Real-time EOM-CCS Green's function method for the core spectral functions

F. D. Vila, J. J. Rehr, B. Peng and K. Kowalski

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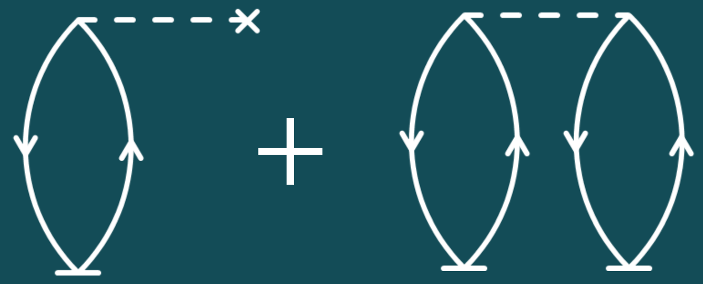

See also: J39.00004, JJ Rehr, FD Vila, JJ Kas, B Peng, and K Kowalski, arXiv: 2002.05841v2

SPEC Collaboration: DOE Office of Science grants DE-FG02-03ER15476, with computer support from DOE - NERSC.

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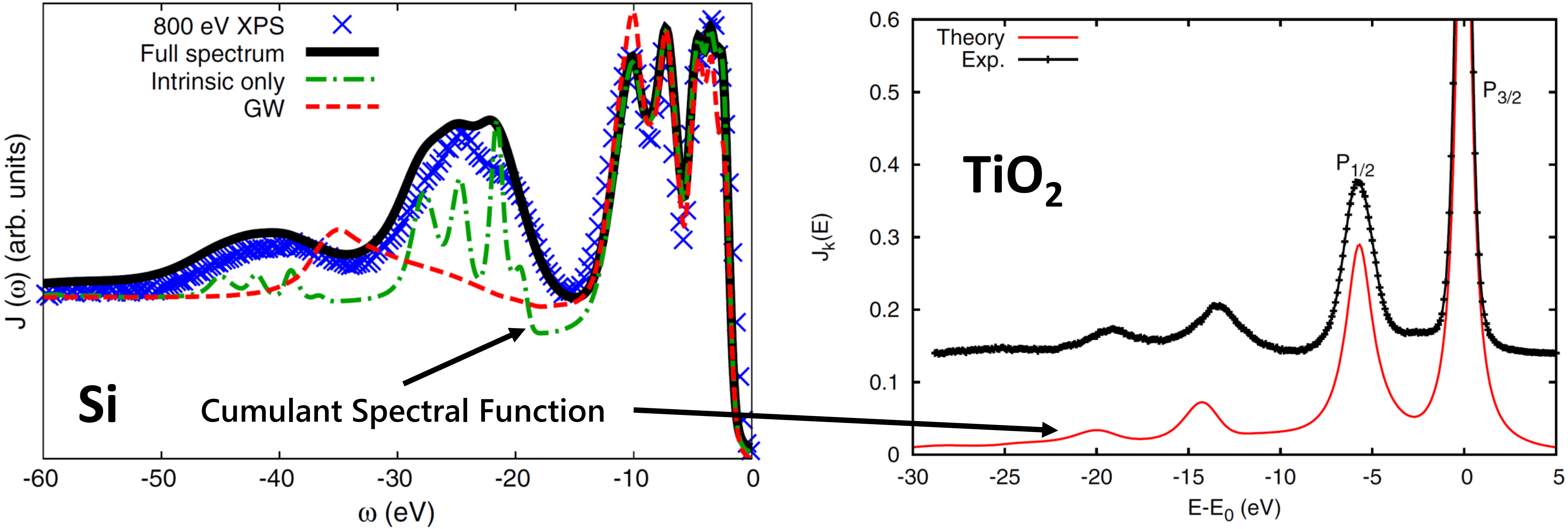
Motivation: The Cumulant Spectral Function

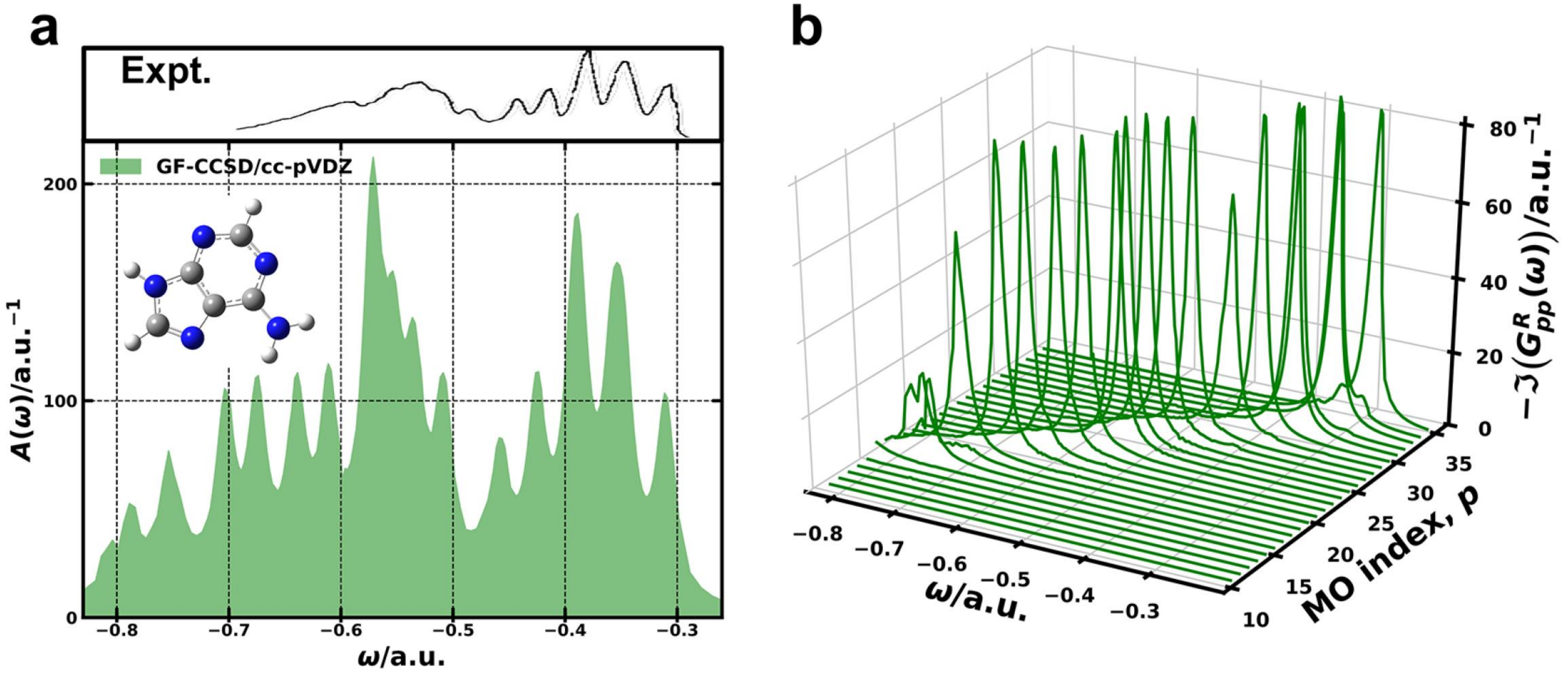


Guzzo et al. PRL ***107****, 166401 (2011)*

Kas et al. PRB ***91****, 121112(R) (2015)*

Efficient, improves many-body satellite effects in cond. matter

Motivation: Coupled Clusters GFs



Peng and Kowalski J. Chem. Theory Comput. ***14***, *4335 (2018)*

Accurate, systematically improvable, applicable to molecular systems

Motivation: Cumulant ←→ CCGF

Is there a relationship between CC and Cumulant approaches?

Can we use it to improve either?

Coupled Clusters Ansatz: $$|0\rangle = e^{T}\,|\Phi_0\rangle$$

Cumulant Ansatz: $$G_k(t) = e^{C_k(t)}\,G_k^0(t)$$

CC and Cumulant: Formally analogous

Is there a relationship between CC and Cumulant approaches?

Can we use it to improve either?

Coupled Clusters Ansatz: $|0\rangle = e^{T} |\Phi_0\rangle$

Correlated

Uncorrelated

Cumulant Ansatz: $G_k(t) = e^{C_k(t)} G_k^0(t)$

CC and Cumulant: Formally analogous

Is there a relationship between CC and Cumulant approaches?

Can we use it to improve either?

Coupled Clusters Ansatz: $|0\rangle = e^{T}|\Phi_0\rangle$

All correlation

Cumulant Ansatz: $G_k(t) = e^{C_k(t)} G_k^0(t)$

Connecting Cumulant and CC: RT-EOM-CCS

Exact retarded GF:

$$G_c^R(t) = -i\Theta(t)e^{iE_0 t}\langle 0|a_c e^{-iHt}a_c^+|0\rangle$$
$$-i\Theta(t)e^{-iE_0 t}\langle 0|a_c^+ e^{iHt}a_c|0\rangle$$

1st approx.: HF Single determinant GS

$$|0\rangle \simeq |\Phi_N\rangle$$
$$|\Phi\rangle \equiv |\Phi_{N-1}\rangle = a_c|\Phi_N\rangle$$

$$e^{iHt}|\Phi\rangle = |\Phi, t\rangle$$

$$G_c^R(t) = -i\Theta(t)e^{-iE_0 t}\langle\Phi|e^{iHt}|\Phi\rangle = -i\Theta(t)e^{-iE_0 t}\langle\Phi|\Phi,t\rangle$$

Connecting Cumulant and CC: RT-EOM-CCS

$$e^{iHt}|\Phi\rangle = |\Phi, t\rangle \quad \Longleftrightarrow \quad -i\frac{d|\Phi, t\rangle}{dt} = H|\Phi, t\rangle$$

Real-time CC ansatz: $|\Phi, t\rangle = N(t)e^{T(t)}|\Phi\rangle$

$$-i\left[\frac{d\ln N(t)}{dt} + \frac{dT(t)}{dt}\right]|\Phi\rangle = \bar{H}(t)|\Phi\rangle$$

where: $\bar{H}(t) = e^{-T(t)}He^{T(t)}$

and: $\langle\Phi|\Phi, t\rangle = N(t)$

Connecting Cumulant and CC: RT-EOM-CCS

$$-i\left[\frac{d\ln N(t)}{dt}+\frac{dT(t)}{dt}\right]|\Phi\rangle=\bar{H}(t)\,|\Phi\rangle$$

Project with: $\langle\Phi|$

$$-i\frac{d\ln N(t)}{dt}=\langle\Phi|\bar{H}_{N-1}(t)|\Phi\rangle+\langle\Phi|H|\Phi\rangle$$

where: $\bar{H}_{N-1}(t)=\bar{H}(t)-\langle\Phi|H|\Phi\rangle$

Connecting Cumulant and CC: RT-EOM-CCS

$$-i\left[\frac{d\ln N(t)}{dt}+\frac{dT(t)}{dt}\right]|\Phi\rangle=\bar{H}(t)|\Phi\rangle$$

Project with: $\langle\Phi|$

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Connecting Cumulant and CC: RT-EOM-CCS

$$-i\left[\frac{d\ln N(t)}{dt}+\frac{dT(t)}{dt}\right]|\Phi\rangle=\bar{H}(t)\,|\Phi\rangle$$

Project with: $\left\langle \Phi_{ij\ldots}^{ab\ldots}\right|$

$$-i\left\langle \Phi_{ij\ldots}^{ab\ldots}\left|\frac{dT(t)}{dt}\right|\Phi\right\rangle=\left\langle \Phi_{ij\ldots}^{ab\ldots}\,|\bar{H}_{N-1}(t)|\,\Phi\right\rangle$$

where: $\bar{H}_{N-1}(t)=\bar{H}(t)-\langle\Phi|H|\Phi\rangle$

Connecting Cumulant and CC: RT-EOM-CCS

$$-i\left[\frac{d\ln N(t)}{dt}+\frac{dT(t)}{dt}\right]|\Phi\rangle=\bar{H}(t)\,|\Phi\rangle$$

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where: $\bar{H}_{N-1}(t)=\bar{H}(t)-\langle\Phi|H|\Phi\rangle$

Connecting Cumulant and CC: RT-EOM-CCS

2nd approx.: Coupled Clusters Singles (CCS) only

$$T(t) = T_1(t) = \sum_{i,a} t_i^a(t)\left\{a_a^+ a_i\right\}'$$

$$\langle\Phi|\bar{H}_N(t)|\Phi\rangle = -\sum_{ia} v_{ci}^{ca} t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab} t_i^a t_j^b$$

$$\left\langle \Phi_i^a \left| \frac{dT(t)}{dt} \right| \Phi \right\rangle = \dot{t}_i^a$$

$$\langle\Phi_i^a|\bar{H}_N(t)|\Phi\rangle = -v_{ac}^{ic} + (\varepsilon_a - \varepsilon_i)t_i^a + \sum_j v_{jc}^{ic} t_j^a - \sum_b v_{ac}^{bc} t_i^b + \sum_{jb} v_{ja}^{bi} t_j^b + \sum_{jb} v_{jc}^{bc} t_i^b t_j^a + \sum_{jbd} v_{aj}^{bd} t_i^b t_j^d - \sum_{jkb} v_{jk}^{ib} t_j^a t_k^b - \sum_{jkbd} v_{jk}^{bd} t_i^b t_j^a t_k^d$$

RT-EOM-CCS: Final equations

$$G_c^R(t) = -i\Theta(t)e^{-i\varepsilon_c t + C^R(t)}$$

Cumulant form!

Pure exponential

$$C^R(t) = i\int_0^t \left(-\sum_{ia} v_{ci}^{ca} t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab} t_i^a t_j^b \right) dt'$$

$$-i\,\dot{t}_i^a = -v_{ac}^{ic} + (\varepsilon_a - \varepsilon_i)\,t_i^a + \sum_j v_{jc}^{ic} t_j^a - \sum_b v_{ac}^{bc} t_i^b + \sum_{jb} v_{ja}^{bi} t_j^b$$
$$+ \sum_{jb} v_{jc}^{bc} t_i^b t_j^a + \sum_{jbd} v_{aj}^{bd} t_i^b t_j^d - \sum_{jkb} v_{jk}^{ib} t_j^a t_k^b - \sum_{jkbd} v_{jk}^{bd} t_i^b t_j^a t_k^d$$

RT-EOM-CCS: Final equations

$$G_c^R(t) = -i\Theta(t)e^{-i\varepsilon_c t + C^R(t)}$$

Cumulant form!

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L NL

$$C^R(t) = i\int_0^t \left(-\sum_{ia} v_{ci}^{ca} t_i^a + \frac{1}{2}\sum_{ijab} v_{ij}^{ab} t_i^a t_j^b \right) dt'$$

Bare S1 S2 S3

$$-i\,\dot{t}_i^a = -v_{ac}^{ic} + (\varepsilon_a - \varepsilon_i)\,t_i^a + \sum_j v_{jc}^{ic} t_j^a - \sum_b v_{ac}^{bc} t_i^b + \sum_{jb} v_{ja}^{bi} t_j^b$$

$$+\sum_{jb} v_{jc}^{bc} t_i^b t_j^a + \sum_{jbd} v_{aj}^{bd} t_i^b t_j^d - \sum_{jkb} v_{jk}^{ib} t_j^a t_k^b - \sum_{jkbd} v_{jk}^{bd} t_i^b t_j^a t_k^d$$

D1 D2 D3 T1

Previous Talk Approximation:

Valence-Core

Bare+S1+S2+D1

RT-EOM-CCS Equations: Numerical Solution

Numerical integration using:

1st to 3rd order Adams-Moulton multistep method

$$y' = f(t, y) \;\Rightarrow\;
\begin{aligned}
y_{n+1} &= y_n + h\left(\frac{1}{2} f(t_{n+1}, y_{n+1}) + \frac{1}{2} f(t_n, y_n)\right)\\
y_{n+2} &= y_{n+1} + h\left(\frac{5}{12} f(t_{n+2}, y_{n+2}) + \frac{2}{3} f(t_{n+1}, y_{n+1}) - \frac{1}{12} f(t_n, y_n)\right)\\
y_{n+3} &= y_{n+2} + h\left(\frac{9}{24} f(t_{n+3}, y_{n+3}) + \frac{19}{24} f(t_{n+2}, y_{n+2}) - \frac{5}{24} f(t_{n+1}, y_{n+1}) + \frac{1}{24} f(t_n, y_n)\right)
\end{aligned}$$

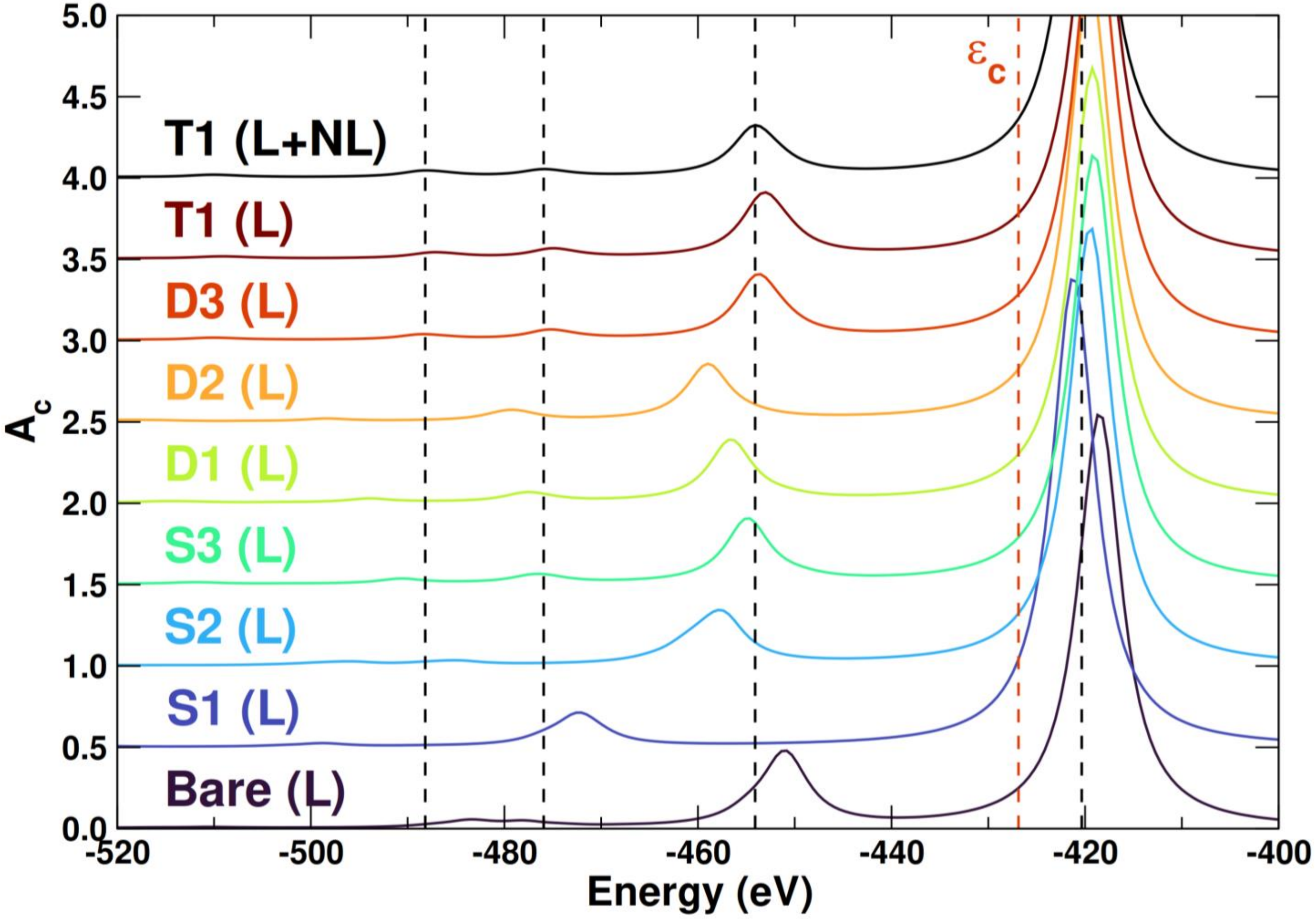
Take advantage of:

Common sum factorization (reduced scaling order)

Removal of cross-spin terms (

Pre-screening of zero cluster amplitudes ($t_i^a = 0$)

Results: Different term effects in N_2

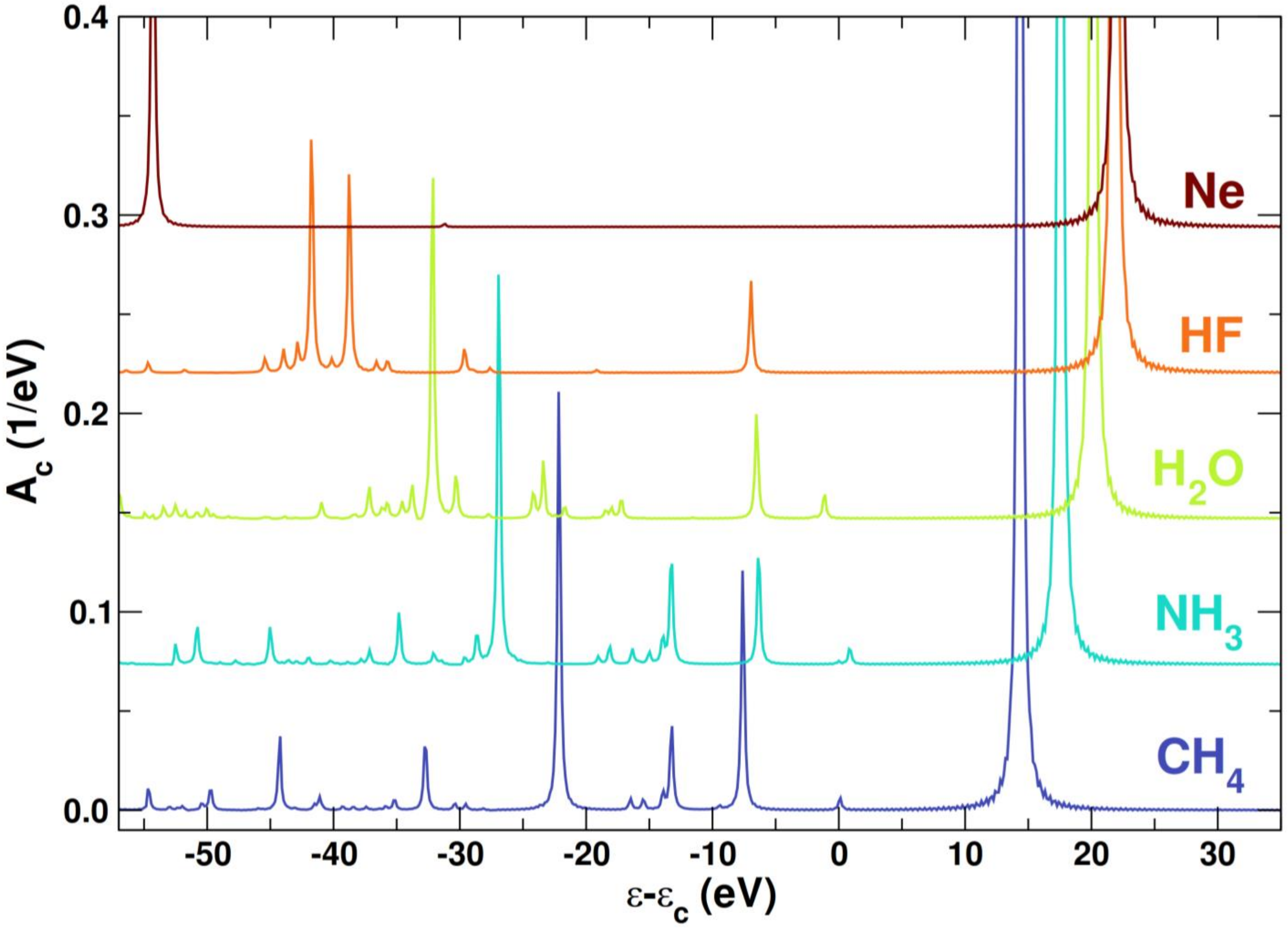


$$A_c^R(\omega) = -\frac{1}{\pi}\Im\left[G_c^R(\omega)\right]$$

t^3 contributions are very small

NL cumulant contribution tends to add an overall shift

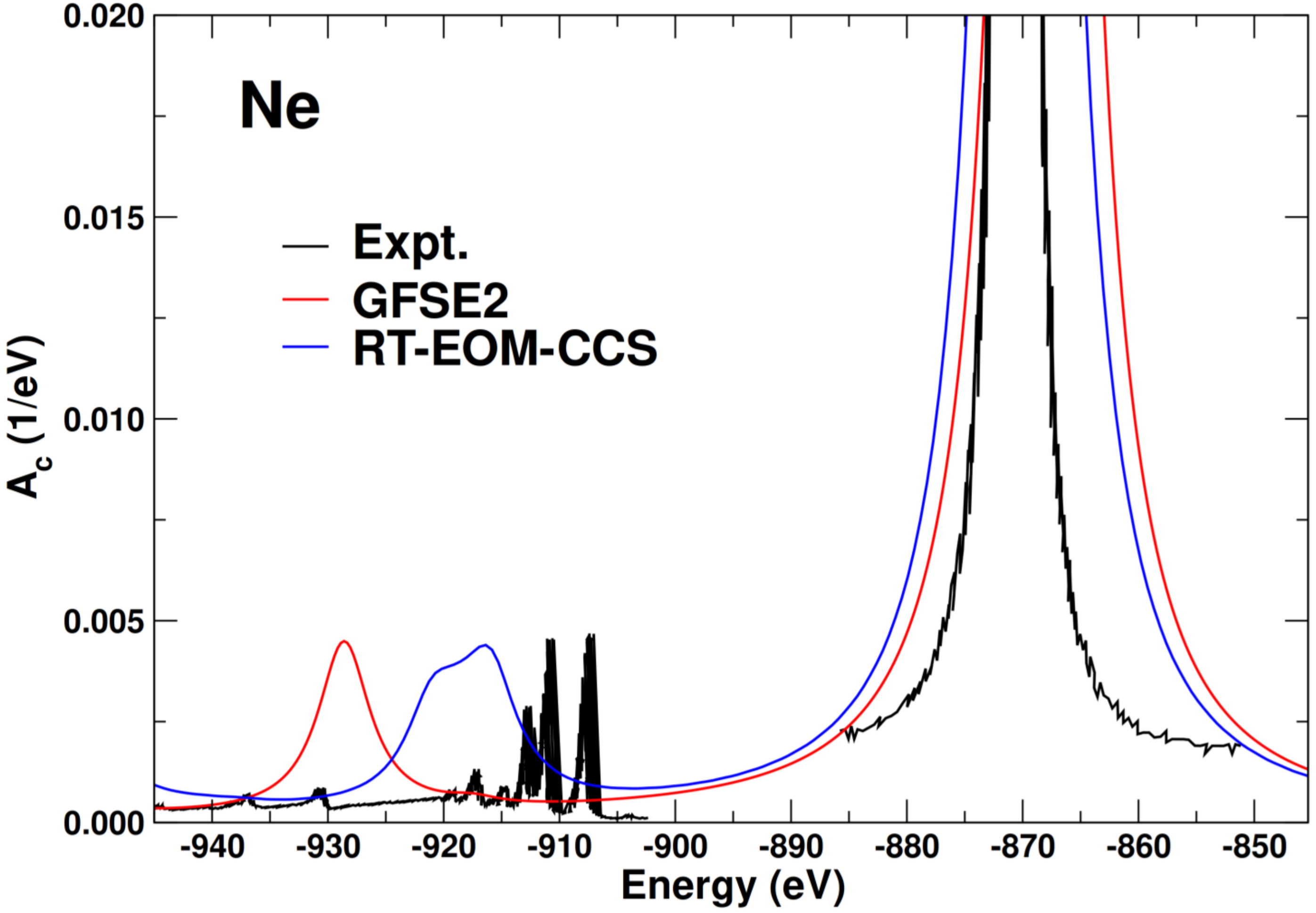
Results: The 10*e* series



QP position dominated by increasing mean core-valence interaction

Increasing core-valence interaction also reflected in increasing QP-satellite gap

Results: Satellites in Ne



Good absolute QP position

Improved satellite position and structure

Need better basis set to capture full relaxation

Summary:

Derived a direct relationship between Cumulant and CC ansatz:

- Only two approximations: Single reference GS, $T \simeq T_1$
- Non-linear Cumulant contribution → energy shift
- Only small contribution from cluster triples

Future developments:

- Derive and implement RT-EOM-CCD and –CCSD approaches
- Implement better (exponential) integrator for longer time-step
- Port to NWChem and TAMM (Tensor Algebra for Many-body Methods)
- Explore simplifications for condensed matter

Thank you for you attention!

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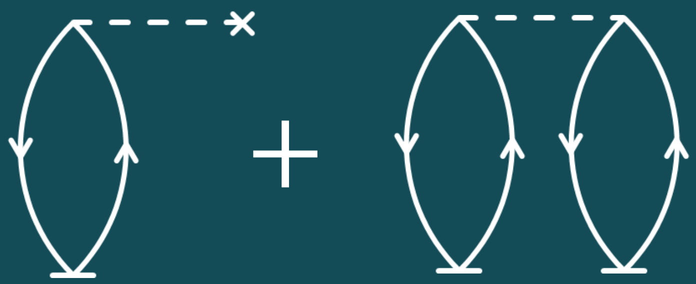

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