

Ionisation energies and electron affinities from a random-phase approximation many-body Green's function approach

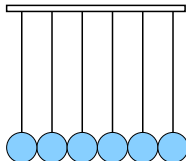
Andreas Heßelmann

Universität Erlangen

April 24, 2017

Random-phase approximation

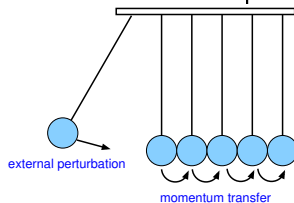
- Bohm and Pines: collective properties of the HEG (Phys. Rev. 82 (1951) 625, 85 (1952) 338, 92 (1953) 609)
- finite 1-dim model of the HEG: Newtons pendulum:



balls in close contact
(high density case)

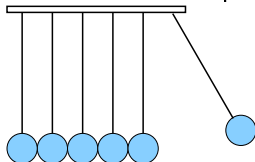
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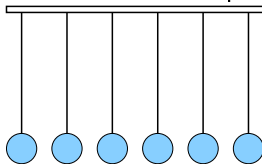
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system oscillates forth and back

Random-phase approximation

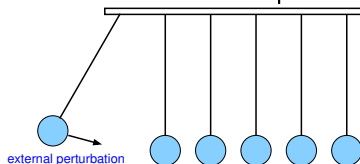
- Bohm and Pines: collective properties of the HEG (Phys. Rev. 82 (1951) 625, 85 (1952) 338, 92 (1953) 609)
- finite 1-dim model of the HEG: Newtons pendulum:



balls have larger distances
(low density case)

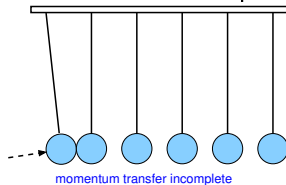
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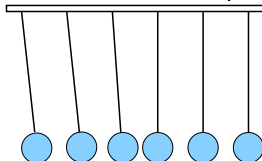
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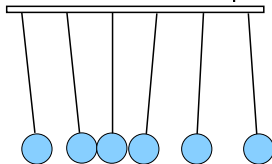
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collective motion damped
balls oscillating in random phases

Random-phase approximation

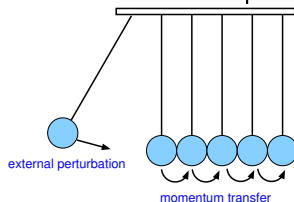
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response tends to average out to zero
for large number of particles

Random-phase approximation

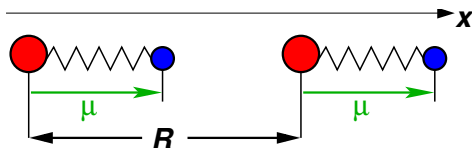
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- finite 1-dim model of the HEG: Newton's pendulum:



- RPA: in the high-density limit the (plasmon) modes can be decoupled from the thermal random motions of the particles in the system and the system can be described solely by collective motions

Coupled quantum Drude oscillator

(T. Odbadrakh, K. Jordan, JCP **144** (2016) 034111)



$$\begin{aligned}\hat{H} &= -\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} + \frac{1}{2} kx_1^2 + \frac{1}{2} kx_2^2 - \frac{2q^2}{R^3} x_1 x_2 \\ &= \hat{H}_0 + \hat{V} = \hat{H}_0 + \gamma x_1 x_2\end{aligned}$$

Exact solution:

$$\begin{aligned}E_{\text{int}} &= -\frac{\omega\gamma^2}{8k^2} - \frac{5\omega\gamma^4}{128k^4} - \dots \\ &= -\frac{1}{2}\alpha^2 \frac{\omega}{R^6} - \frac{5}{8}\alpha^4 \frac{\omega}{R^{12}} - \dots\end{aligned}$$

Coupled quantum Drude oscillator

(T. Odbadrakh, K. Jordan, JCP **144** (2016) 034111)

- CI using just the $|00\rangle$ and $|11\rangle$ configuration gives:

$$E = 2\omega - \frac{\omega\gamma^2}{8k^2} + \frac{\omega\gamma^4}{128k^4} - \dots$$

which is exact only through 2nd order

- Adiabatic connection fluctuation-dissipation theorem:

$$E_{int} = -\frac{1}{2\pi} \int_0^\infty d\nu \int dx_1 \int dx_2 \hat{V} \times \left(\frac{1}{2} \chi_0 \hat{V} \chi_0 - \frac{1}{3} \chi_0 \hat{V} \chi_0 \hat{V} \chi_0 + \dots \right)$$

- Response function of noninteracting system for coupled Drude oscillator (Hamiltonian real-valued, so need only real-valued part):

$$\chi_0(x_1, x_2, i\nu) = - \sum_{nm} \frac{2(E_{nm} - E_{00})}{(E_{nm} - E_{00})^2 + \nu^2} \langle \Psi_0 | \hat{\rho}(x_1) | \Psi_{nm} \rangle \langle \Psi_0 | \hat{\rho}(x_2) | \Psi_{nm} \rangle$$

with $E_{nm} = \omega(n + \frac{1}{2}) + \omega(m + \frac{1}{2})$

Coupled quantum Drude oscillator

- Due to symmetry (orthogonality of harmonic oscillator wave functions ϕ) $\Psi_{11} = |11\rangle$ can not contribute to the response function (the same for all excited states Ψ_{nm} with $n \neq 0 \wedge m \neq 0$). When all higher excited states are neglected the response function reads

$$\chi_0(x_1, x_2, i\nu) = -\frac{2\omega}{\omega^2 + \nu^2} (|01\rangle\langle 01| + |10\rangle\langle 10|)$$

- $E_{int}^{(2)} = -\frac{\delta^2}{2\omega} \quad \left(\frac{\gamma}{2\omega} = \delta\right)$
- $E_{int}^{(3)} = 0 \quad \left(\text{since } \langle 01|\hat{V}|01\rangle = 0 \text{ and } \langle 10|\hat{V}|10\rangle = 0\right)$
- $E_{int}^{(4)} = -\frac{5}{8} \frac{\delta^4}{\omega^3}$
- $E_{int}^{(n)} = -\frac{1 \cdot 3 \cdot 5 \cdots (2n-3)}{n(n-1)!} \cdot \frac{\delta^n}{\omega^{n-1}}$

Coupled quantum Drude oscillator

- Why is this result exact, i.e., why do the oscillators not couple in higher modes. Recall that the interaction matrix elements all have to be of the type

$$\begin{aligned}\langle 0n|\hat{V}|m0\rangle &= \langle 0n|\gamma x_1 x_2|m0\rangle \\ &= \gamma \langle 0|x_1|m\rangle \langle n|x_2|0\rangle\end{aligned}$$

with $m, n = 1, 2, \dots$

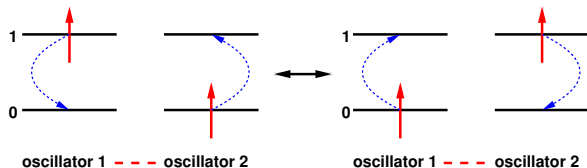
- Consider the matrix elements:

$$\begin{aligned}\langle 0|x|n\rangle &\sim \int_{-\infty}^{\infty} dx H_0(\sqrt{\omega}x) \cdot x \cdot H_n(\sqrt{\omega}x) e^{-\omega x^2} \quad |\sqrt{\omega}x \rightarrow y \\ &\sim \int_{-\infty}^{\infty} dy H_0(y) H_{n+1}(y) e^{-y^2} + (2n+1) \int_{-\infty}^{\infty} dy H_0(y) H_{n-1}(y) e^{-y^2} \\ &\sim \sqrt{\pi} \delta_{0,(n+1)} + (2n+1) \sqrt{\pi} \delta_{0,(n-1)} \\ &\sim (2n+1) \sqrt{\pi} \delta_{0,(n-1)}\end{aligned}$$

which is zero for all n except $n = 1$.

Coupled quantum Drude oscillator

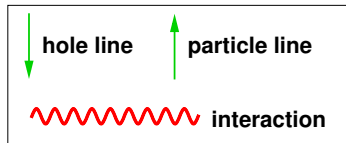
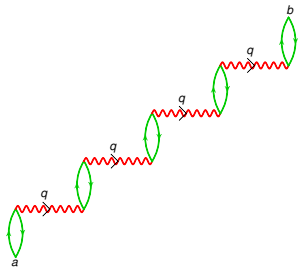
- This means that the above given form of the response function is sufficient if the interaction between the oscillators is a coupled dipole-interaction.



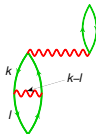
- This means that in this system the oscillators can interact only when they are 'in-phase' with each other. Since this actually is the approximation usually made within the random phase approximation, the RPA is exact for this particular model system.

Ring approximation

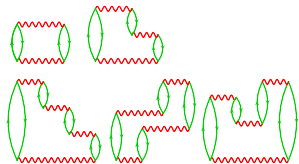
polarisation propagator in the RPA



not described within the RPA:

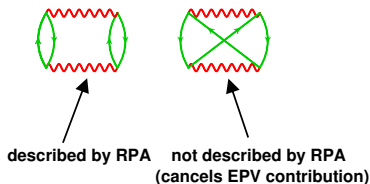
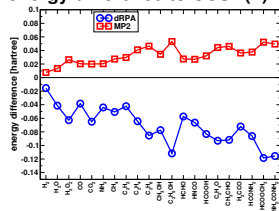


correlation energy (Gell-Mann and Brueckner (1957))



RPA correlation energy including exchange interactions

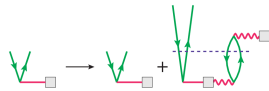
energy difference to CCSD(T):



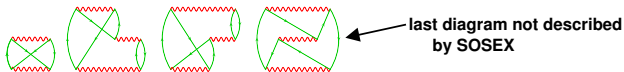
second-order screened exchange:
(SOSEX)
(Grueneis, Kresse et al. (2009))



antisymmetrise during iterations:
(RPAX2) (A.H. (2012))



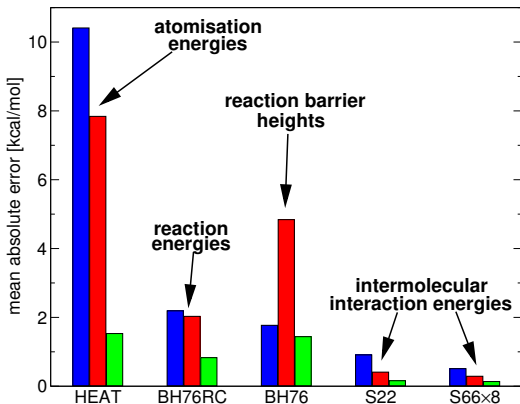
exchange contributions to correlation energy through 3rd order:



Performance of Kohn-Sham RPA methods

reference determinant: PBE

reference: CCSD(T)/cbs



(A.H., *Top. Curr. Chem.* **365** (2015) 97

A.H., RPA chapter, *Non-cov. Int. in Quant. Chem. and Phys.*, Elsevier (2017))

Green's function method

(Szabo, Ostlund, *Modern Quantum Chemistry*, Dover Press, chapter 7)

- Solution to matrix equation

$$(\omega \mathbf{1} - \mathbf{H}_0) \mathbf{a} = \mathbf{b}$$

can be obtained by knowledge of the resolvent

$$\mathbf{G}_0(\omega) = \frac{1}{\omega \mathbf{1} - \mathbf{H}_0} \quad (\mathbf{G}_0(\omega))_{ij} = \sum_{\alpha} \frac{c_i^{\alpha} c_j^{\alpha*}}{E - E_{\alpha}^{(0)}}$$

- Hartree-Fock Green's function

$$\mathbf{G}_0(\omega) = \frac{1}{\omega \mathbf{1} - \varepsilon}$$

with: ε : diagonal matrix containing the HF orbital energies

- Koopman's theorem: occupied HF orbital energies are associated with the molecular ionisation energies and virtual ones with the electron affinities of the molecule

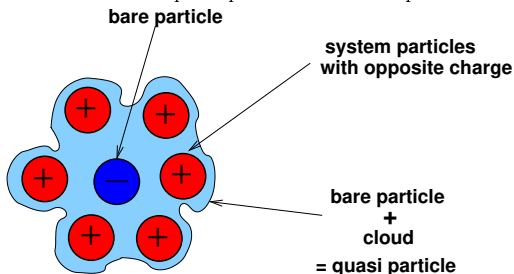
Green's function for interacting many-body system

- Dyson equation:

$$\begin{aligned} \mathbf{G}(\omega) &= \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\mathbf{\Sigma}(\omega)\mathbf{G}(\omega) \\ &= \frac{\mathbf{1}}{\omega\mathbf{1} - \epsilon - \mathbf{\Sigma}(\omega)} \end{aligned}$$

$\mathbf{\Sigma}(\omega)$: self-energy matrix

- self-energy: $\epsilon_{\text{quasi particle}} - \epsilon_{\text{bare particle}} = \epsilon_{\text{self}}$



particle 'interacts with itself' via the many-body system

Green's function for interacting many-body system

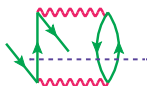
- poles of the many-body Green's function correspond to the 'exact' ionisation energies and electron affinities
- diagonal approximation:

$$\omega = \varepsilon_i + \Sigma_{ii}(\omega)$$

- first-order solution:

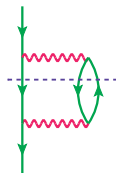
$$\omega = \varepsilon_i + \Sigma_{ii}(\varepsilon_i)$$

- second-order self-energy contributions:



correlation contribution

$$\Sigma_{\mathbf{p}\mathbf{q}}^{\text{corr}}(\omega) = -2 \sum_{i,a,b} \frac{(\mathbf{p}a|j\mathbf{b})(j\mathbf{b}|a\mathbf{q})}{\omega + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$



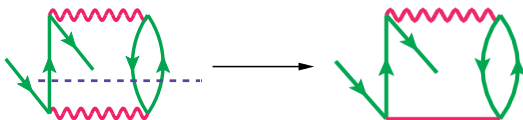
relaxation contribution

$$\Sigma_{\mathbf{p}\mathbf{q}}^{\text{relax}}(\omega) = -2 \sum_{i,j,b} \frac{(\mathbf{p}i|j\mathbf{b})(j\mathbf{b}|i\mathbf{q})}{\varepsilon_i + \varepsilon_j - \omega - \varepsilon_b}$$

Correlation contribution to self-energy

Σ_{CORR} on the RPA level:

replace second-order amplitudes (associated with the neutral system) by the RPA (RPAX2) amplitudes:

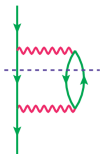


The correlation term Σ_{CORR} stabilises the neutral system relative to the anion/cation. Correspondingly it

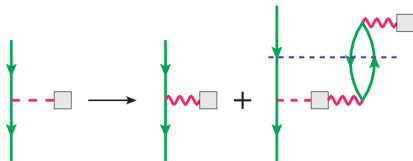
- leads to an increase of the ionisation energy
- reduces the electron affinity

Relaxation contribution to self-energy

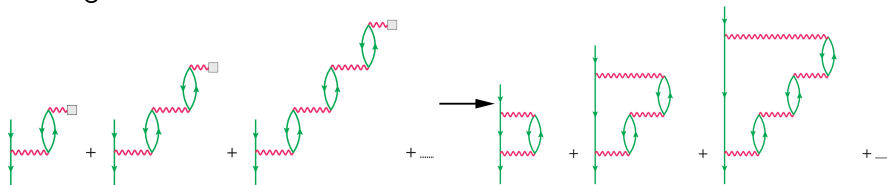
Σ_{relx} in second order:



Generate all time-forward ring-diagram contributions via:

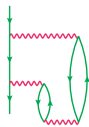


which gives

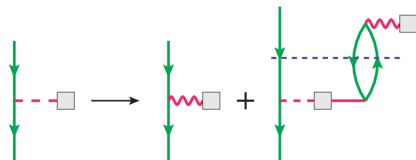


Relaxation contribution to self-energy

To take into account terms which include self-energy independent fragments like



the equation above is modified to

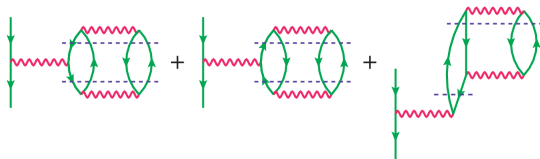


The relaxation contribution to Σ

- leads to a reduction of the ionisation energy
- increases the electron affinity

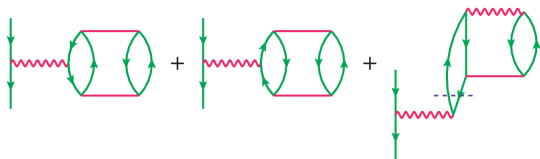
Static self-energy contributions

In third (and higher orders) the self-energy contains ω -independent contributions of the form:



These describe the interaction of the extra electron with a nonlocal correlation potential describing additional screening contributions (to the HF potential).

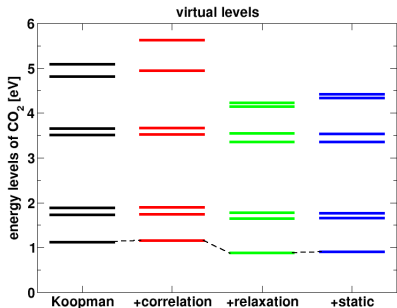
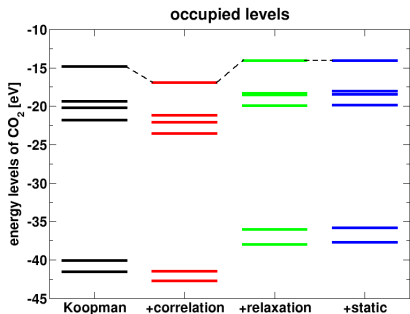
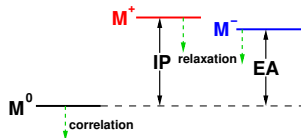
Generalisation to the RPA:



Quasiparticle energies of CO₂

reference determinant: HF

electron correlation level: RPAX2



Reference ionisation energies

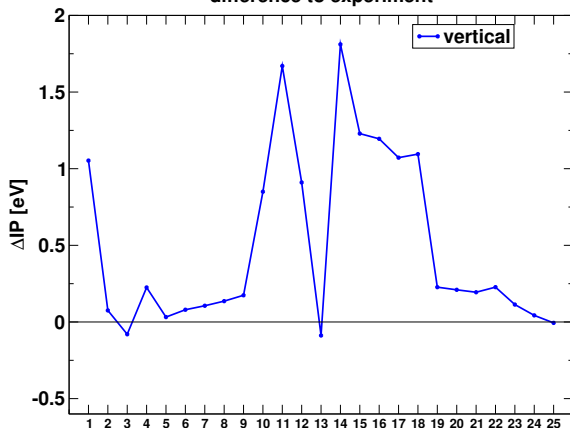
GW27 set of molecules (*M. van Setten et al., JCTC 9 (2013) 232*)

(H_2 , Li_2 , F_2 , BF , H_2O , NH_3 , SiH_4 , SF_4 , Au_2 , Au_4 , acetone, CH_4 , C_4H_{10} , naphthalene, naphthalene, ...)

structures: MP2/cc-pVTZ

energies: CCSD(T)/cbs

difference to experiment



Reference ionisation energies

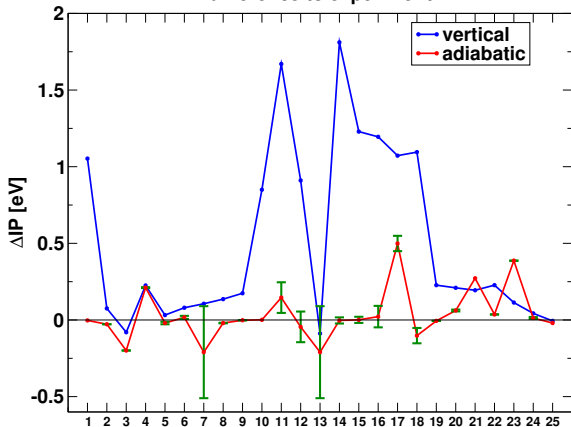
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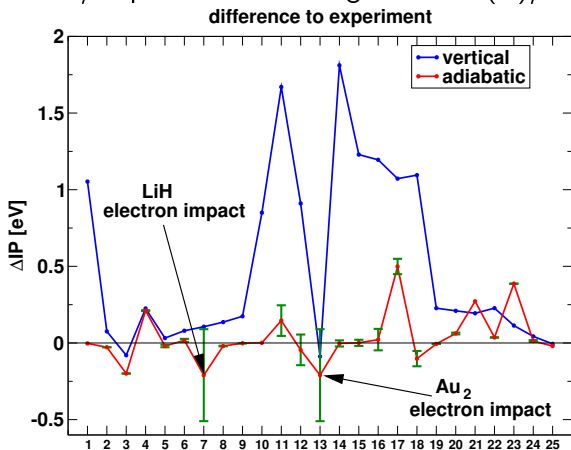
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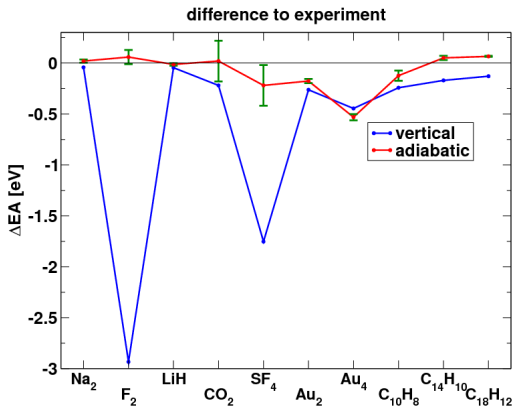
Reference electron affinities

GW27 set of molecules (*M. van Setten et al., JCTC* **9** (2013) 232)

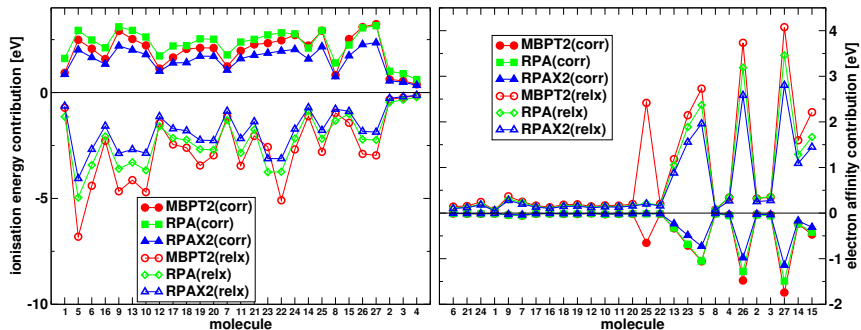
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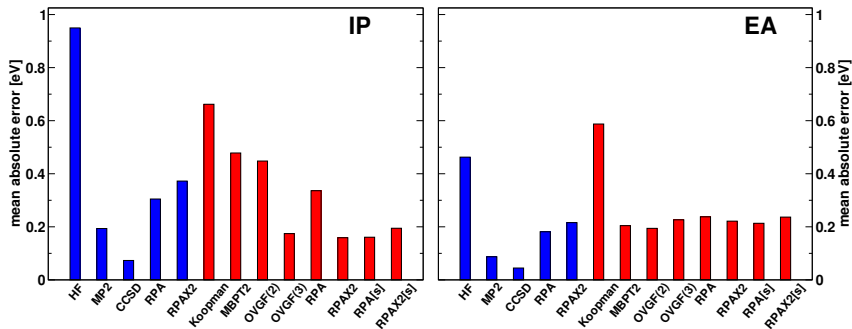
GW27: correlation & relaxation



- 2nd order self-energy contribution overestimates relaxation contribution to occupied and virtual energy levels
- RPA overestimates both, Σ_{corr} and Σ_{relx}
- $\Sigma_{\text{corr}}^{\text{RPA}} + \Sigma_{\text{relx}}^{\text{RPA}} \approx \Sigma_{\text{corr}}^{\text{RPAX2}} + \Sigma_{\text{relx}}^{\text{RPAX2}}$
- the correlation contribution is less important relative to the relaxation contribution for the unoccupied levels

GW27: deviations to CCSD(T) reference energies

- blue bars: energy difference methods
- red bars: Green's function methods
- all methods: HF reference
- reference IP's and EA's: extrapolated CCSD(T)



Summary

- RPA is exact for systems where incomplete momentum transfers of particle interactions are negligible
examples: HEG at high density, coupled Drude oscillator with dipole-dipole interaction
- for molecular systems RPA methods with additional exchange interactions can significantly improve the accuracy for thermokinetic properties
- self-energy corrections to ionisation energies and electron affinities on the RPA and RPAX2 level are very similar because the strong overestimation of the correlation contribution with RPA is largely corrected by the relaxation contribution
- accuracies of IP's and EA's with RPA/RPAX2 are similar to results using a 3rd-order propagator