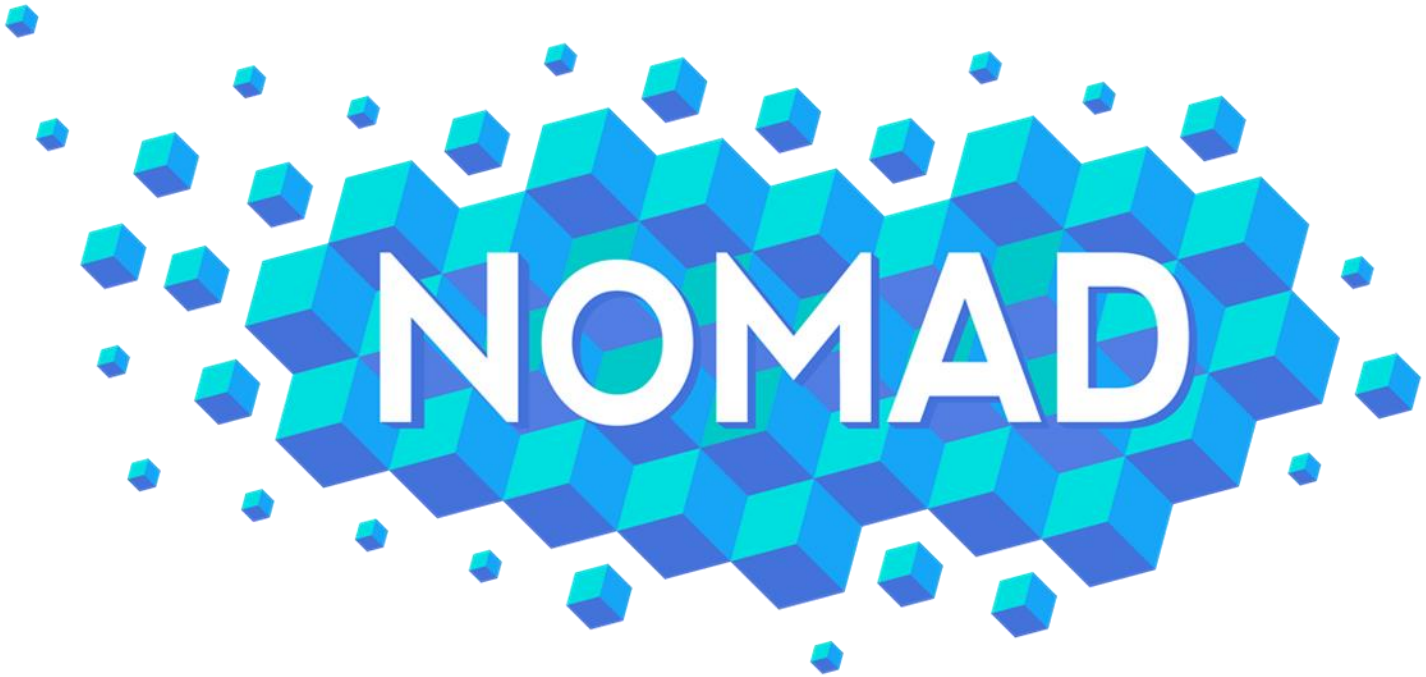

NOVEL MATERIALS DISCOVERY

European Center of Excellence

NOMAD CoE receives funding from the European Union's Horizon program under the grant agreement № 951786.

Time-frequency component of the Green-X library: minimax grids for efficient RPA and GW calculations

Maryam Azizi

Université Catholique de Louvain, Louvain-la-Neuve, Belgium

October 2023

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Outline

- Brief introduction and background
- Space-time G_0W_0 method, low scaling algorithm
- Green-X library
- MINIMAX grids for RPA and GW calculations
- Cosine and sine transformation for low scaling
- Accuracy of the grids
- Low-scaling algorithms for molecules
- Low-scaling algorithms for solids
- Green-X on GitHub

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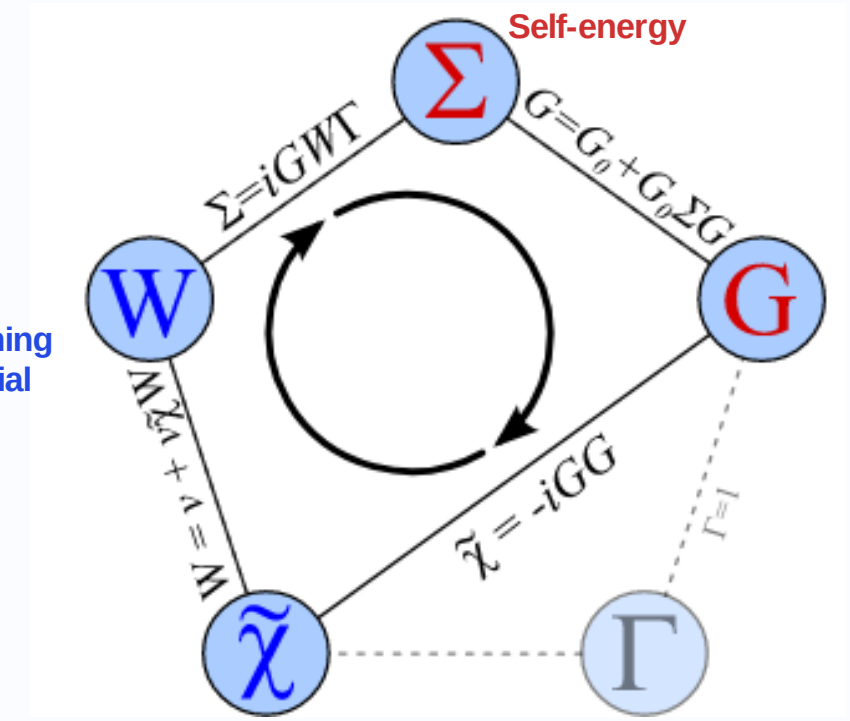
GW calculations based on Hedin's equations



EXPENSIVE CALCULATIONS!

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Space-time G_0W_0 method helps!

Canonical $\mathcal{O}(N^4)$ G_0W_0

1. Compute density response in $\mathcal{O}(N^4)$

$$\chi(r,r',i\omega) = \Sigma_{ia}\psi_a(r')\,\psi_i(r')\,\psi_i(r)\,\psi_a(r)\,\frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}$$

2. Compute dielectric function

$$\epsilon(r,r',i\omega) = \delta(r,r') - \int dr''\, v(r,r'')\chi(r'',r',i\omega)$$

3. Compute screened Coulomb interaction

$$W_0(r,r',i\omega) = \int dr''\, \epsilon^{-1}(r'',r',i\omega)v(r'',r')$$

4. Compute self-energy

$$\Sigma(r,r',i\omega) = -\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}G_0(r,r',i\omega-i\omega')W_0(r,r',i\omega')$$

5. Compute G_0W_0 quasi-particle energies

$$\varepsilon_n^{G_0W_0} = \varepsilon_n + <\chi_n|Re\Sigma(\varepsilon_n^{G_0W_0}) - V^{XC}|\chi_n>$$

$\mathcal{O}(N^3)$ G_0W_0 space-time method

1. Compute density response in $\mathcal{O}(N^3)$

$$\chi(r,r',i\tau) = \Sigma_{ia}\psi_a(r')\,\psi_i(r')\,\psi_i(r)\,\psi_a(r)\,e^{-(\varepsilon_a-\varepsilon_i)|\tau|}$$
$$= \left(\Sigma_i^{occ}\psi_i(r')\,\psi_i(r)\,e^{\varepsilon_i|\tau|}\right)\left(\Sigma_a^{unocc}\psi_a(r')\,\psi_a(r)\,e^{-\varepsilon_a|\tau|}\right)$$

2. Compute dielectric function

$$\epsilon(r,r',i\tau) = \delta(r,r') - \int dr''\, v(r,r'')\chi(r'',r',i\tau)$$

3. Compute screened Coulomb interaction

$$W_0(r,r',i\tau) = \int dr''\, \epsilon^{-1}(r'',r',i\tau)v(r'',r')$$

4. Compute self-energy

$$\Sigma(r,r',i\tau) = -G_0(r,r',i\tau)W_0(r,r',i\tau)$$

5. Compute G_0W_0 quasi-particle energies

$$\varepsilon_n^{G_0W_0} = \varepsilon_n + <\chi_n|Re\Sigma(\varepsilon_n^{G_0W_0}) - V^{XC}|\chi_n>$$

The space-time method calculates the polarizability and self-energy in the real space and imaginary time.

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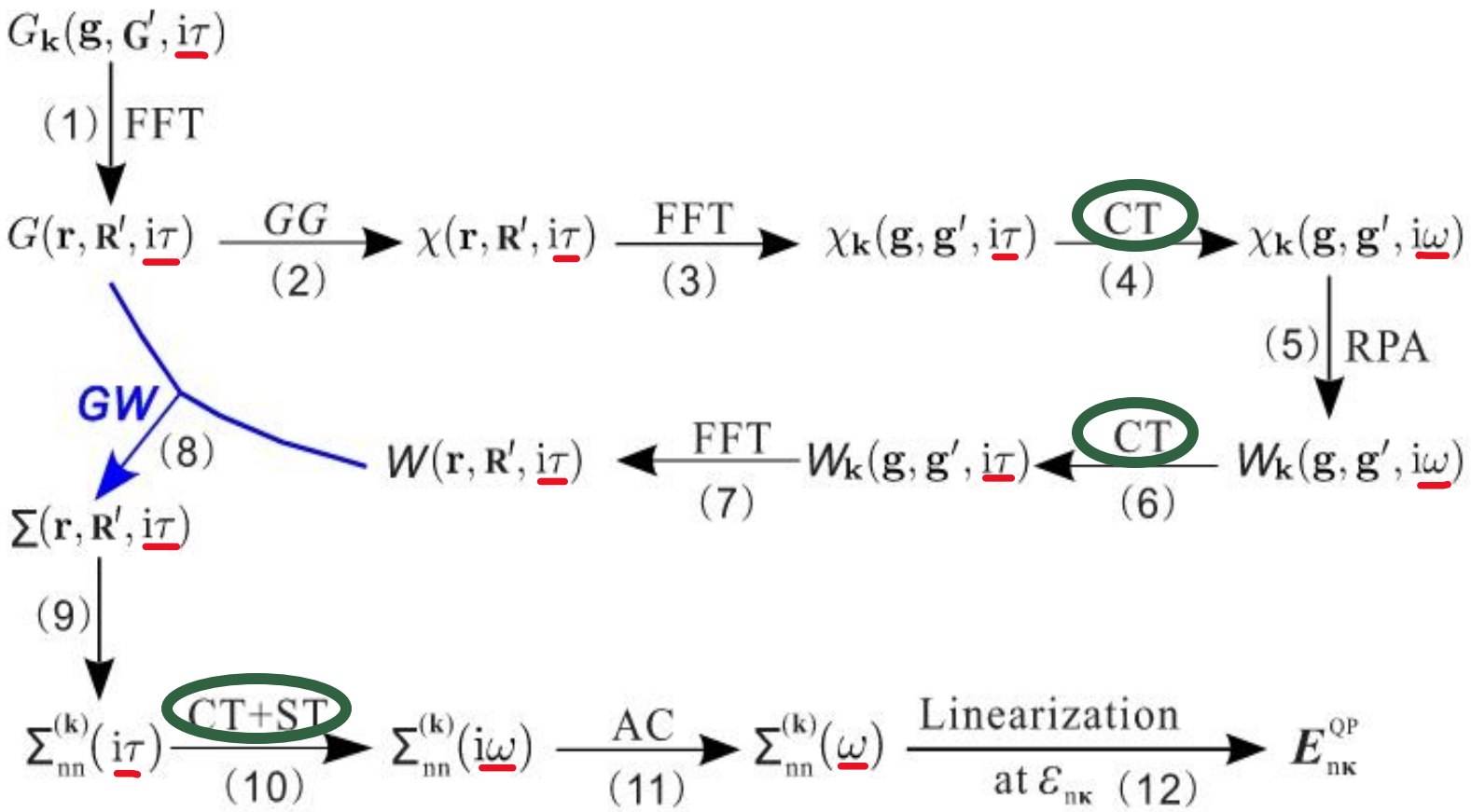
Schematic workflow for the low-scaling GW quasi-particle calculations



Fast Fourier transformation (**FFT**)
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Peitao Liu, Merzuk Kaltak, Jiří Klimeš, and Georg Kresse, *Phys. Rev. B* 94, 165109 (2016)

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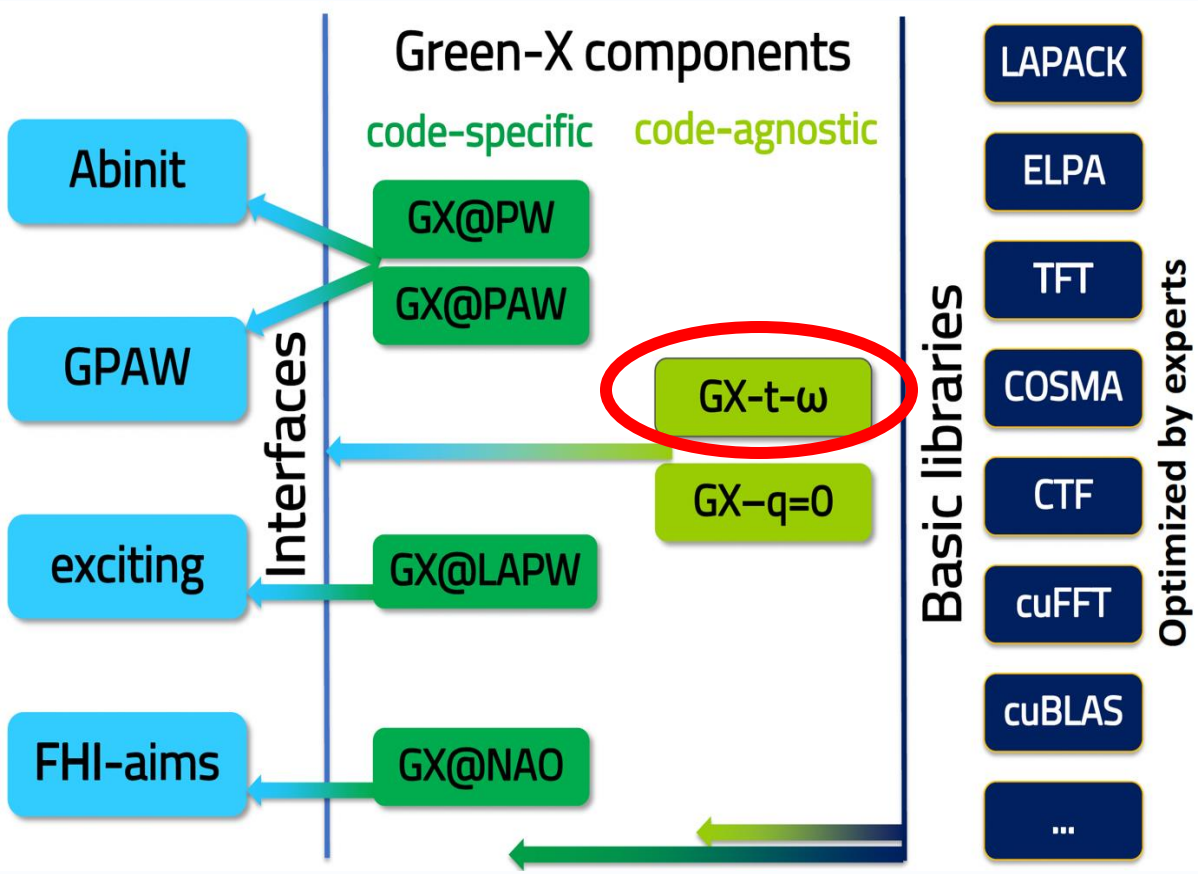
Green-X library

SCAN ME

https://github.com/nomad-coe/greenX

Open Source distributed under the Apache license (Freely available)

More features in progress!



- Green-X provides Time and frequency grids and corresponding integration weights to compute correlation energies for Green's function implementations.
- Fourier weights to convert between imaginary time and imaginary frequency.
- The library can be used for low-scaling RPA and GW implementations, or BSE codes, which use (low-scaling) GW as input. The minimax grids are also suitable for RPA implementations with conventional scaling.

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Why non-uniform grids?

Since the polarizability is sharply peaked around the origin and then decays slowly, homogeneous time and frequency grids are inefficient.

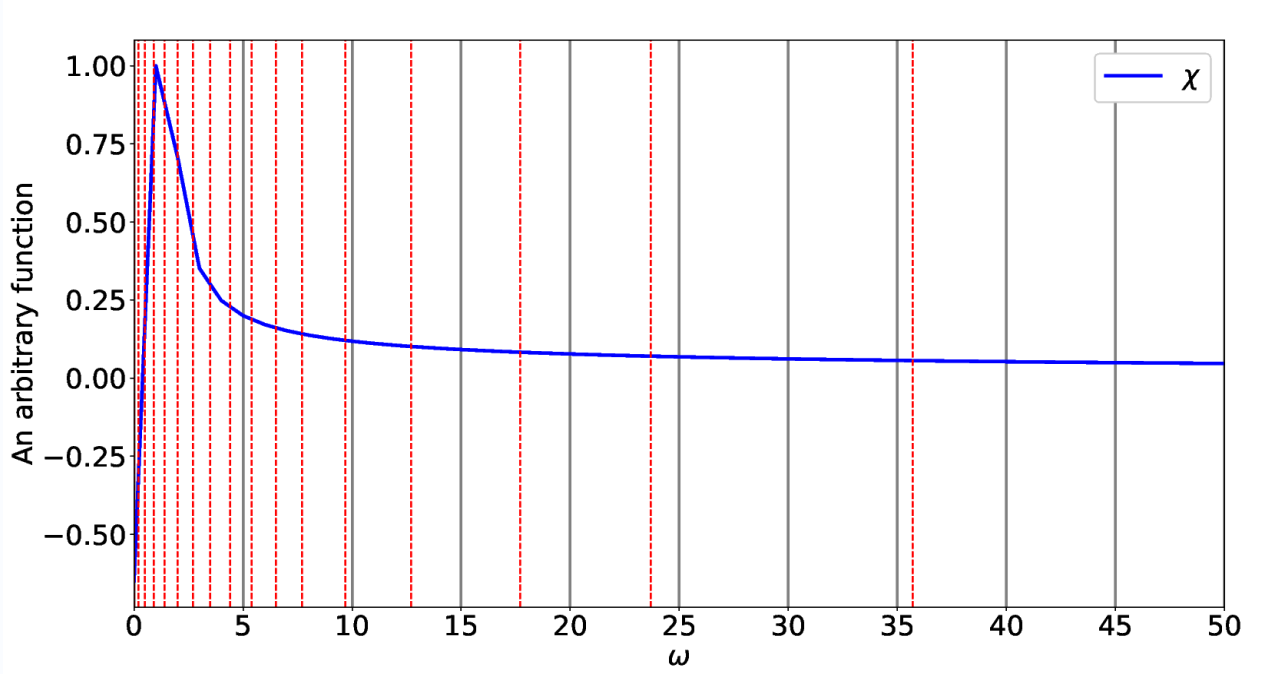
For this reason, non-uniform grids like Gauss-Legendre, modified Gauss-Legendre and Green-X grids are used.

Minimax grids are more compact than the others resulting in a reduction of the computational prefactor, while yielding same accuracy.

small number of points is needed to reach reasonable convergence **(about 20 number of points).**

$$\hat{\chi}^0(\mathbf{r},\mathbf{r}',i\tau) = \sum_j^{\text{occ}} \psi_j(\mathbf{r}')\,\psi_j^*(\mathbf{r})\,e^{\varepsilon_j|\tau|} \times \sum_a^{\text{unocc}} \psi_a^*(\mathbf{r}')\,\psi_a(\mathbf{r})\,e^{-\varepsilon_a|\tau|}.$$

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \sum_j^{\text{occ}} \sum_a^{\text{unocc}} \psi_a^*(\mathbf{r}')\,\psi_j(\mathbf{r}')\,\psi_j^*(\mathbf{r})\,\psi_a(\mathbf{r}) \frac{2(\varepsilon_j-\varepsilon_a)}{\omega^2+(\varepsilon_j-\varepsilon_a)^2},$$



Comput. Phys. Commun., 117 (3), 211–228
New J. Phys., 14(5), 053020
Chem. Theory Comput., 10(6), 2498–2507

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Minimax approximation

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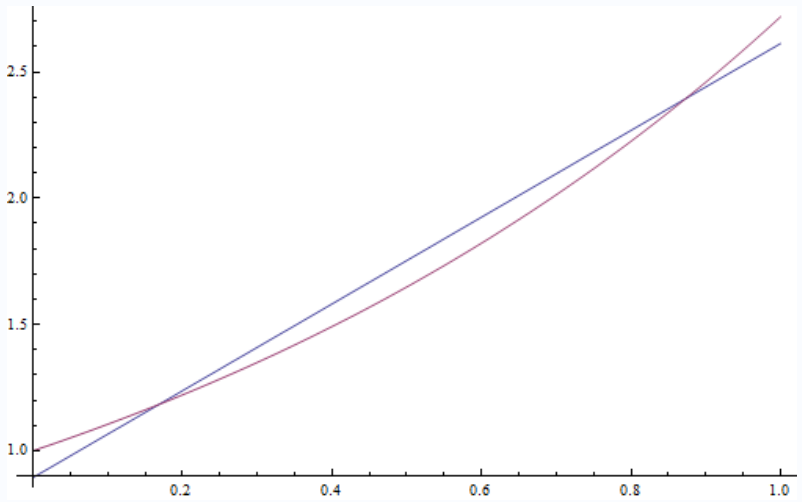
Consider the graph of $f(x)=e^x$ and a best possible linear approximation of $y=mx+b$.



Clearly, $f(x)$ and $y(x)$ must be equal at two points c, d in $[0, 1]$, where $0 \leq c < d \leq 1$. Therefore,

$$e^c - y(c) = e^d - y(d) = 0.$$

The maximum error must be attained at exactly three points $0, 1$, and some point a in $(0, 1)$. The minimax theory tells us that we must have:

$$\rho = Max_{0 \leq x \leq 1} \left(e^x - (mx + b)\right)$$

All of these observations give us:

$$e^0 - b = \rho, e^1 - (m + b) = \rho,\ e^a - (ma + b) = -\rho.$$

We have four variables and this is only three equations, so we add one more equation. Since $w(x) = e^x - (mx + b)$ has a local minimum at a, we have $w'(a) = e^a - m = 0$.

These four equations yield:

- $m = e - 1 \approx 1.718282$
- $b = \dfrac{e - (e - 1)\ln(e - 1)}{2} \approx 0.894067$
- $a = \ln(e - 1) \approx 0.541325$
- $\rho = 1 - b \approx 0.105933.$

This gives us the linear approximation:

$$y(x) = 1.718282x + 0.894067.$$

This intersects the exponential function at $c = 0.168371$ and $d = 0.873066$.

Minimax approximation

$$E_c^{\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty \mathrm{d}\nu\ \mathrm{Tr}\{\ln(1-\chi(i\nu)V)+\chi(i\nu)V\}$$

with $\chi(i\nu) = \chi(-i\nu)$

$$\ln(1-x)+x = -x^2/2 - x^3/3 - \ldots$$

The lowest order in an RPA correlation energy expansion

$$E_c^{(2)} = -\frac{1}{4}\sum_{\mu\mu'} \mathrm{Tr}\{\chi_\mu V \chi_{\mu'} V\}\frac{1}{x_\mu + x_{\mu'}}$$

$$E_c^{(2)} = -\frac{1}{4\pi}\int_0^\infty d\omega\ \mathrm{Tr}\{(\chi(i\omega)V)^2\} = -\frac{1}{4\pi}\sum_{\mu\mu'}\mathrm{Tr}\{\chi_\mu V\chi_{\mu'}V\}\int_0^\infty d\omega\ \phi_\omega(x_\mu)\,\phi_\omega(x_{\mu'})$$

$$E_c^{(2)} = -\frac{1}{2}\int_0^\infty d\tau\ \mathrm{Tr}\{(\hat{\chi}(i\tau)V)^2\} = -\frac{1}{2}\sum_{\mu\mu'}\mathrm{Tr}\{\chi_\mu V\chi_{\mu'}V\}\int_0^\infty d\tau\ \hat{\phi}_\tau(x_\mu)\,\hat{\phi}_\tau(x_{\mu'})$$

Which are the ideal starting point to construct time and frequency grids.

Peitao Liu, Merzuk Kaltak, Jiří Klimeš, and Georg Kresse, *Phys. Rev. B* 94, 165109 (2016)

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Minimax approximation

We aim to minimize the error function

Error function

$$\eta(\vec{\alpha}, \vec{\beta}, x) = f(x) - \sum_{i=1}^{N} \beta_i \varphi(\alpha_i, x)$$

Infinity norm

$$||\eta||_\infty = \max\{|\eta(\vec{\alpha}, \vec{\beta}, x)| \in \mathbb{R} : x \in I\}$$

$$\eta_{\vec{\gamma},\vec{\omega}}(x) = \frac{1}{x} - \frac{1}{\pi} \sum_{k=1}^{N} \gamma_k \phi^2_{\omega_k}(x)$$

$$\hat{\eta}_{\vec{\sigma},\vec{\tau}}(x) = \frac{1}{2x} - \sum_{i=1}^{N} \sigma_i \hat{\phi}^2_{\tau_i}(x)$$

Peitao Liu, Merzuk Kaltak, Jiří Klimeš, and Georg Kresse, *Phys. Rev. B* 94, 165109 (2016)
Jan Wilhelm, Patrick Seewald, and Dorothea Golze, *J. Chem. Theory Comput* 17, 1662−1677 (2021)

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Minimax approximation

Constructing minimax time and frequency grids

$$\eta_{\vec{\gamma},\vec{\omega}}(x) = \frac{1}{x} - \frac{1}{\pi}\sum_{k=1}^{N}\gamma_k\phi^2_{\omega_k}(x) \qquad \phi_\omega(x) := \frac{2x}{x^2+\omega^2}$$

$$\hat{\eta}_{\vec{\sigma},\vec{\tau}}(x) = \frac{1}{2x} - \sum_{i=1}^{N}\sigma_i\hat{\phi}^2_{\tau_i}(x) \qquad \hat{\phi}_\tau(x) := e^{-x|\tau|}$$

$$x \in I^* = \left[\min(\epsilon_a - \epsilon_j), \max(\epsilon_a - \epsilon_j)\right] := [1, R] \qquad R := \frac{\epsilon_{\max}}{\epsilon_{\min}}$$

Remez algorithm

The grids (and coefficients) depends on number of grid points (N) and energy range (R)

$\vec{\omega} = \{\omega_k\}_{k=1}^N$ $\vec{\tau} = \{\tau_i\}_{i=1}^N$ — **grids**

$\vec{\gamma} = \{\gamma_k\}_{k=1}^N$ $\vec{\sigma} = \{\sigma_i\}_{i=1}^N$ — **integration weights**

Peitao Liu, Merzuk Kaltak, Jiří Klimeš, and Georg Kresse, *Phys. Rev. B* 94, 165109 (2016)
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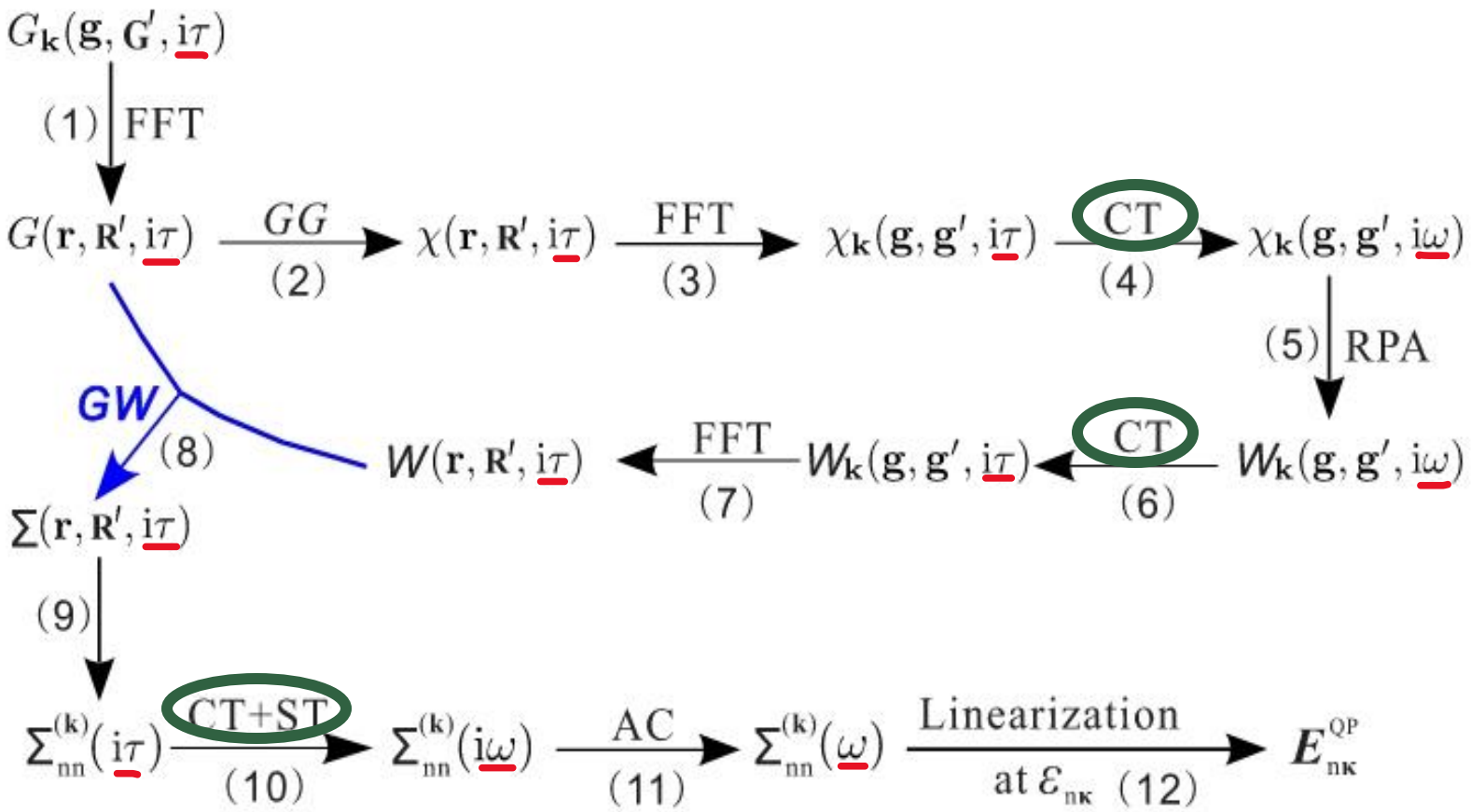
Schematic workflow for the low-scaling GW quasi-particle calculations



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Nonuniform cosine and sine transformations

$$F(i\omega_k) = \sum_{j=1}^{N} \gamma_{kj} \cos(\omega_k \tau_j) F(i\tau_j)$$

$$F(i\tau_j) = \sum_{k=1}^{N} \xi_{jk} \cos(\tau_j \omega_k) F(i\omega_k)$$

The matrix $\xi \cos(\tau\omega)$ is the inverse of the matrix $\gamma \cos(\omega\tau)$.

$$\sum_k \eta_{j'k} \cos(\tau_{j'} \omega_k) \cdot \delta_{kj} \cos(\omega_k \tau_j) \neq (\mathbb{I})_{j'j}$$

$$F(i\omega_k) = i \sum_{j=1}^{N} \lambda_{kj} \sin(\omega_k \tau_j) F(i\tau_j)$$

$$F(i\tau_j) = -i \sum_{k=1}^{N} \zeta_{jk} \sin(\tau_j \omega_k) F(i\omega_k)$$

The matrix $\zeta \sin(\tau\omega)$ is the inverse of the matrix $\lambda \sin(\omega\tau)$.

The implementation and associated Python scripts is available in Green-X library.

sloppy Remez algorithm needs quadruple precision, and is rather unstable

For each target number of points and ratio of energies, human effort has to be dedicated to the production of the grids

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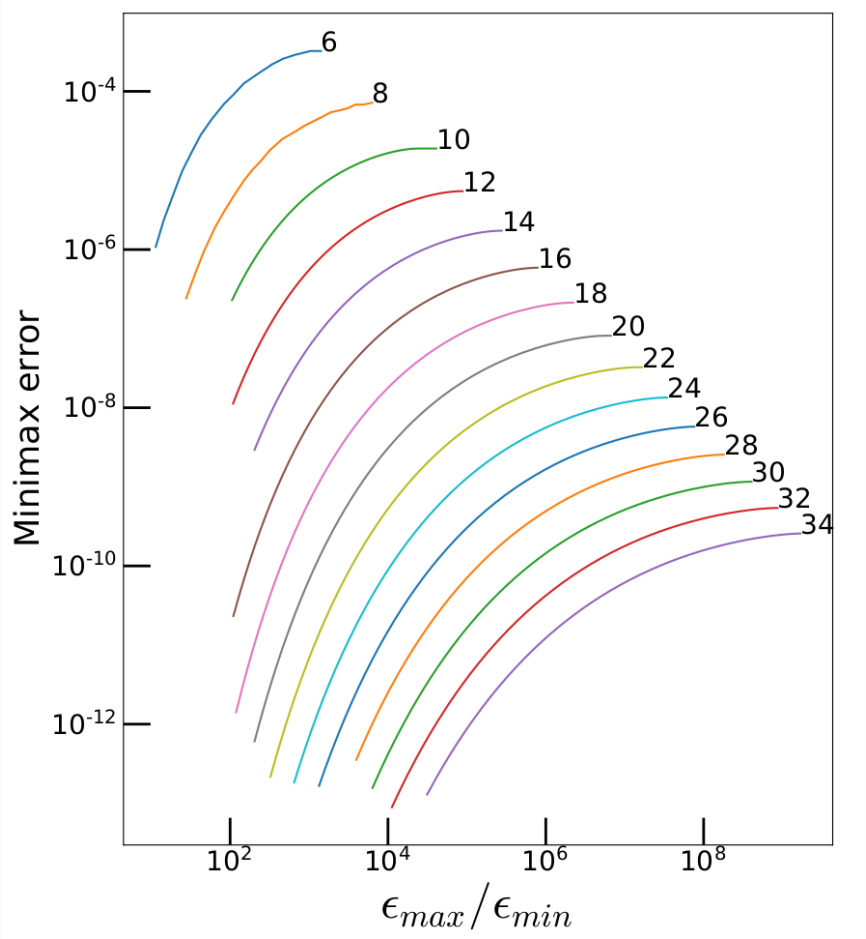
Absolute maximum and minimum error of η(x) as a function of energy range for different number of frequency points.



Starting from CP2K routines, the routines have been improved with respect to the accuracy of the grids.

"One key result of this work"

This plot provides a rough estimation of the error in the final RPA energy for a given pair (N, energy range).

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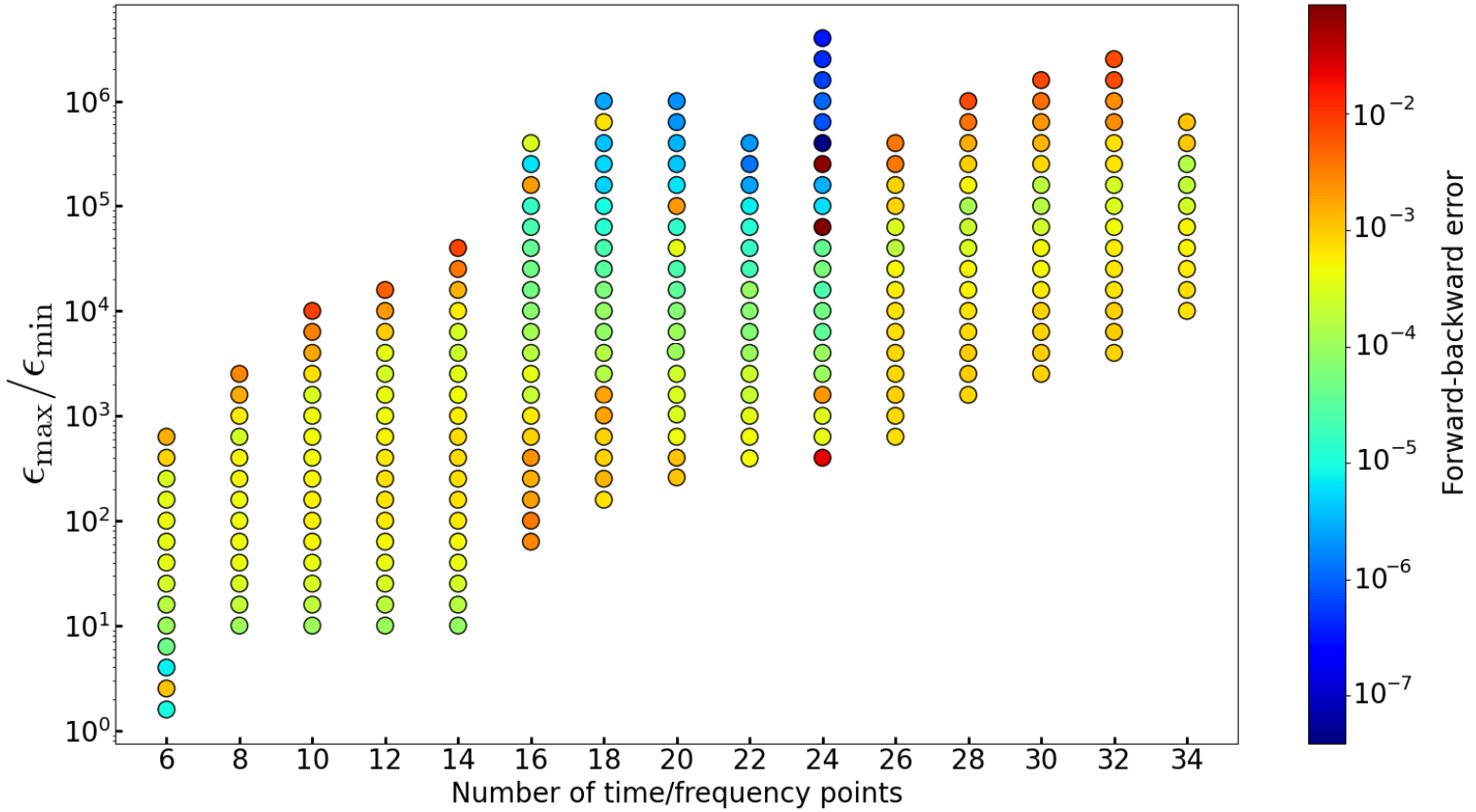
Forward-backward error for the different sets provided by Green-X

$$\Delta_{\mathrm{FB}} = \max_{j'j} \left| \sum_{k} \eta_{j'k} \cos(\tau_{j'}\omega_k) \cdot \delta_{kj} \cos(\omega_k \tau_j) - (\mathbb{I})_{j'j} \right|$$



$$F(i\omega_k) = \sum_{j=1}^{N} \gamma_{kj} \cos(\omega_k \tau_j) F(i\tau_j)$$

$$F(i\tau_j) = \sum_{k=1}^{N} \xi_{jk} \cos(\tau_j \omega_k) F(i\omega_k)$$

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GW100 benchmark: accuracy check Linking Green-X with CP2K

Convergence of HOMO and LUMO energies of the GW100 benchmark set computed with the low-scaling algorithm at the G_0W_0@PBE level as a function of the number of minimax points N.

	MAD (eV)		AD $\leq$ 0.01 eV		AD $\leq$ 0.02 eV	
N	HOMOs	LUMOs	HOMOs	LUMOs	HOMOs	LUMOs
10	0.11	0.091	15	18	30	34
12	0.087	0.010	30	41	48	79
14	0.065	0.017	27	60	40	84
16	0.038	0.019	29	53	41	73
18	0.032	0.008	28	62	49	91
20	0.025	0.011	28	66	60	94
22	0.020	0.011	47	79	75	92
24	0.013	0.008	70	87	86	94
26	0.016	0.008	70	90	83	95
28	0.006	0.006	84	93	90	96
30	0.008	0.004	87	97	92	100
32	0.008	0.008	85	96	92	98

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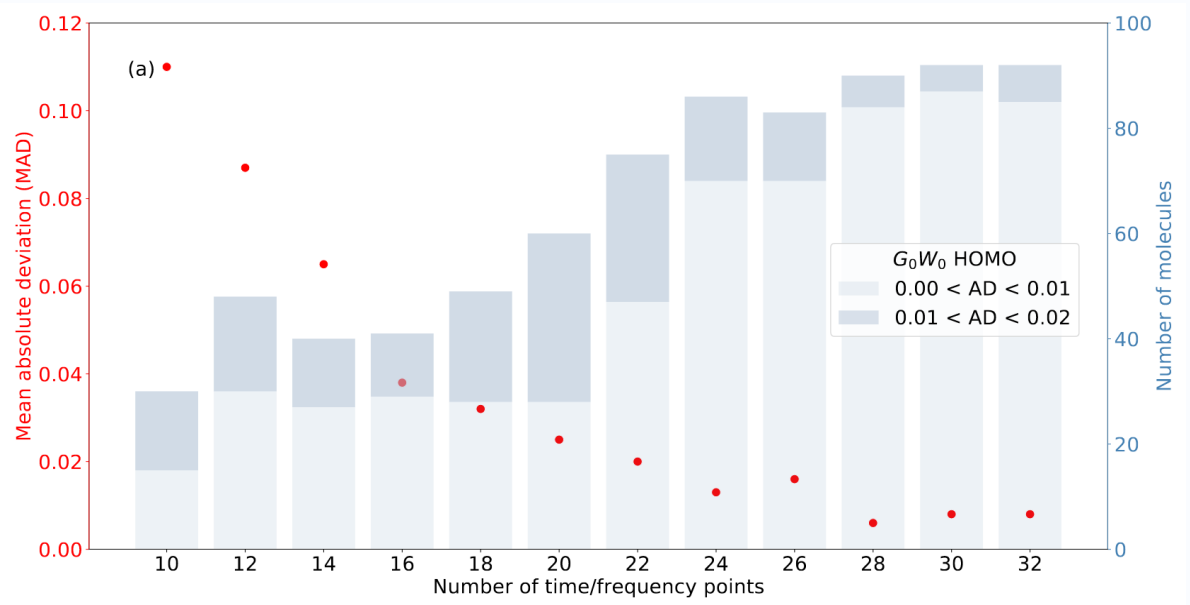
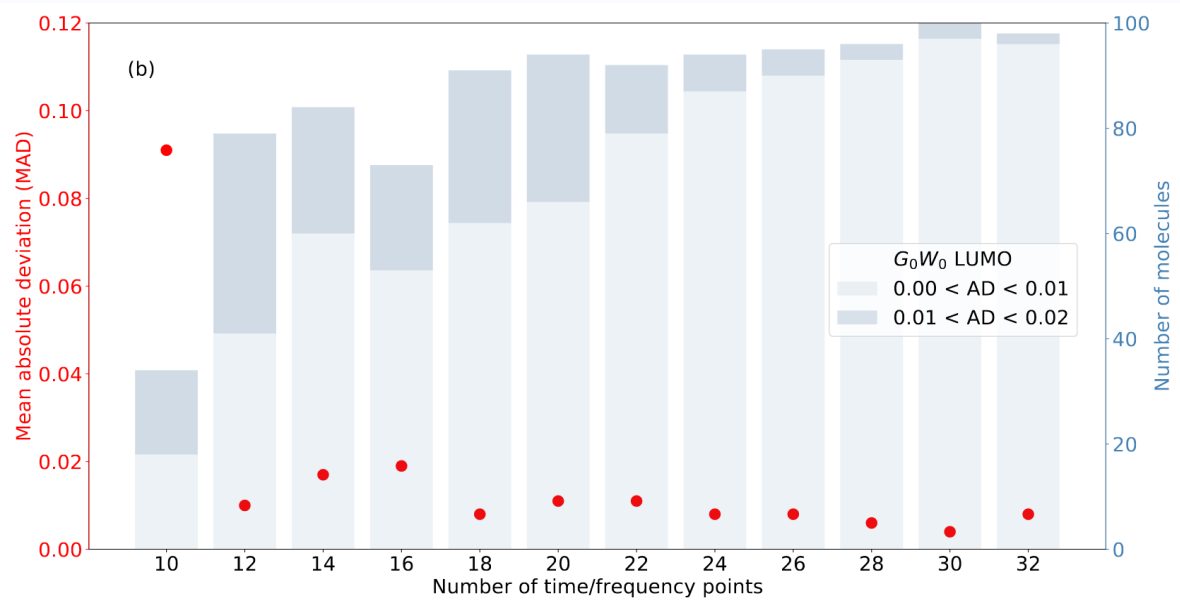
Low-scaling GW for molecules

GW 100 benchmark of the G_0W_0@PBE energies computed with the low-scaling algorithm for (a) HOMOs and (b) LUMOs.

The bars represent the number of molecules with a given absolute deviation from the FHI-aims values reported in Ref. Comput. Phys. Commun. 255, 107242 (2020).

The variation of mean absolute deviation (MAD) as a function of number of time/frequency points is given by the orange dots.





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NOVEL MATERIALS DISCOVERY

JOSS
The Journal of Open Source Software

Time-frequency component of the GreenX library: minimax grids for efficient RPA and *GW* calculations

Maryam Azizi [1], **Jan Wilhelm** [2], **Dorothea Golze** [3], **Matteo Giantomassi** [1], **Ramón L. Panadés-Barrueta** [3], **Francisco A. Delesma** [4], **Alexander Buccheri** [5], **Andris Gulans** [6], **Patrick Rinke** [4], **Claudia Draxl** [5], **and Xavier Gonze** [1]

1 Institute of Condensed Matter and Nanoscience, UCLouvain, B-1348 Louvain-la-Neuve, Belgium
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4 Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Finland
5 Institut für Physik und Iris Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 2, 12489 Berlin, Germany
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DOI: 10.21105/joss.05570

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Summary

- GW space-time method

$$\chi(i\tau) \rightarrow \chi(i\omega) \rightarrow \varepsilon(i\omega) \rightarrow W(i\omega) \rightarrow W(i\tau) \rightarrow \Sigma(i\tau) \rightarrow \Sigma(i\omega) \rightarrow \Sigma(\omega)$$

- GX-TimeFrequency provides time and frequency grids and corresponding integration weights to compute correlation energies for Green's function implementations. It also provides Fourier weights to convert between imaginary time and imaginary frequency.
- They are more compact than, e.g., Gauss-Legendre grids, resulting in a reduction of the computational prefactor, while yielding same accuracy.
- The library has been already linked to ABINIT, CP2K, exciting and FHI-AIMS. The results seem to be promising.

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Supplementary

$$W(i\tau) = \int_{-\infty}^{\infty} e^{i\omega t} W(i\omega) = \int_{-\infty}^{\infty} (\cos(\omega t) + i \sin(\omega t)) W(i\omega)$$

$$= \int_{-\infty}^{\infty} \cos(\omega t)\, W(i\omega)$$

$$E^{(2)} = -\int_0^\infty \frac{d\omega}{4\pi} \mathrm{Tr}([\chi(i\omega)v]^2).$$

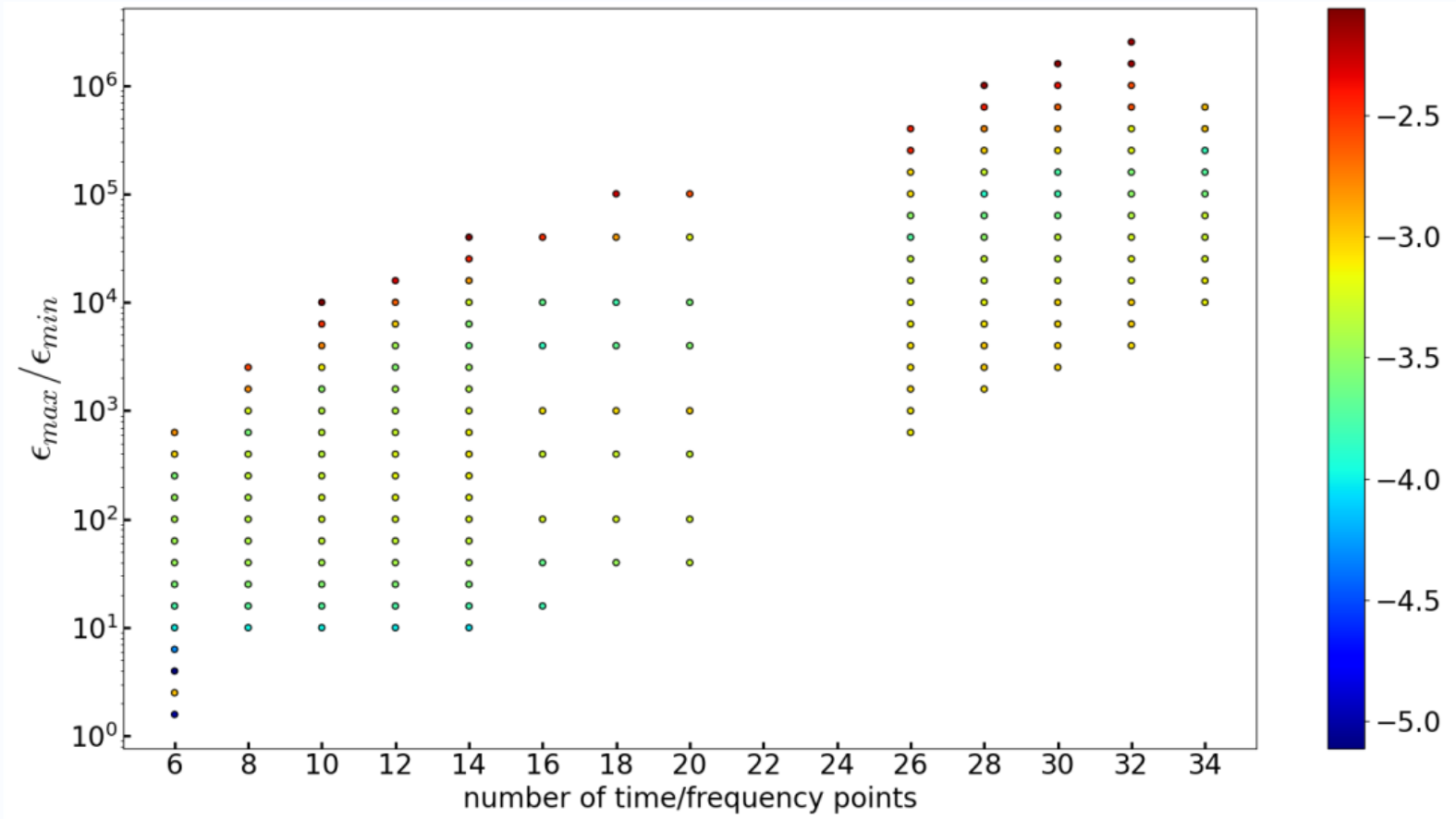
$$\chi_{\mathbf{k}}(\mathbf{g},\mathbf{g}',i\omega_k) = \sum_{ia} \xi_{ia}(i\omega_k)\langle\psi_i|e^{i(\mathbf{g}+\mathbf{k})\mathbf{r}}|\psi_a\rangle \times \langle\psi_a|e^{-i(\mathbf{g}'+\mathbf{k})\mathbf{r}'}|\psi_i\rangle$$

$$\xi_{ia}(i\omega_k) = \frac{2(\epsilon_a - \epsilon_i)}{(\epsilon_a - \epsilon_i)^2 + \omega_k^2}$$

$$E^{(2)} = \frac{1}{2}\sum_{ijab} \frac{|\langle\psi_i\psi_j|v|\psi_a\psi_b\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

Forward-backward error for the different sets provided CP2k

$$\Delta_{\mathrm{FB}} = \max_{j'j} \left| \sum_{k} \eta_{j'k} \cos(\tau_{j'}\omega_k) \cdot \delta_{kj} \cos(\omega_k \tau_j) - (\mathbb{I})_{j'j} \right|$$



$$F(i\omega_k) = \sum_{j=1}^{N} \gamma_{kj} \cos(\omega_k \tau_j) F(i\tau_j)$$

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