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Examining the Nonlinear Response of Quantum Electrons with the Assistance of the Wigner Distribution Function

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Center of Advanced Systems Understanding, Helmholtz-Zentrum Dresden-Rossendorf

My previous visit of Budapest

HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF
TECHNISCHE UNIVERSITÄT DRESDEN
CBG Max Planck Institute of Molecular Cell Biology and Genetics
UFZ HELMHOLTZ Centre for Environmental Research
Uniwersytet Wrocławski
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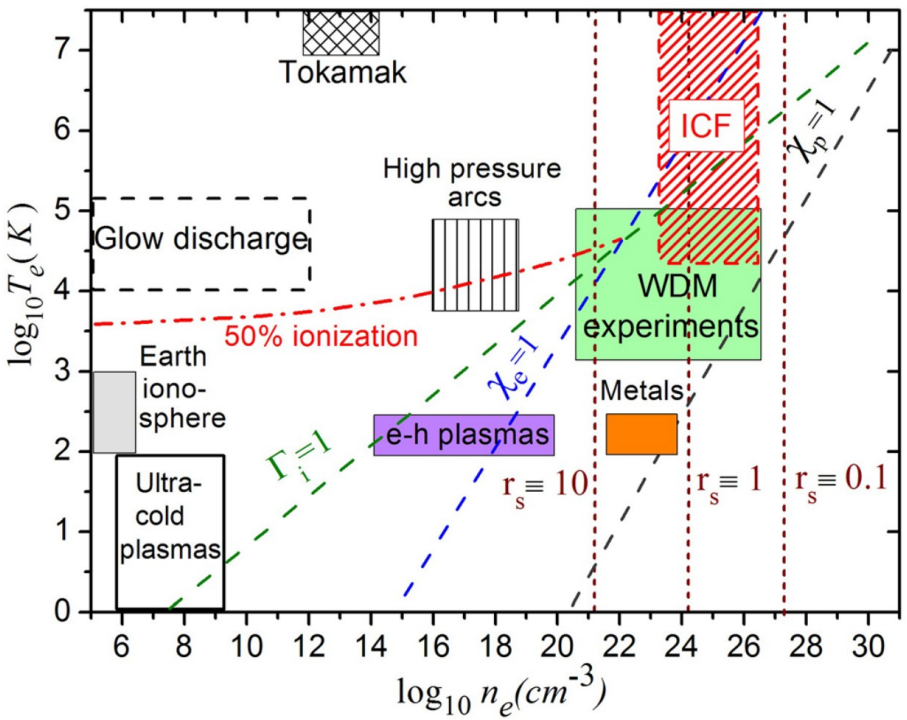
Freistaat SACHSEN

The Presentation Plan

- **Linear Response Theory of Correlated Quantum Electrons**
- **Extension to a Non-Linear Response Regime**
- **General solution for Non-Linear Response functions of Electron Gas using Wigner Distribution Functions**

Research Object: **Warm Dense Matter**



Wigner-Seitz radius $r_s = \frac{d}{a_B} = \left(\frac{3}{4\pi n_0}\right)^{1/3} \frac{me^2}{\hbar^2}$

M. Bonitz, Zh. A. Moldabekov and T. S. Ramazanov, Phys. Plasmas 26, 090601 (2019)

Experimental Facilities:

The National Ignition Facility (Livermore)
European XFEL (Hamburg)
SLAC National Accelerator Laboratory (Stanford)
Omega Laser Facility (Rochester)
...

https://photon-science.desy.de

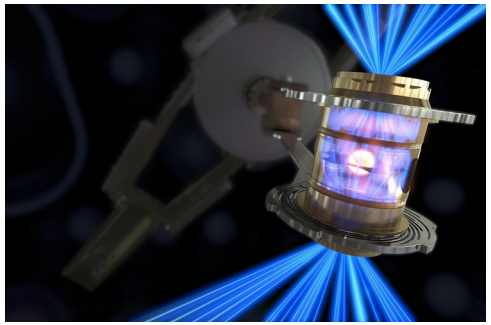
Applications:

Laboratory Astrophysics

Materials Under Extreme Conditions

Hot Electron Chemistry

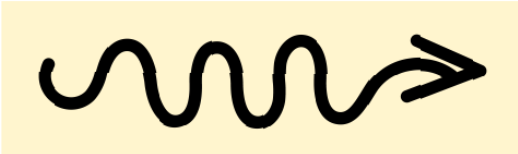
Inertial Confinement Fusion



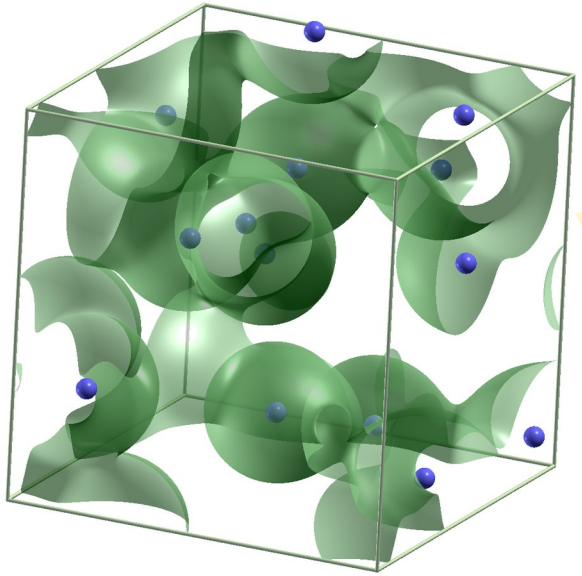
(artist's conception)
J. Jett and J. Long, LLNL

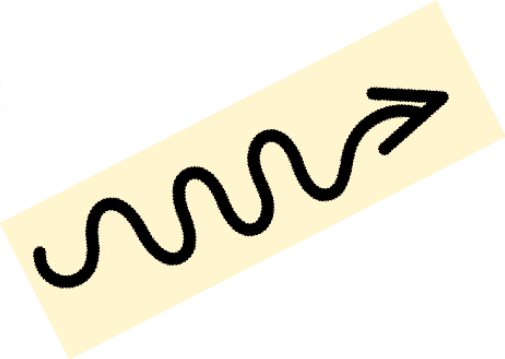
Linear Response Theory

Probe



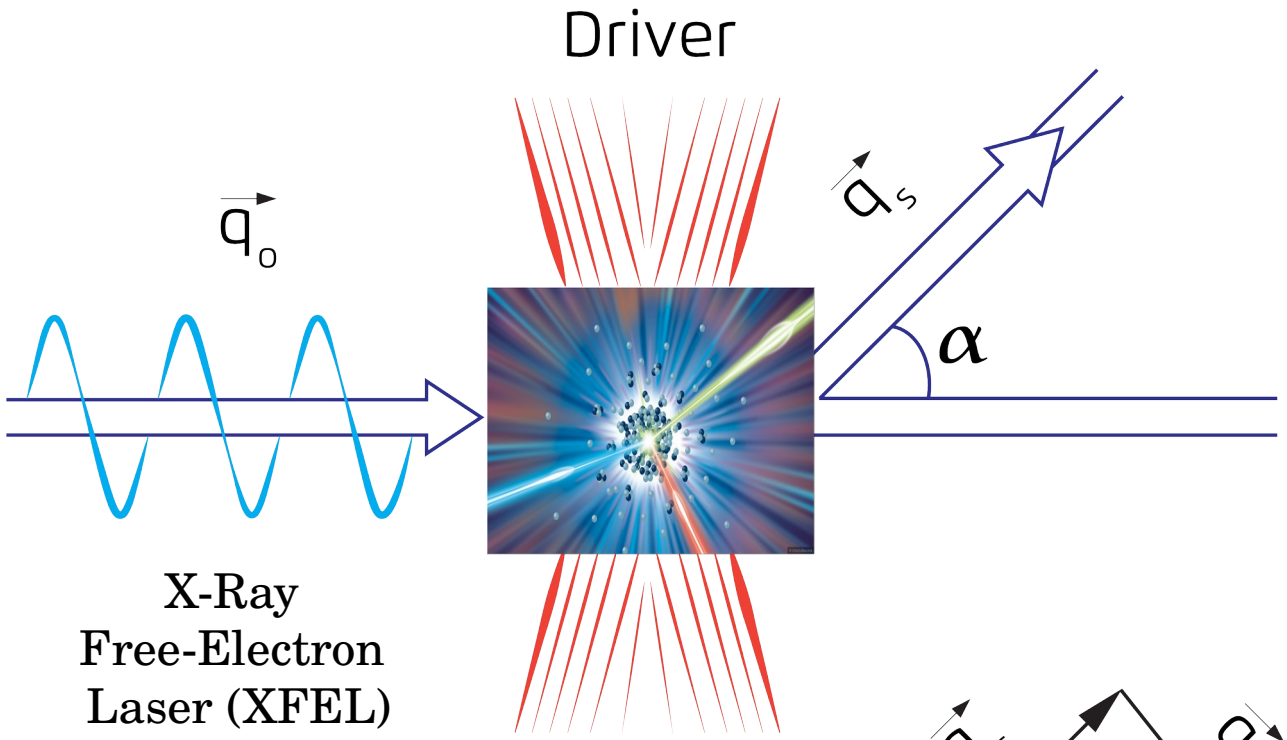
A weak perturbation

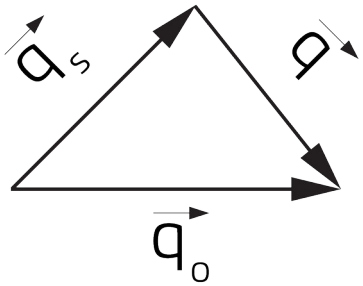


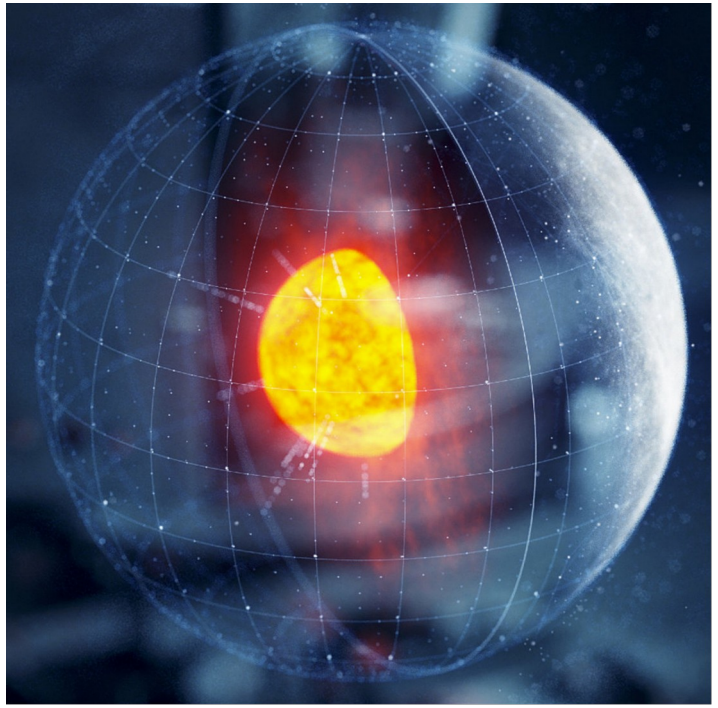


Measure disturbances

Linear Response Theory for **Warm Dense Matter**







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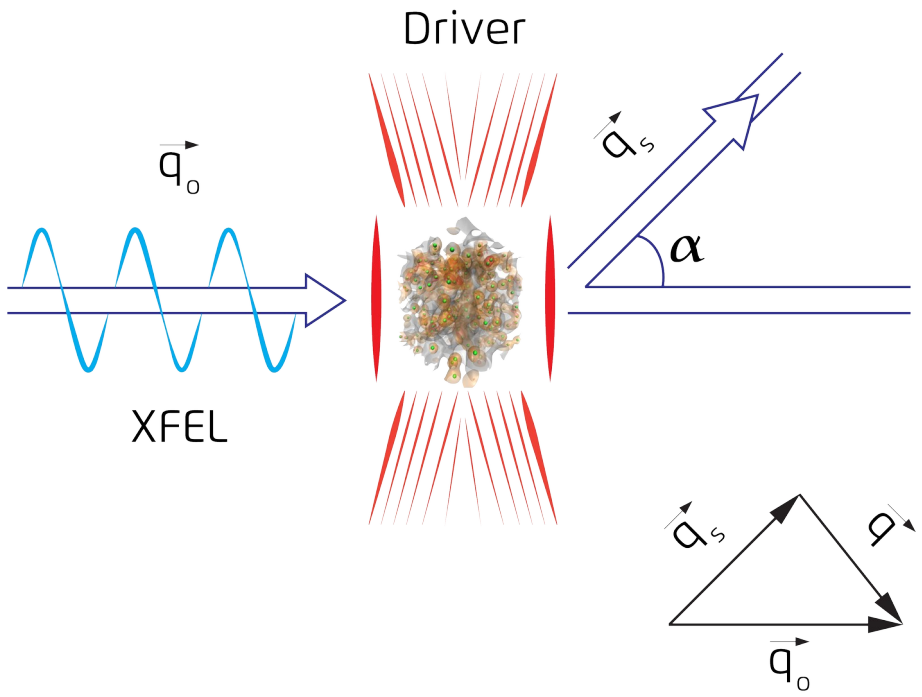
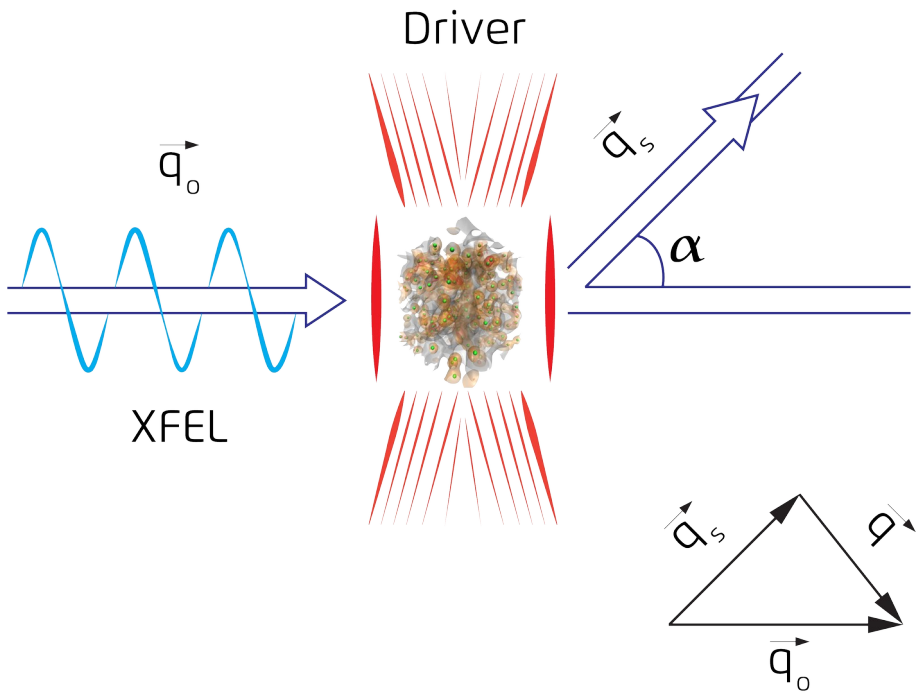
M. Böhme, **Z. A. Moldabekov**, J. Vorberger, and T.Dornheim PRL 129, 066402 (2022)

Linear Response Theory for
Warm Dense Matter (WDM)



$$\Delta\rho(\mathbf{r},t) = \int_{-\infty}^{t} dt' \int d^3\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}',t-t')\, V_{\text{ext}}(\mathbf{r}',t')$$

Linear Response Theory for
Warm Dense Matter (WDM)



$$\Delta\rho(\mathbf{r},t) = \int_{-\infty}^{t} dt' \int d^3\mathbf{r}'\, \chi(\mathbf{r},\mathbf{r}',t-t')\, V_{\text{ext}}(\mathbf{r}',t')$$

WDM parameters

$r_s = a_W/a_B \sim 1$

$\theta = T/T_F \sim 1$

Ab initio **methods** for equilibrium

- Linear-response time-dependent density functional theory (LR-TDDFT):
- can be used for complex materials;
- an approximation to exchange-correlation.

- Real-time time-dependent density functional theory:
- can be used for complex materials;
- an approximation to exchange-correlation.

- Path integral Quantum Monte Carlo (QMC):
- exact;
- restricted to “simple” systems.

Exchange-correlation (XC) functionals

DFT Heaven

*

Fully Non-local

Hybrid Meta GGA

Hybrid GGA

Meta GGA

GGA

LDA

Jacob's Ladder

LR-TDDFT applications for **extended systems**

XC kernel for extended systems as a second order functional derivative with respect to density

* Photo credit: Getty Images

What we need?

Macroscopic Dynamic density response function

$$\chi(\mathbf{q},\omega) = \frac{\chi_0(\mathbf{q},\omega)}{1 - [v(q) + K_{\mathrm{xc}}(\mathbf{q},\omega)]\,\chi_0(\mathbf{q},\omega)}$$

a known reference function

χ_0

the Lindhard function

Dense plasmas, uniform electron gas (UEG) model

the KS response function

LR-TDDFT simulations of real materials

XC-kernel

*

Applications

the dynamic structure factor, the dielectric properties,

the transport properties, the stopping power ...

* Picture Credit: Grommik // Shutterstock

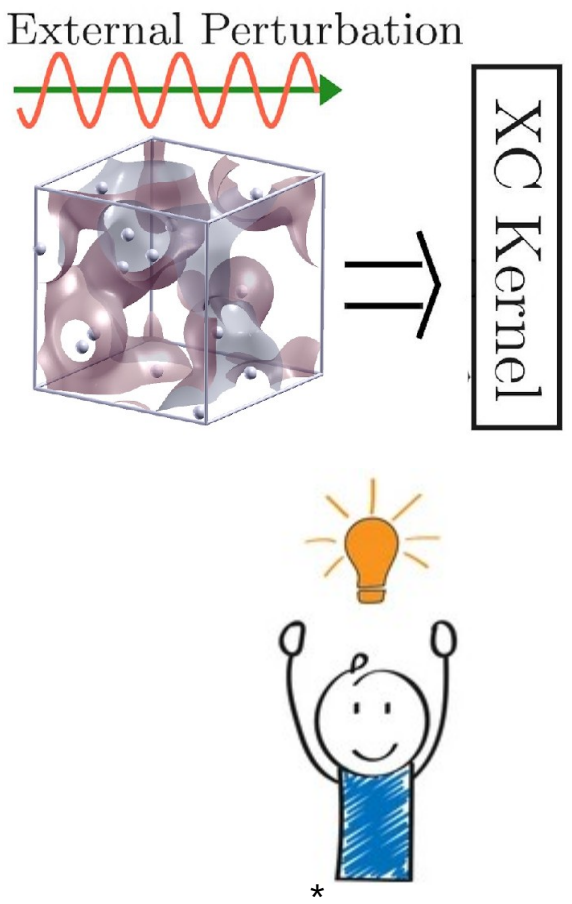
Static XC-kernel

$$K_{\mathrm{xc}}(\mathbf{q}) = K_{\mathrm{xc}}(\mathbf{q}, 0)$$

$$K_{\mathrm{xc}}(\mathbf{q}) = -\left\{ v(q) + \left(\frac{1}{\chi(\mathbf{q})} - \frac{1}{\chi_0(\mathbf{q})} \right) \right\}$$

Utility: Dynamic response in the adiabatic (*static) approximation*

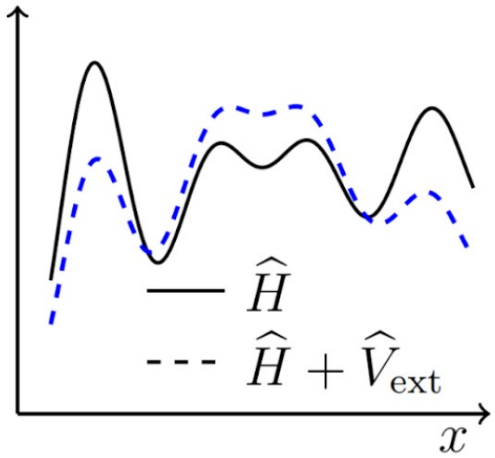
$$\chi_{\mathrm{stat}}(\mathbf{q}, \omega) = \frac{\chi_0(\mathbf{q}, \omega)}{1 - [v(q) + K_{\mathrm{xc}}(\mathbf{q})]\, \chi_0(\mathbf{q}, \omega)}$$



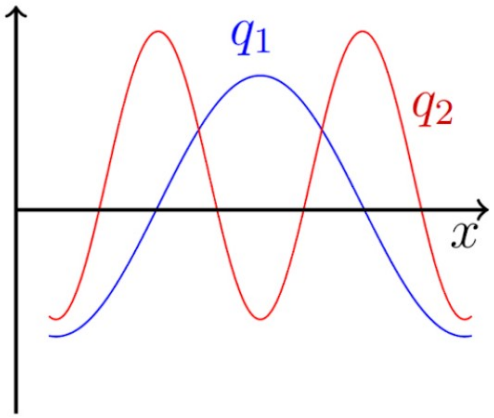
* Picture Credit: Grommik // Shutterstock

Ab Initio Static XC Kernel across Jacob's Ladder without Functional Derivatives

DFT : Single particle density $n(x)$

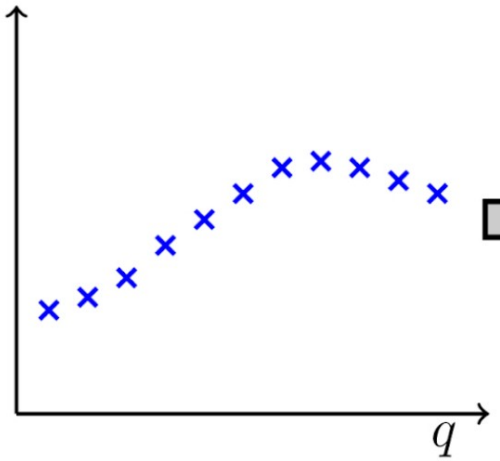


Harmonic perturbations $\Delta n(x)$



$$\Delta n_e(\mathbf{r})_{\mathbf{q},A} = 2A\cos(\mathbf{q}\cdot\mathbf{r})\,\chi(\mathbf{q})$$

Exact e − e correlations $K_{\text{xc}}(q)$



$$K_{\text{xc}}(\mathbf{q}) = -\left\{v(q) + \left(\frac{1}{\chi(\mathbf{q})} - \frac{1}{\chi_0(\mathbf{q})}\right)\right\}$$

Applications :

$S(q,\omega)$, $\epsilon(q,\omega)$,

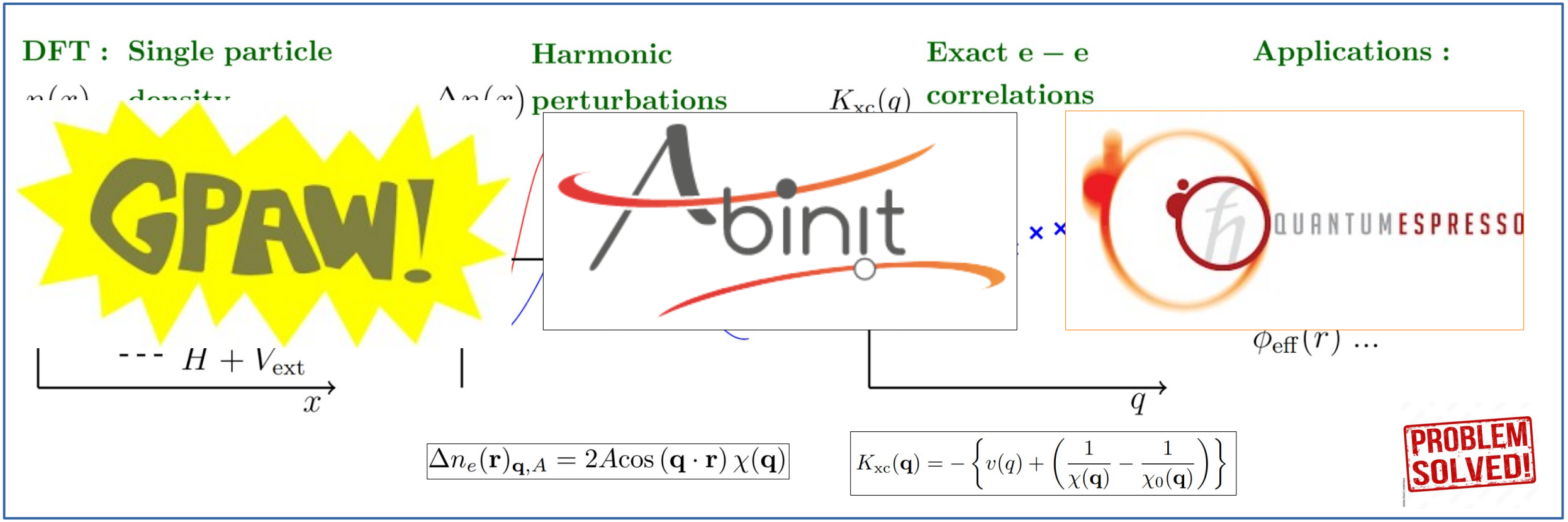
$\sigma_{\text{el}}(q,\omega), \sigma_{\text{th}}(q,\omega)$,

$\frac{\delta E}{\delta l}$, $S(q)$, $g(r)$,

$\phi_{\text{eff}}(r)$ ...

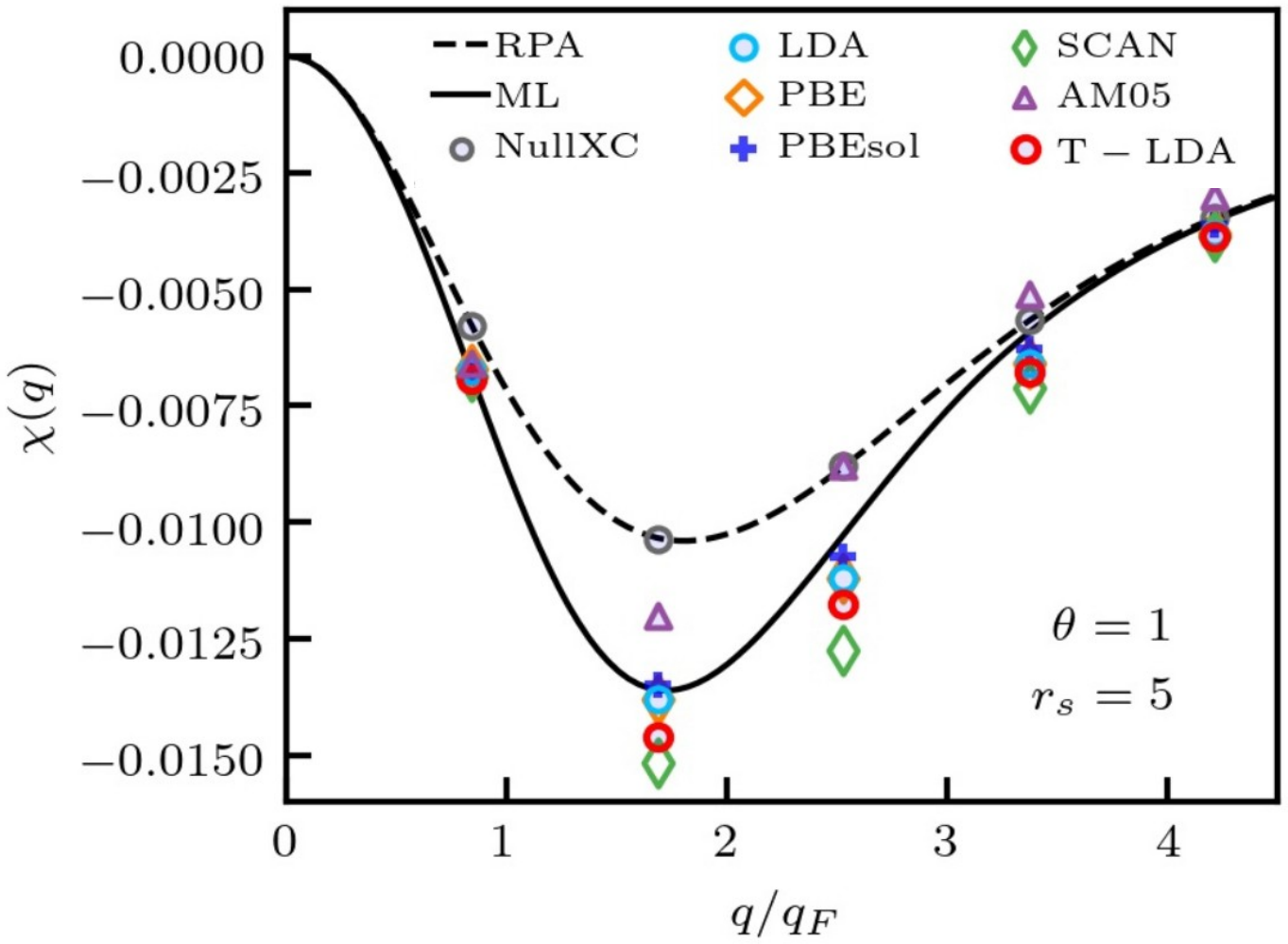
Zhandos A. Moldabekov, et al ., ***Journal of Chemical Theory and Computation*** 19, 1286 (2023).

Ab Initio Static XC Kernel across Jacob's Ladder without Functional Derivatives



Zhandos A. Moldabekov, et al ., ***Journal of Chemical Theory and Computation*** 19, 1286 (2023).

Finite temperature LDA performs worse than its ground state version !!!



[LDA] J. P. Perdew and Y. Wang, PRB (1992)

[PBE] J. P. Perdew, K. Burke, and M. Ernzerhof, PRL (1996).

[PBEsol] J. P. Perdew et. al., PRL (2008).

[SCAN] J. Sun, A. Ruzsinszky, and J. P. Perdew, PRL (2015).

[T-LDA] S. Groth et. al., PRL 119, 135001 (2017)

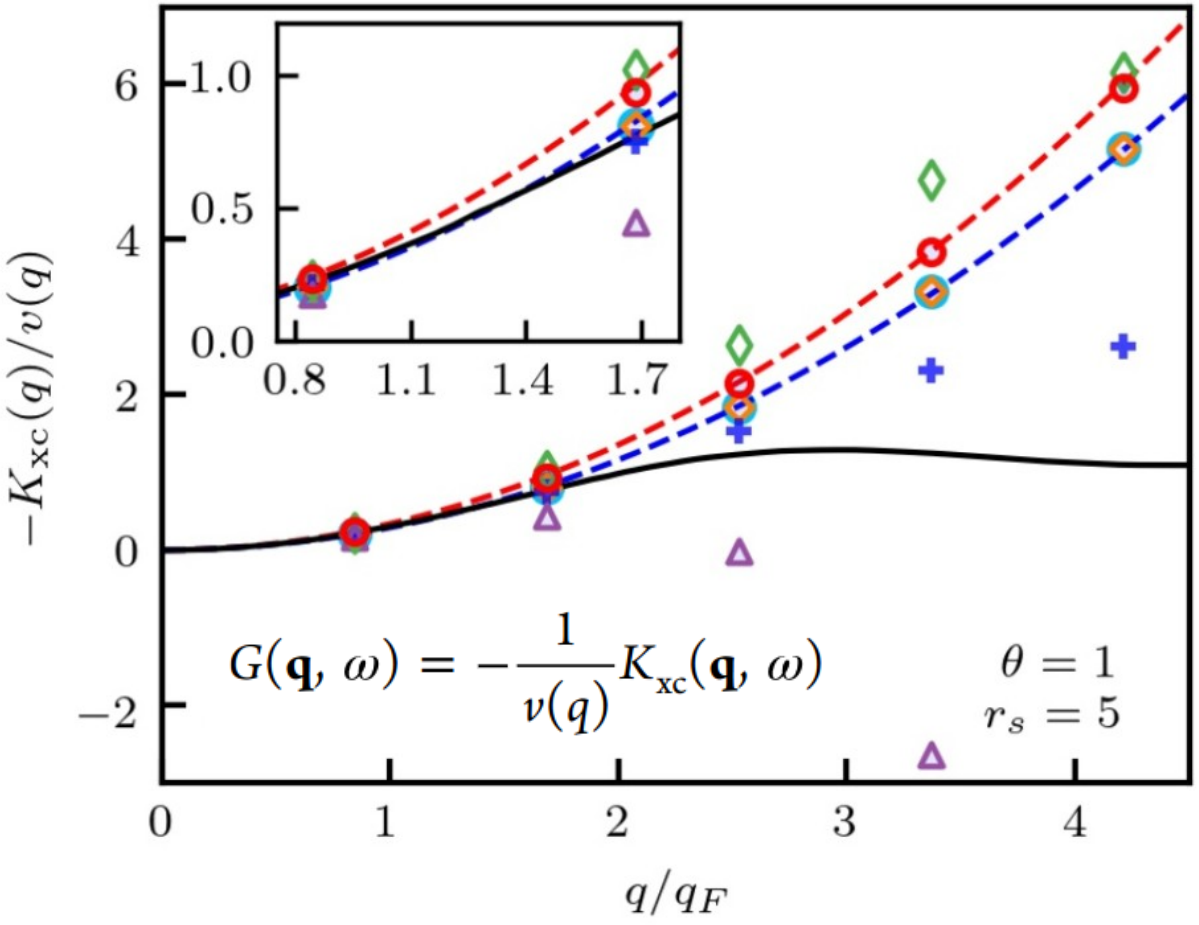
[ML] **PIMC based parameterization**, see T. Dornheim et. al., JCP (2019)

Uniform Electron Gas (**UEG**)
T=12.4 eV

Zhandos A. Moldabekov, et al ., ***Journal of Chemical Theory and Computation*** 19, 1286 (2023).

Finite temperature LDA performs worse than its ground state version !!!

In theory of quantum liquids: **Local Field Correction**



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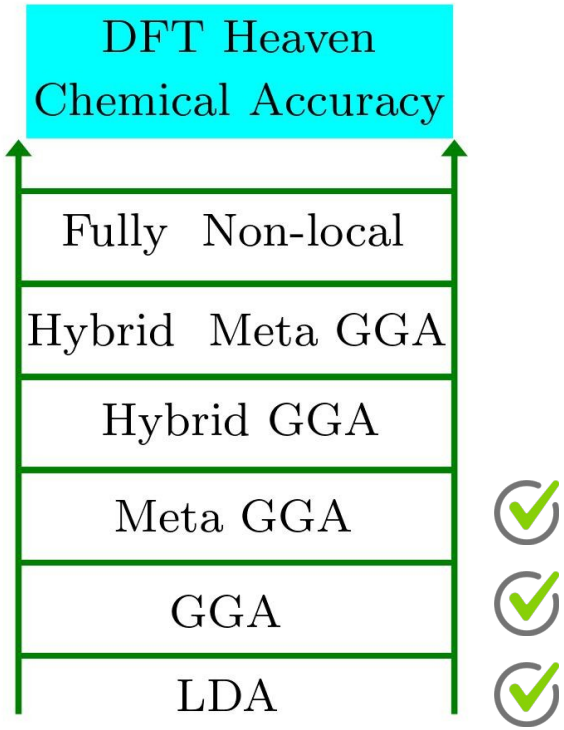
[T-LDA] S. Groth et. al., PRL 119, 135001 (2017)

[ML] **PIMC based parameterization**, see T. Dornheim et. al., JCP (2019)

Uniform Electron Gas (**UEG**)

T=3 eV

Zhandos A. Moldabekov, et al ., ***Journal of Chemical Theory and Computation*** 19, 1286 (2023).



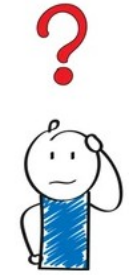
Let's take a look at hybrid XC functionals !

Note, ✓ means to a certain extent

Non-empirical mixing coefficient for hybrid XC functionals ?

$$E_{\mathrm{xc}}[\rho_\sigma, n] = E_{\mathrm{c}}^{\mathrm{DF}}[n] + aE_x^{\mathrm{HF}}[\rho_\sigma] + (1-a)E_{\mathrm{x}}^{\mathrm{DF}}[n]$$

Problem:
How to choose the mixing parameter ?



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If conditions vary, as in WDM experiments, why keep the mixing coefficient constant?

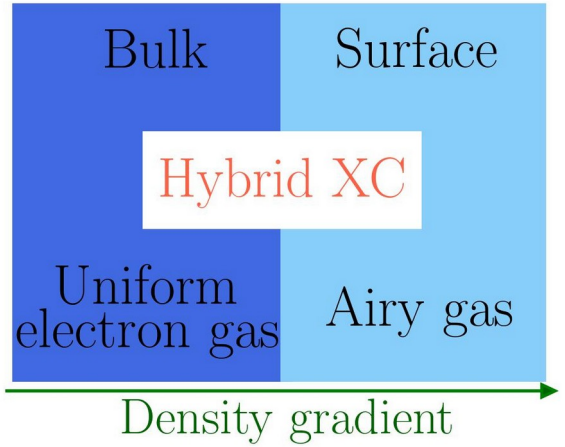
Zhandos A. Moldabekov, et al
J. Phys. Chem. Lett. 14, 1326 (2023).

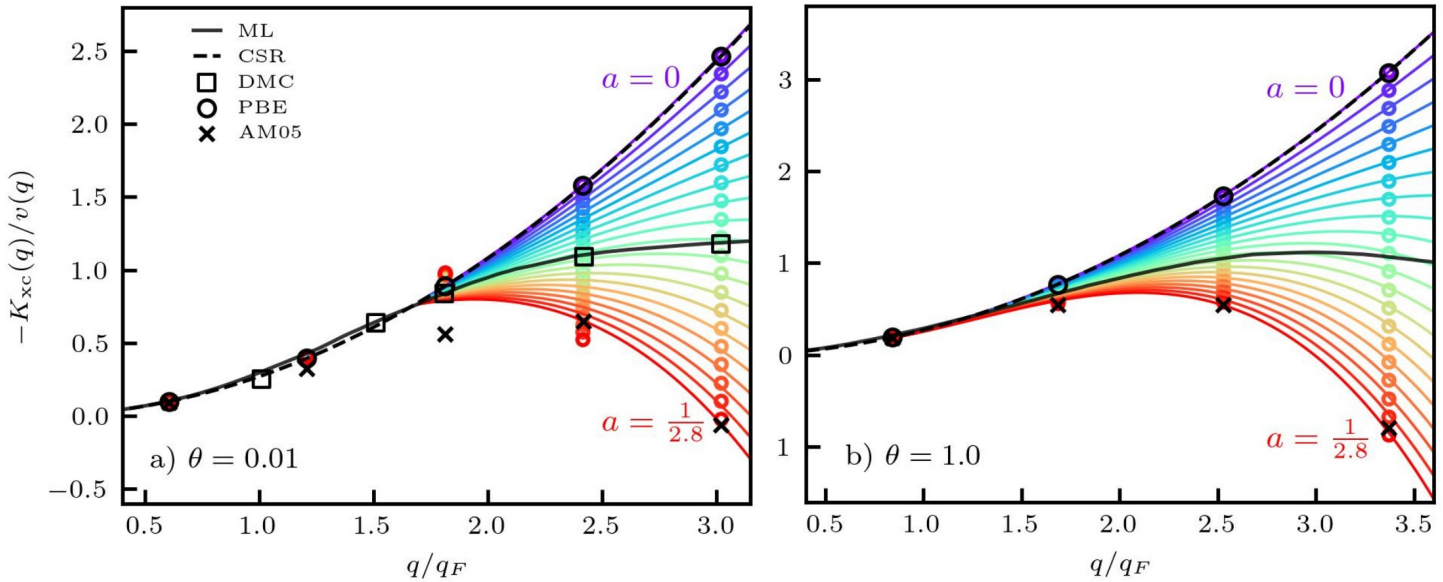
* Picture Credit: Grommik // Shutterstock

A subsystem functional approach for mixing coefficient

$$K_{xc}(q, a) = K_{xc}^{PBE_c}(q) + aK_{xc}^{HF}(q) + (1 - a)K_{xc}^{PBE_x}(q)$$

*





UEG for bulk & the Airy gas for surface regions

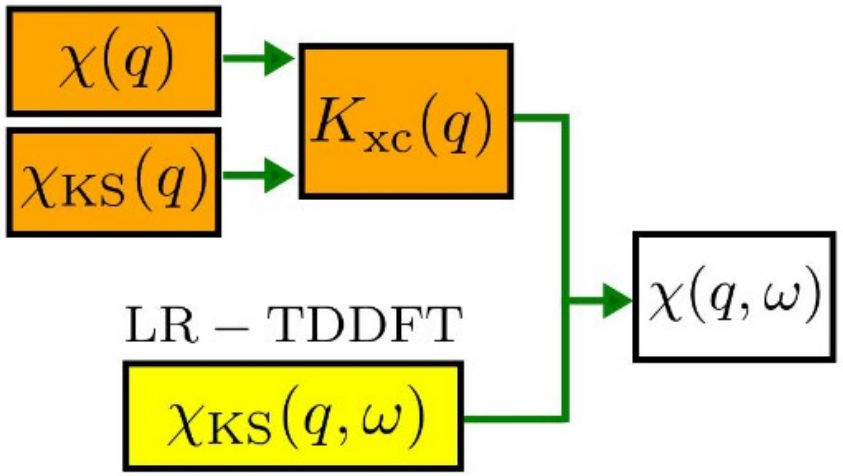
Zhandos A. Moldabekov, et al
J. Phys. Chem. Lett. 14, 1326 (2023)

* Picture Credit: Grommik // Shutterstock

LR-TDDFT with adiabatic (static) XC kernels

$$\chi(\mathbf{q},\omega) = \frac{\chi_{\mathrm{KS}}(\mathbf{q},\omega)}{1-\left[v(q)+K_{\mathrm{xc}}(\mathbf{q})\right]\chi_{\mathrm{KS}}(\mathbf{q},\omega)}$$

The direct perturbation method



Dynamic KS response function

$$\chi_{\mathrm{KS}}(\mathbf{q},\omega) = \frac{1}{v(q)}\left(1-\varepsilon_M^{\mathrm{RPA}}(\mathbf{q},\omega)\right)$$

$$\varepsilon_M^{\mathrm{RPA}}(\mathbf{q},\omega) = \frac{1}{1+\frac{4\pi}{|\mathbf{q}|^2}\chi_{\mathbf{GG}}^{\mathrm{RPA}}(\mathbf{k},\omega)}.$$

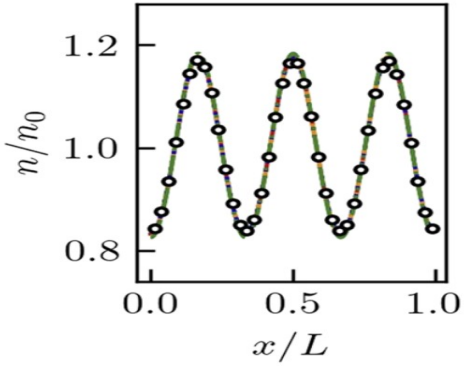
$$\chi_{\mathbf{GG}'}^{\mathrm{RPA}}(\mathbf{k},\omega) = \chi_{\mathbf{GG}'}^{0}(\mathbf{k},\omega) + \sum_{\mathbf{G}_1}\chi_{\mathbf{GG}_1}^{0}(\mathbf{k},\omega)\frac{4\pi}{|\mathbf{k}+\mathbf{G}_1|^2}\chi_{\mathbf{G}_1\mathbf{G}'}^{\mathrm{RPA}}(\mathbf{k},\omega)$$

Z. A. Moldabekov, Phys. Rev. Research 5, 023089 (2023)

Extension to a Non-Linear Response Regime

Theory of non-linear response

$$\hat{H} = \hat{H}_{\mathrm{UEG}} + 2\,A \sum_{i}^{N} \cos(\boldsymbol{r}_i \cdot \boldsymbol{q})$$



Linear response regime: $\delta n(\mathbf{r}) = 2\,A \cos(\boldsymbol{r} \cdot \boldsymbol{q}) \chi(\mathbf{q})$ $|\delta n_(\mathbf{r})|/n_0 \ll 1$

General non-linear response result:

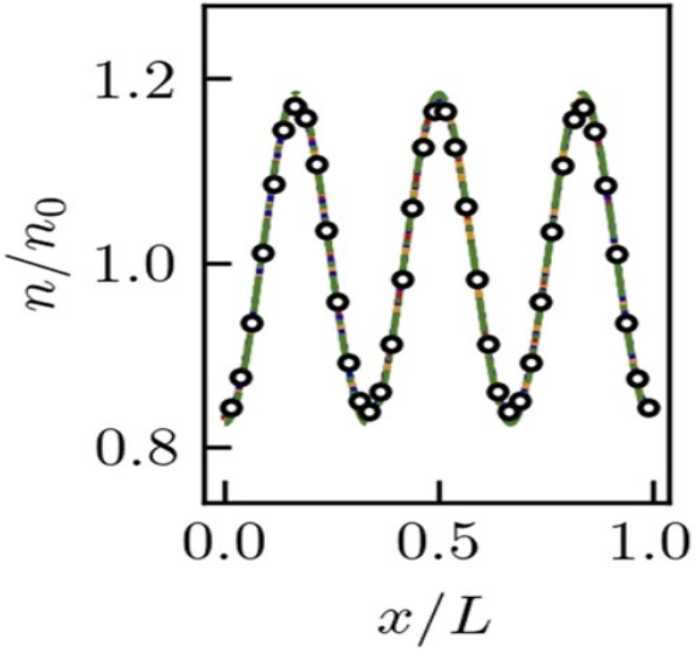
$$\delta n(\mathbf{r}) = 2\,\rho^{(1)} \cos(\boldsymbol{r} \cdot \boldsymbol{q}) + 2\,\rho^{(2)} \cos(\boldsymbol{r} \cdot 2\boldsymbol{q}) + 2\,\rho^{(3)} \cos(\boldsymbol{r} \cdot 3\boldsymbol{q}) + \ldots$$

Theory of non-linear response

General non-linear response result:

$$\delta n(\mathbf{r}) = 2\,\rho^{(1)}\cos(\boldsymbol{r}\cdot\boldsymbol{q}) + 2\,\rho^{(2)}\cos(\boldsymbol{r}\cdot 2\boldsymbol{q}) + 2\,\rho^{(3)}\cos(\boldsymbol{r}\cdot 3\boldsymbol{q}) + \ldots$$

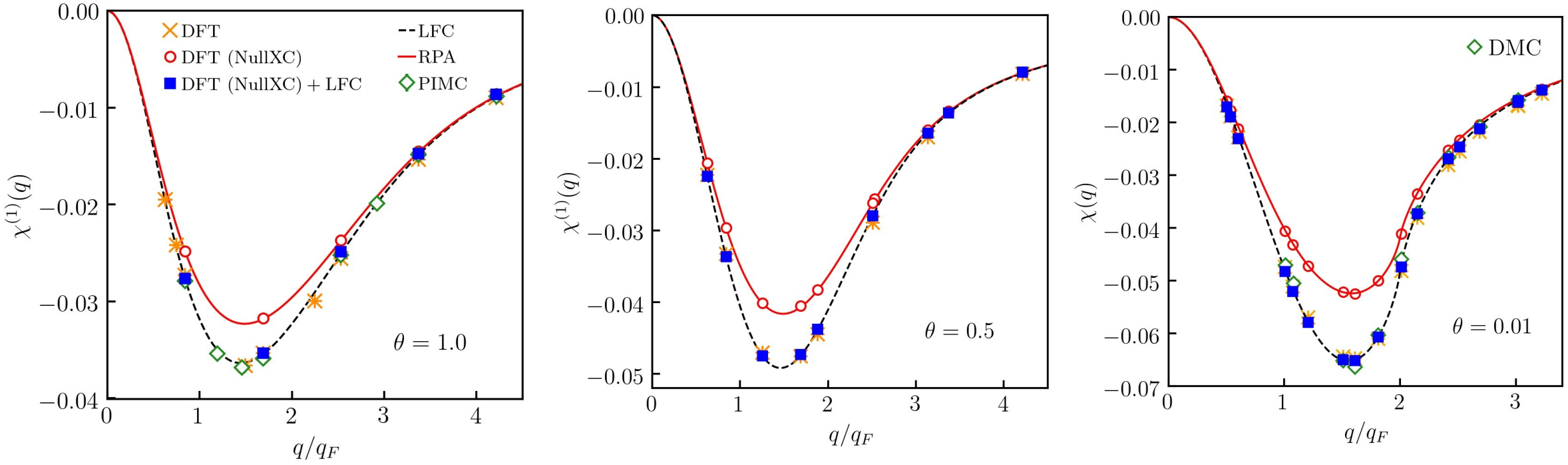
- $\rho^{(1)} = \chi^{(1)}(\mathbf{q})\ A + \chi^{(1,\mathrm{cubic})}(\mathbf{q})\ A^3$
- $\rho^{(2)} = \chi^{(2)}(\mathbf{q})\ A^2$
- $\rho^{(3)} = \chi^{(3)}(\mathbf{q})\ A^3$



[1] T. Dornheim, M. Böhme, **Z. A. Moldabekov**, J. Vorberger, and M. Bonitz, Phys. Rev. Research 3, 033231 (2021)

Linear static density response function for rs = 2

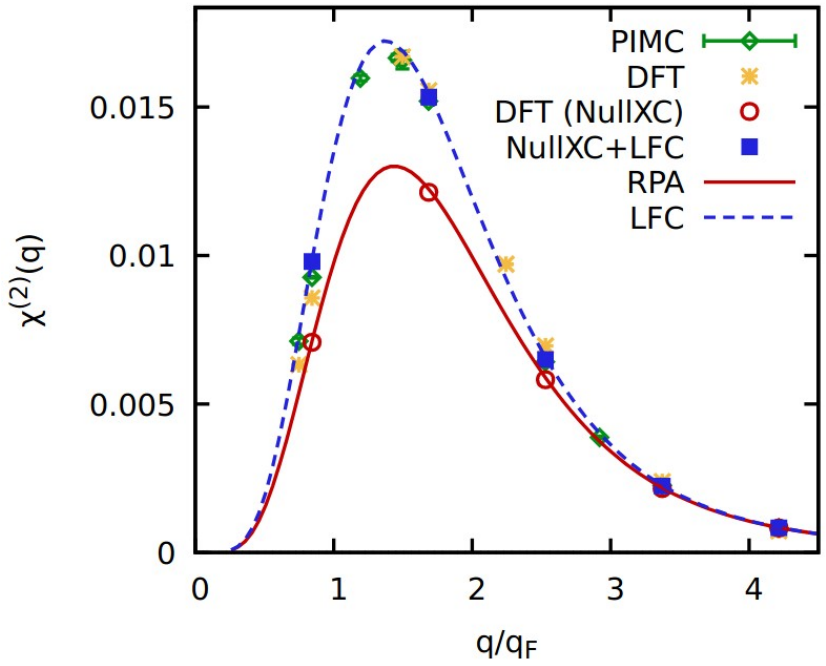
$$\delta n(\mathbf{r}) = 2\,A\cos(\boldsymbol{r}\cdot\boldsymbol{q})\chi(\mathbf{q})$$



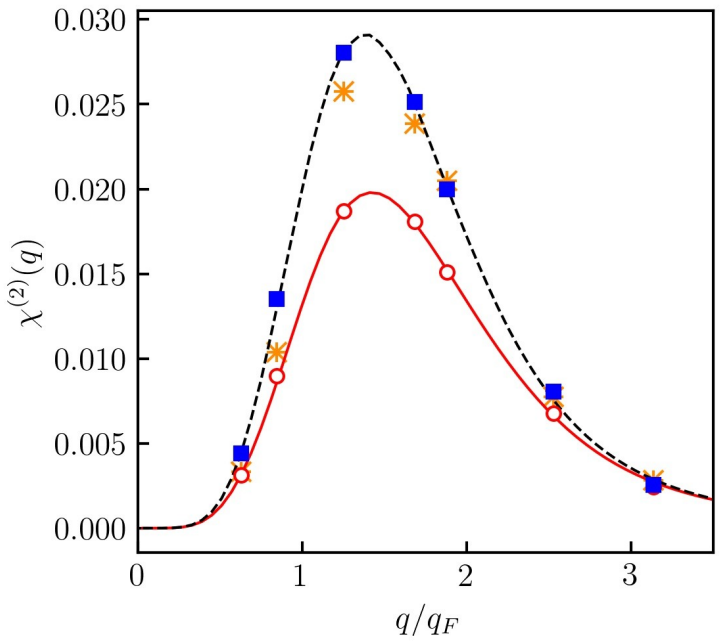
[1] **Zhandos Moldabekov**, Jan Vorberger, Tobias Dornheim, **J. Chem. Theory Comput.** 2022, 18, 5, 2900–2912

Quadratic static density response function for rs = 2

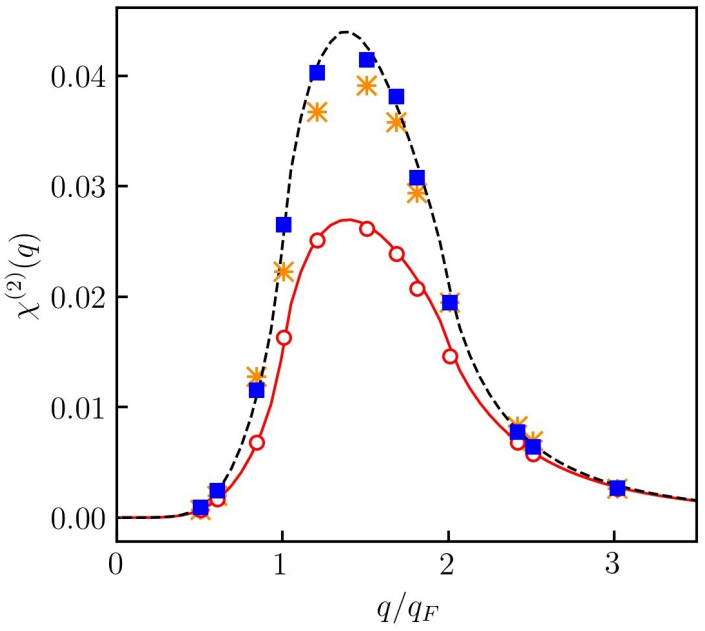
$$\rho^{(2)} = \chi^{(2)}(\mathbf{q})\ A^2$$



θ = 1



θ = 0.5

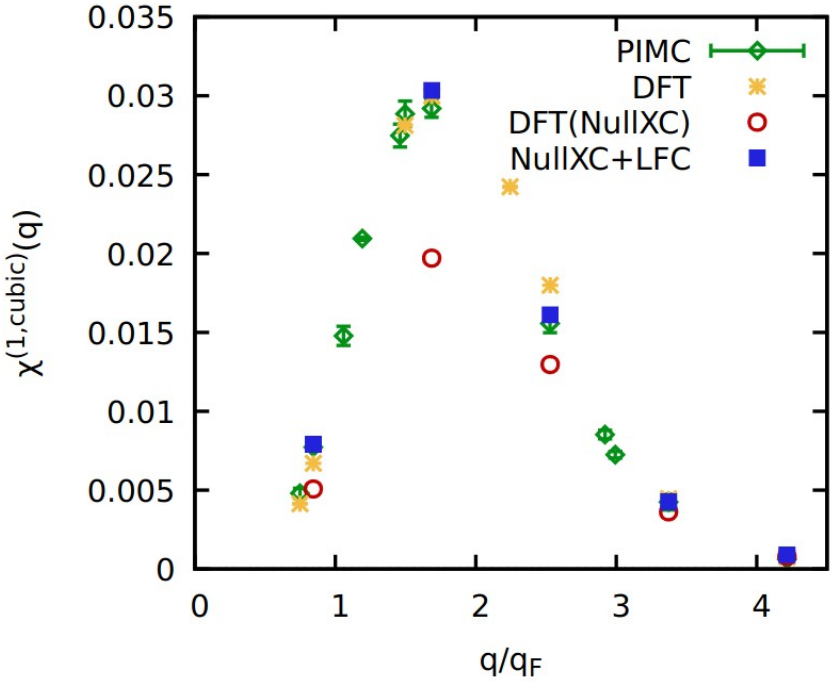


θ = 0.01

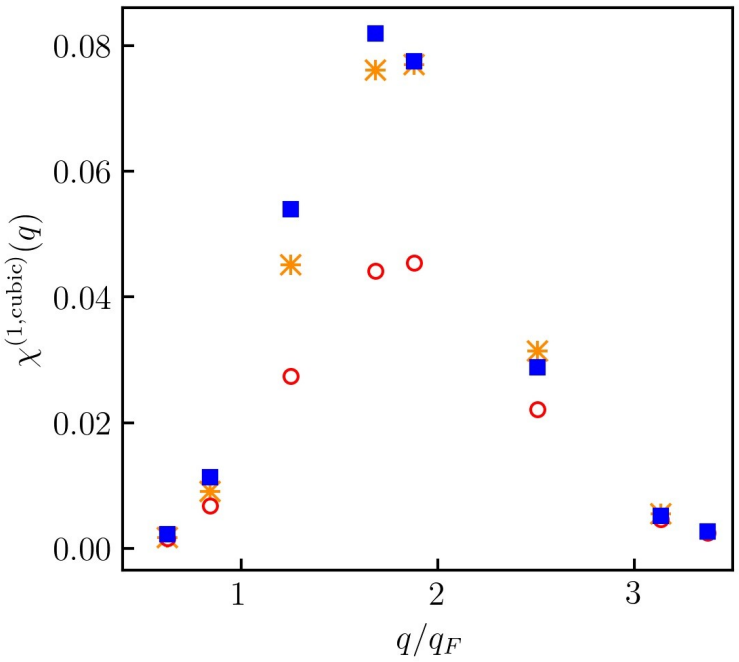
[1] **Zhandos Moldabekov**, Jan Vorberger, Tobias Dornheim, **J. Chem. Theory Comput.** 2022, 18, 5, 2900–2912

Cubic static density response function at the first harmonic for rs = 2

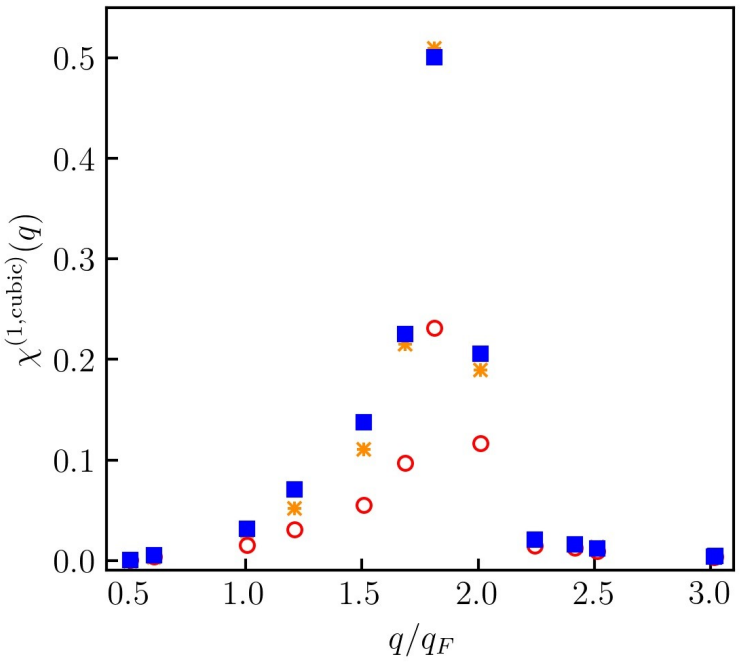
$$\rho^{(1)} = \chi^{(1)}(\mathbf{q})\ A + \chi^{(1,\mathrm{cubic})}(\mathbf{q})\ A^3$$



θ = 1



θ = 0.5

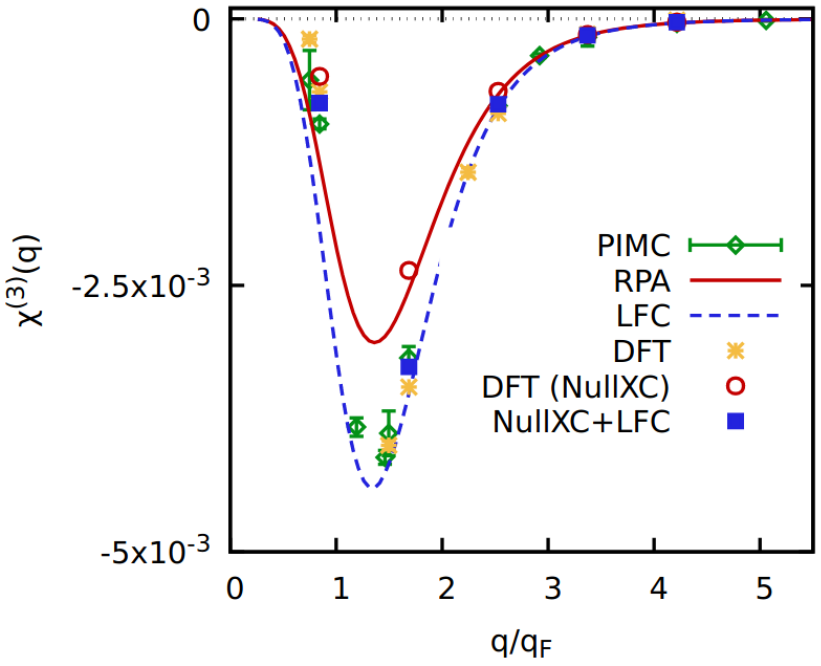


θ = 0.01

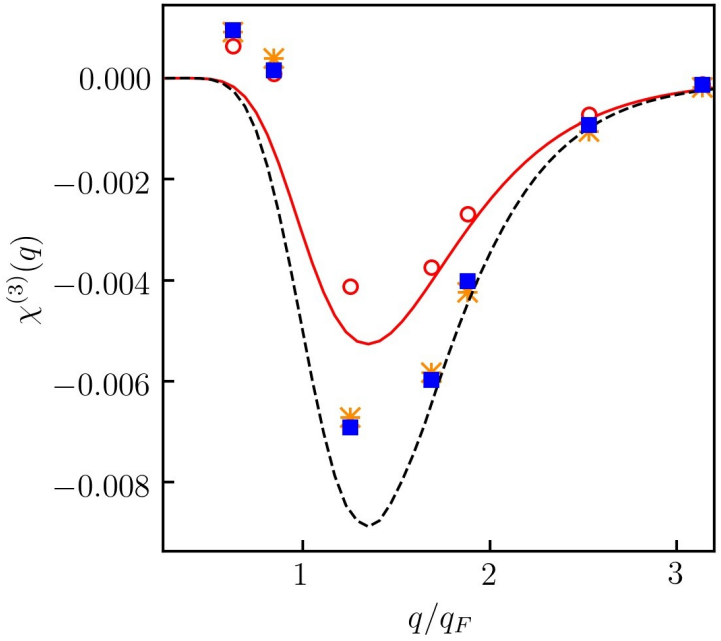
[1] **Zhandos Moldabekov**, Jan Vorberger, Tobias Dornheim, **J. Chem. Theory Comput.** 2022, 18, 5, 2900–2912

Cubic static density response function at the third harmonic for rs = 2

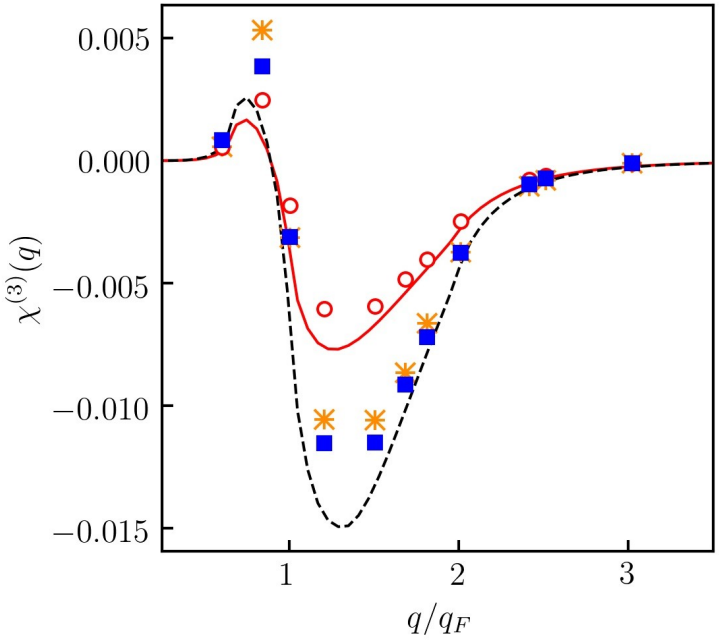
$$\rho^{(3)} = \chi^{(3)}(\mathbf{q})\ A^3$$



θ = 1



θ = 0.5



θ = 0.01

[1] **Zhandos Moldabekov**, Jan Vorberger, Tobias Dornheim, **J. Chem. Theory Comput.** 2022, 18, 5, 2900–2912

General solution for Non-Linear Response functions of Electron Gas using Wigner Distribution Functions

Quantum kinetic theory in the Wigner representation for the calculation of nonlinear ideal density responses

$$\left\{\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\frac{\partial}{\partial \boldsymbol{r}}\right\} f(\boldsymbol{r},\boldsymbol{p},t)=\frac{\imath}{\hbar}\int\frac{\mathrm{d}^3\lambda\mathrm{d}^3\bar{p}}{(2\pi)^3}\exp\left[\imath\left(\boldsymbol{p}-\bar{\boldsymbol{p}}\right)\cdot\boldsymbol{\lambda}\right]$$
$$\times\left[U_{\mathrm{ext}}\left(\boldsymbol{r}+\frac{\hbar}{2}\boldsymbol{\lambda},t\right)-U_{\mathrm{ext}}\left(\boldsymbol{r}-\frac{\hbar}{2}\boldsymbol{\lambda},t\right)\right]f(\boldsymbol{r},\bar{\boldsymbol{p}},t).$$

$$\widetilde{\chi}_0^{(l,l)}(\boldsymbol{x},Z)=\frac{1}{(l-1)!}\frac{1}{l!}\frac{\Theta^{l-1}}{x^{2l-2}}\left[l\widetilde{\chi}_0(l\boldsymbol{x},lZ)+\sum_{m=1}^{l-1}a_{m,l}\times\widetilde{\chi}_0(m\boldsymbol{x},mZ)\right].$$

The paper on 6 pages and
with derivations in the supplementary material on 169 pages !

P. Tolias, T. Dornheim, **Z. Moldabekov**, and J. Vorberger, **EPL** 142 , 44001 (2023).

Note: The expressions for l=2 and l= 3 were derived by Mikhailov [PRL, 027405 (2014)].

Putting it all together: an example of a quadratic density reaction

1. Ideal $$\chi_0^{(2)}(q) = \frac{2}{q^2}(\chi_0^{(1)}(2q) - \chi_0^{(1)}(q))$$

2. RPA

$$\chi_{\mathrm{RPA}}^{(2)}(q) = \frac{\chi_0^{(2)}(q)}{[1 - v(q)\chi_0^{(1)}(q)]^2[1 - v(2q)\chi_0^{(1)}(2q)]}$$

3. Correlated system

$$\chi_{\mathrm{LFC}}^{(2)}(q) = \chi_0^{(2)}(q)[1 - v(q)[1 - G(q)]\chi_0^{(1)}(q)]^{-2} \times [1 - v(2q)[1 - G(2q)]\chi_0^{(1)}(2q)]^{-1}$$

$$G(\mathbf{q}, \omega) = -\frac{1}{v(q)}K_{\mathrm{xc}}(\mathbf{q}, \omega)$$

Generalization for real materials using KS-DFT simulations:

1. Use the KS response as an ideal density response

2. Use the XC kernel from KS-DFT

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