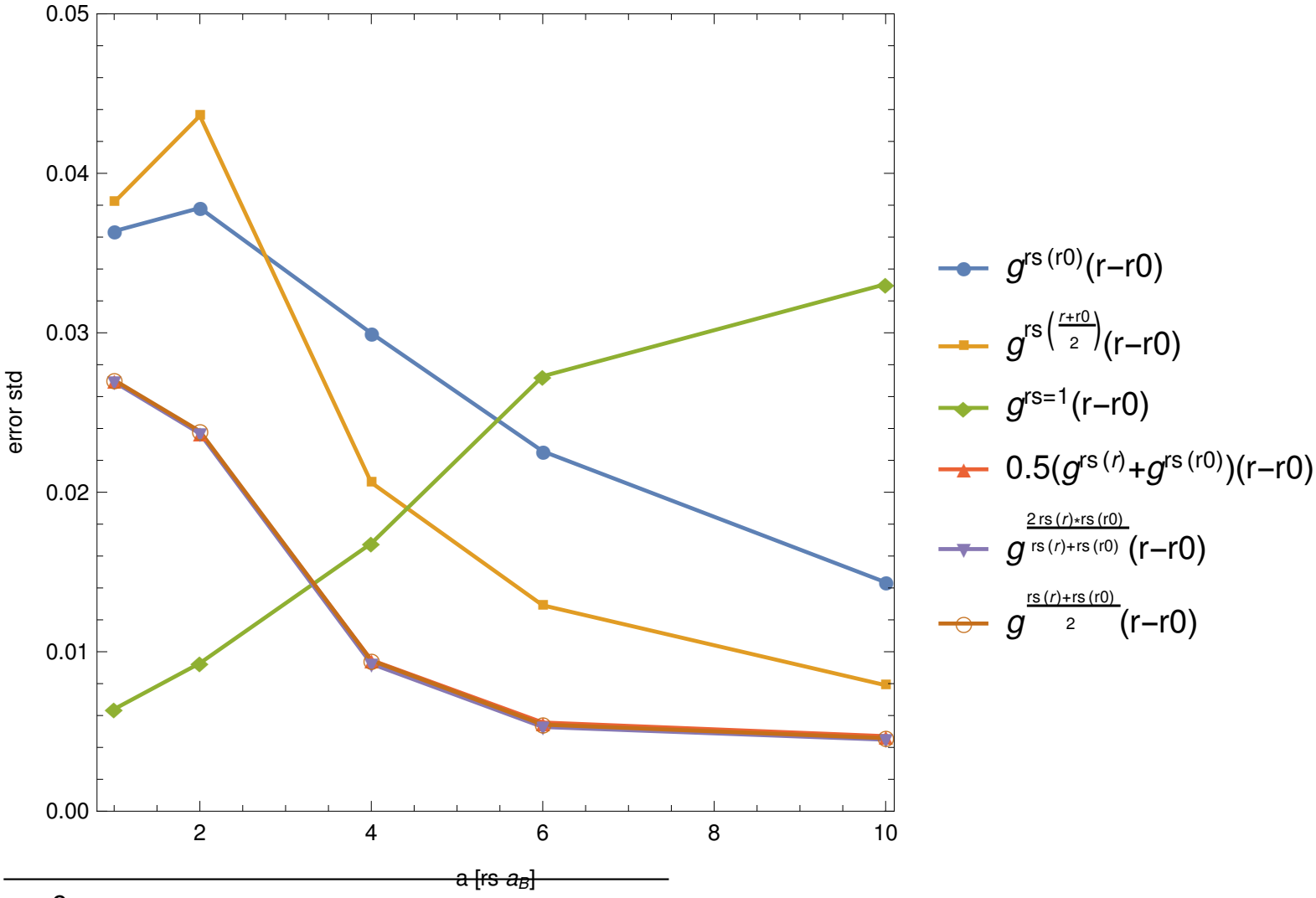
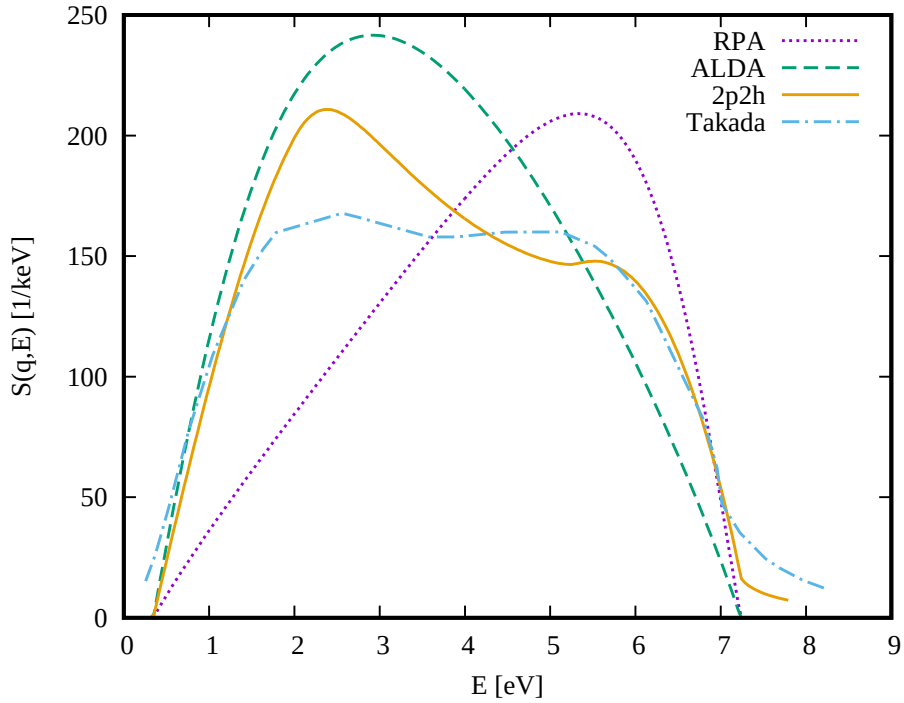


[9] M. Panholzer, Journal of Low Temperature Physics **187**, 639–645 (2017), M. Panholzer et al., Physical Review Letters **120**, 166402 (2018).

Excitations

Having a ground state for realistic solids, allows us to do excitations in the same way as we did for homogeneous systems.[10] To obtain e.g. $S(q, \omega)$ at $r_s = 8, q = 2.2k_F$[11]



[10] M. Panholzer et al., Physical Review Letters **120**, 166402 (2018), H. M. Böhm et al., Physical Review B **82**, 224505 (2010), H. Godfrin et al., Nature **483**, 576–579 (2012).

[11] Y. Takada, Phys. Rev. B **94**, 245106 1–14 (2016).

Summary

- Simple FHNC approximation
- Strategy to extend the KS idea to the pair distribution function
- First results in 1D

Outlook

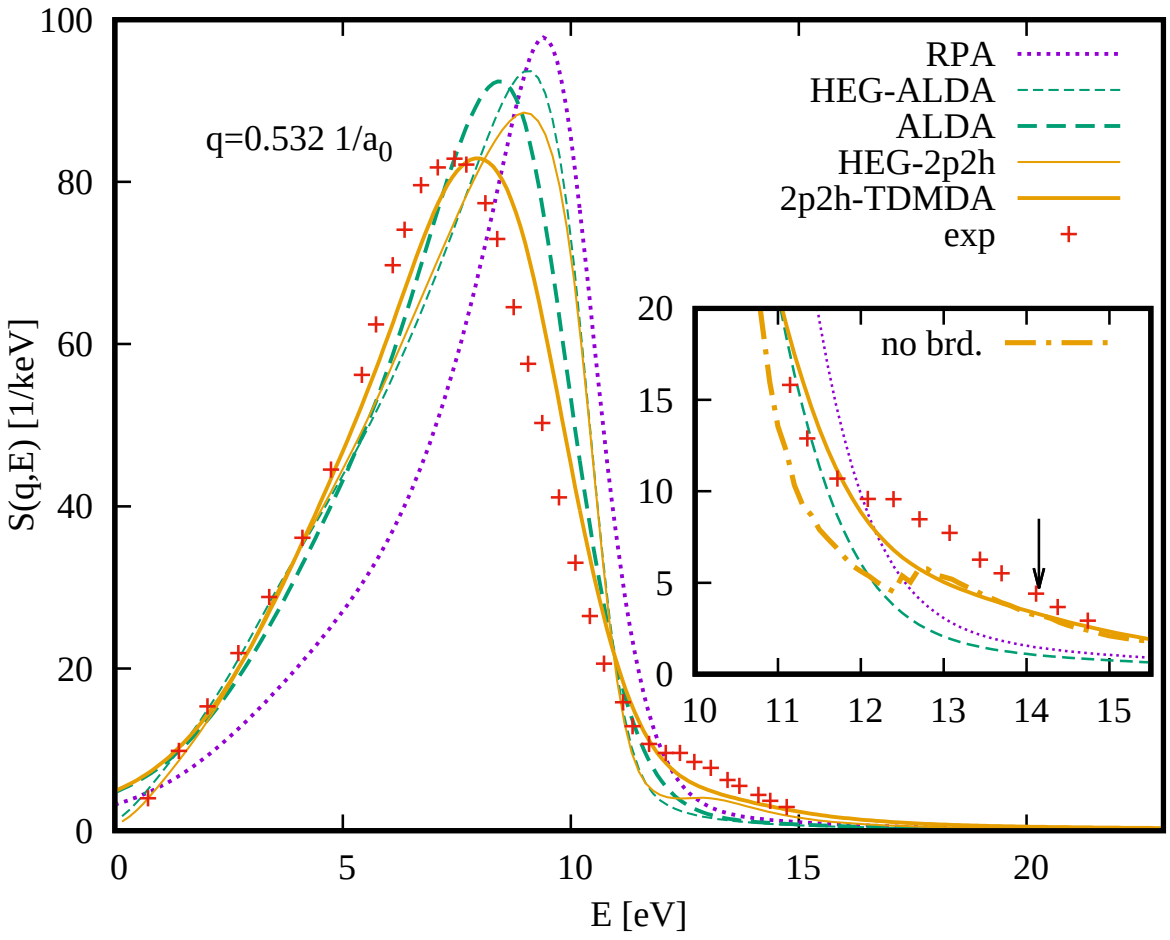
- A lot of different approximations possible
- Systematically improvable
- Accurate description of excitations

Acknowledgments

- Theoretical spectroscopy group Palaiseau, esp. Lucia Reining and Matteo Gatti, Marco Vanzini, Jaakko Koskelo, Ayoub Aouina
- Institute for Theoretical Physics JKU: Robert Zillich, Helga Bohm and Arthur Ernst, Eckhard Krotscheck
- ZONA, JKU: Kurt Hingerl
- Funding: FWF-Schrödinger Fellowship J 3855-N27

Absorption Na

$r_s = 4$



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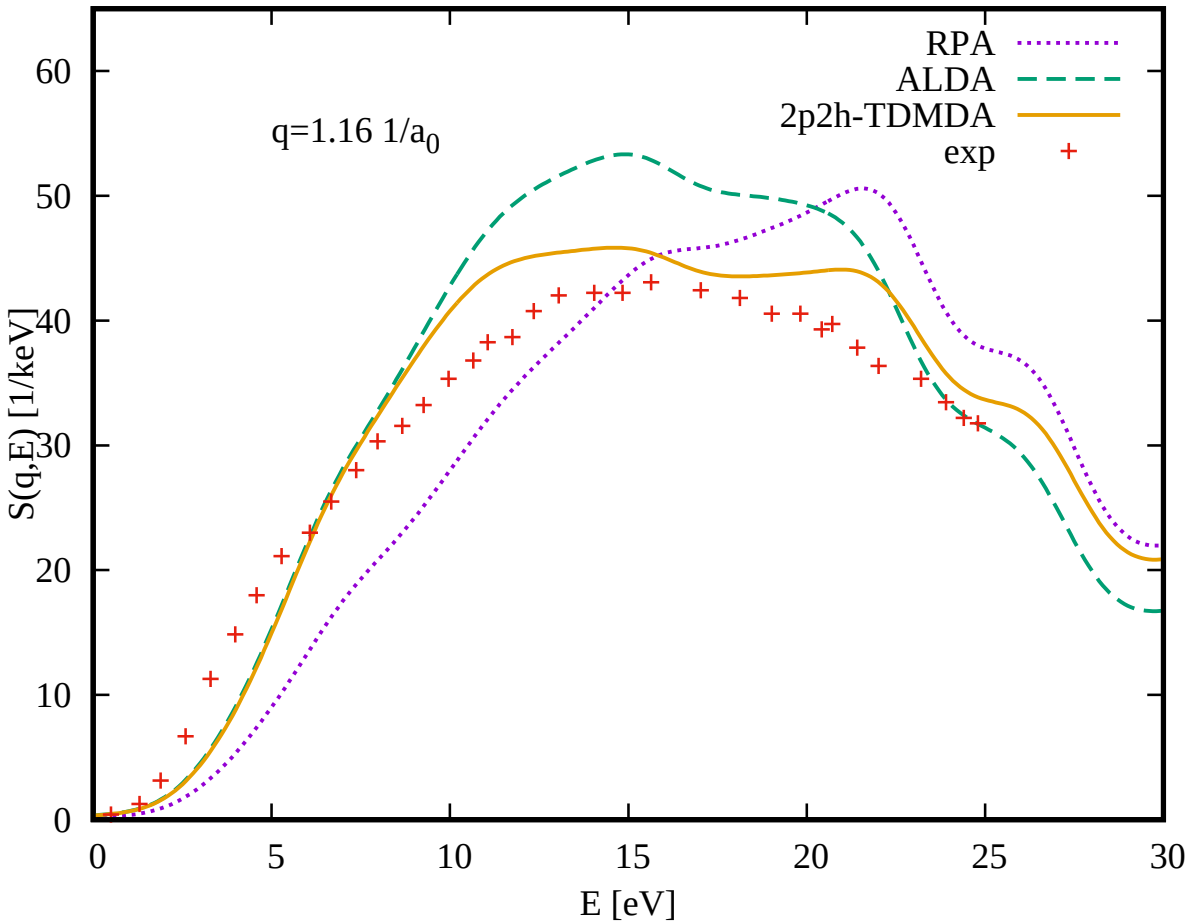
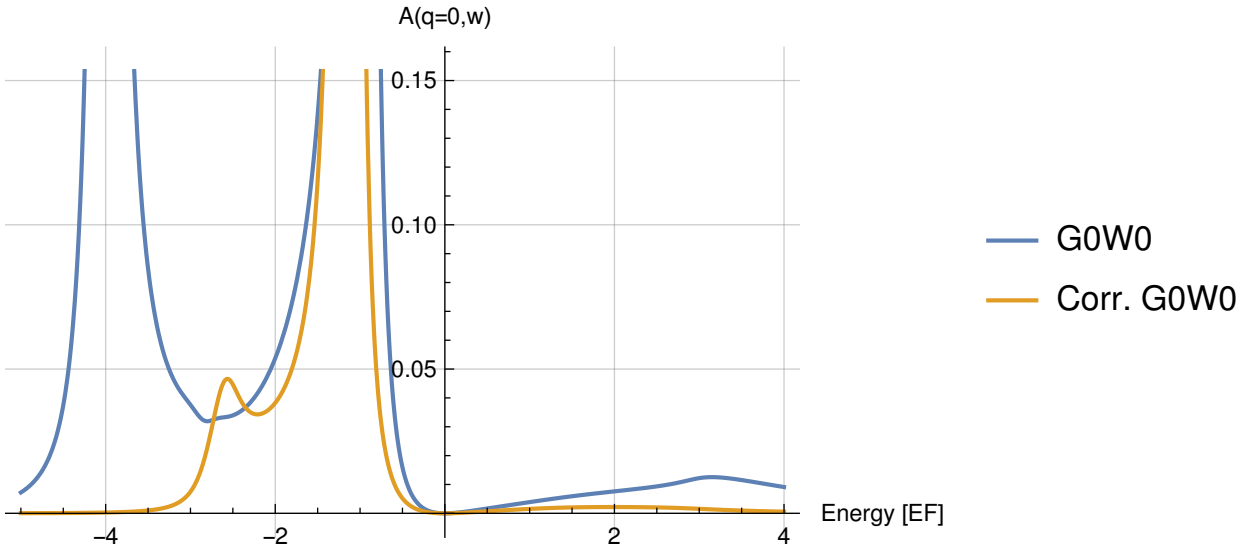


Spectral function

$q = 0, r_s = 4$



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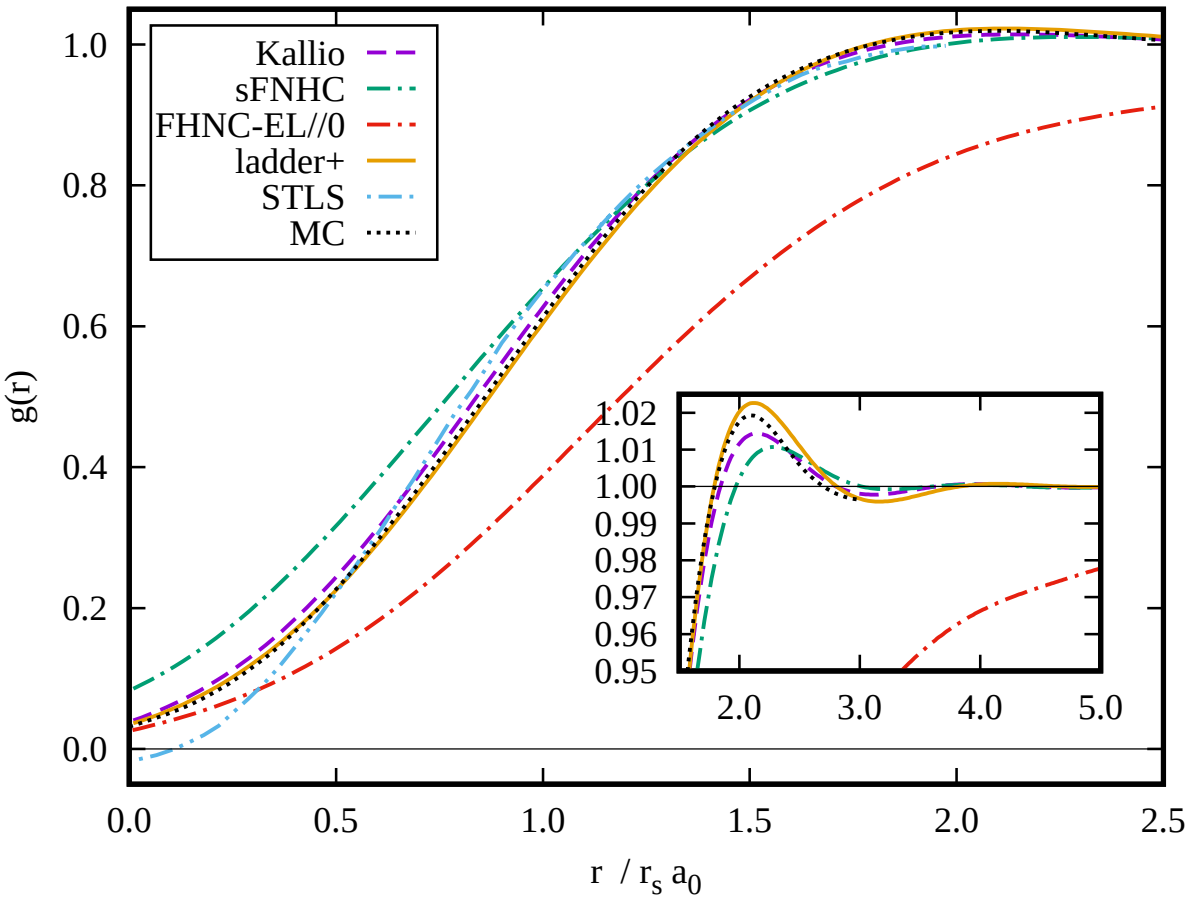
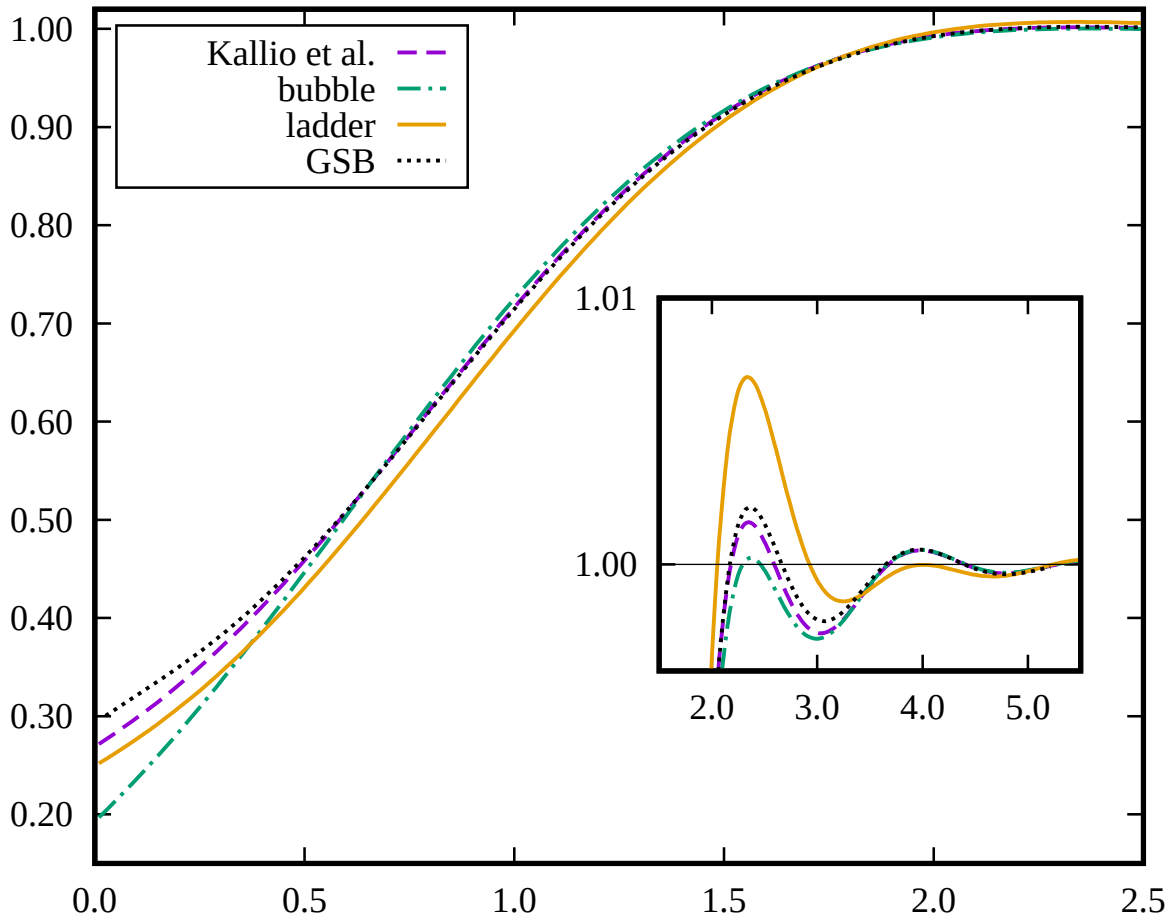
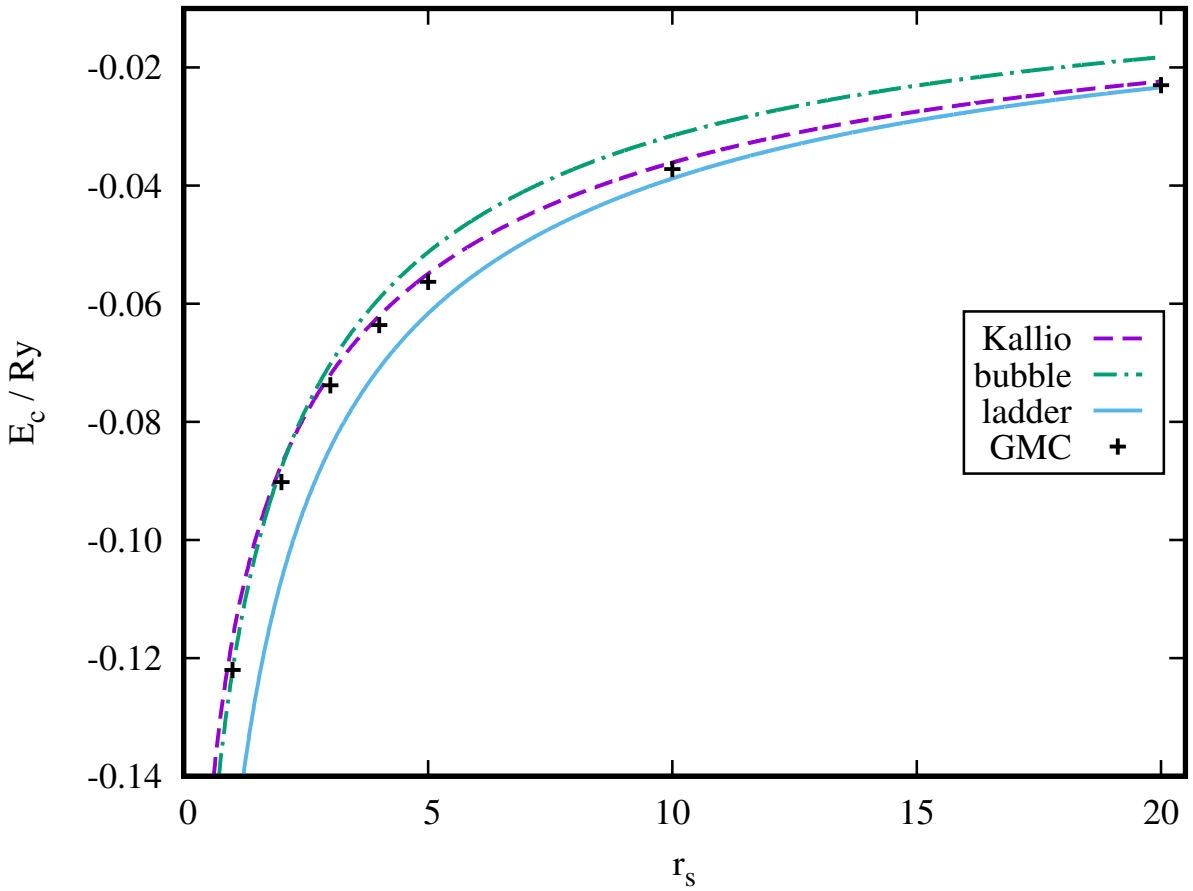


Pair distribution function 3D

$r_s = 1$



Correlation energy 3D



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