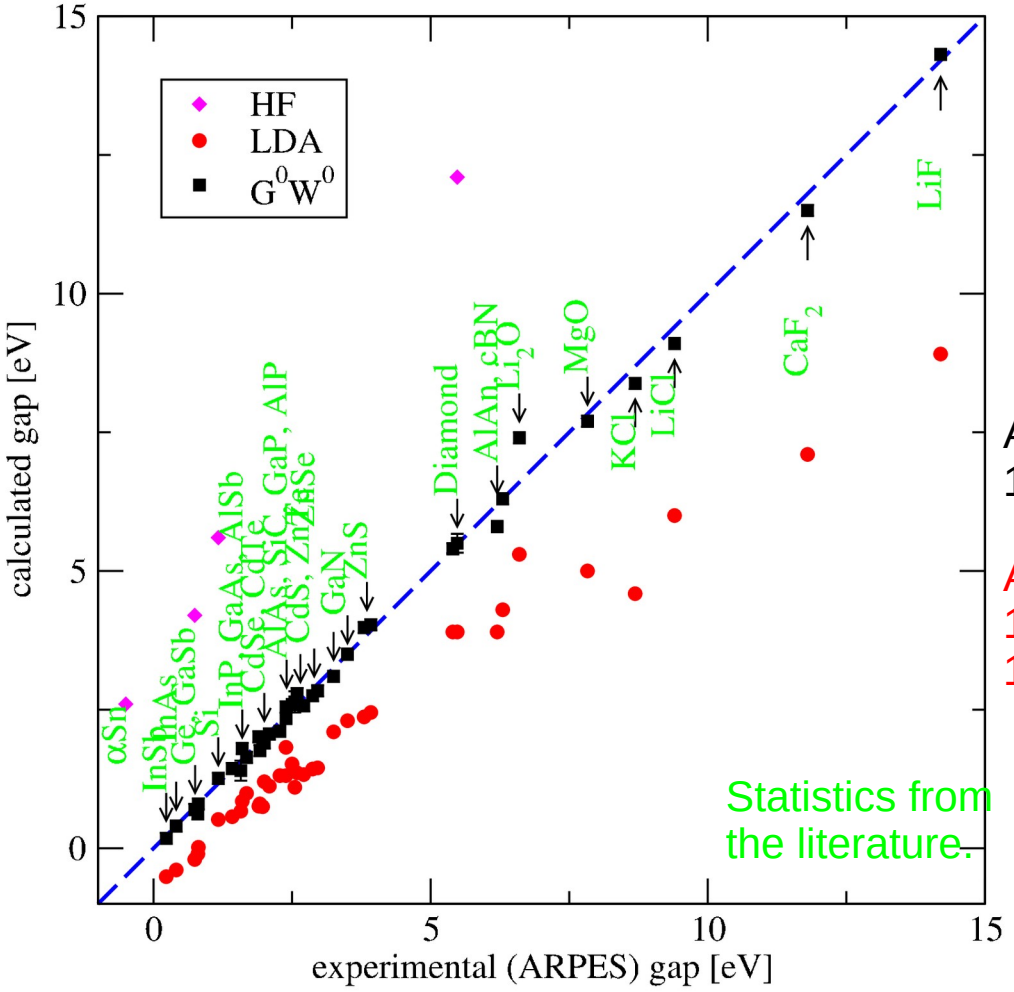
dRPA, RPAx, SRPA, SCRPA, rRPA, ...: tell me who you are and I will tell your RPA

Valerio Olevano
in memory of Peter Schuck

Background

- We need a **benchmark** for many-body theories & approx.

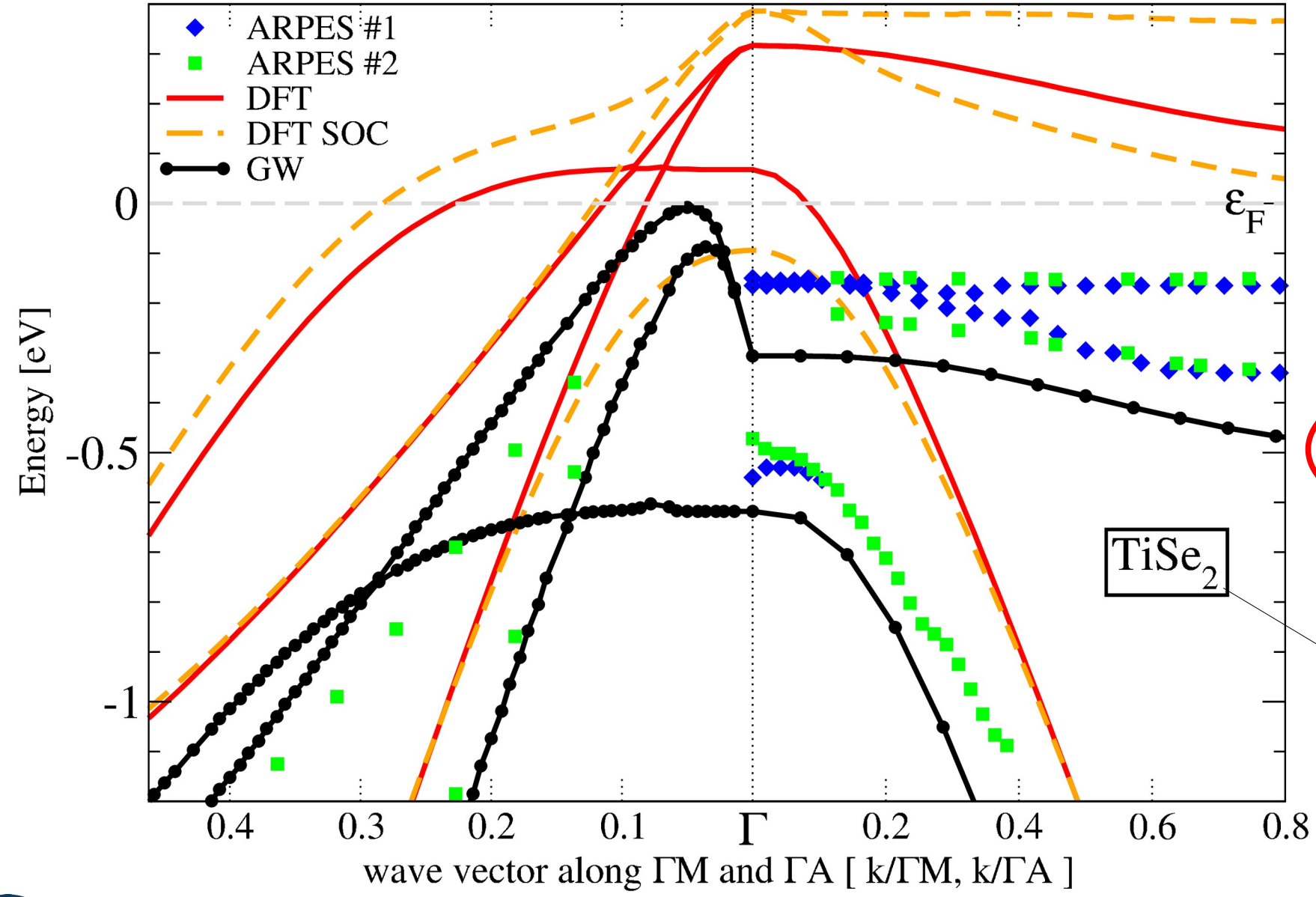


Ab initio GW on top of HF:
1980: Strinati, Mattausch, Hanke

Ab initio GW on top of DFT-LDA:
1985: Hybertsen, Louie
1986: Godby, Schlueter, Sham

- Is the **Experiment** a good **benchmark**?

What about Relativistic Effects?



Band gap:

0.2 eV

spin-orbit split:

0.2 eV

first 3d elements

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and electron-phonon, 0-point motion correction to the gap?

Computational Materials Science 83 (2014) 341–348

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Verification of first-principles codes: Comparison of total energies, phonon frequencies, electron–phonon coupling and zero-point motion correction to the gap between ABINIT and QE/Yambo

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in diamond:

0.4 eV

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 16 November 2013
Accepted 19 November 2013
Available online 12 December 2013

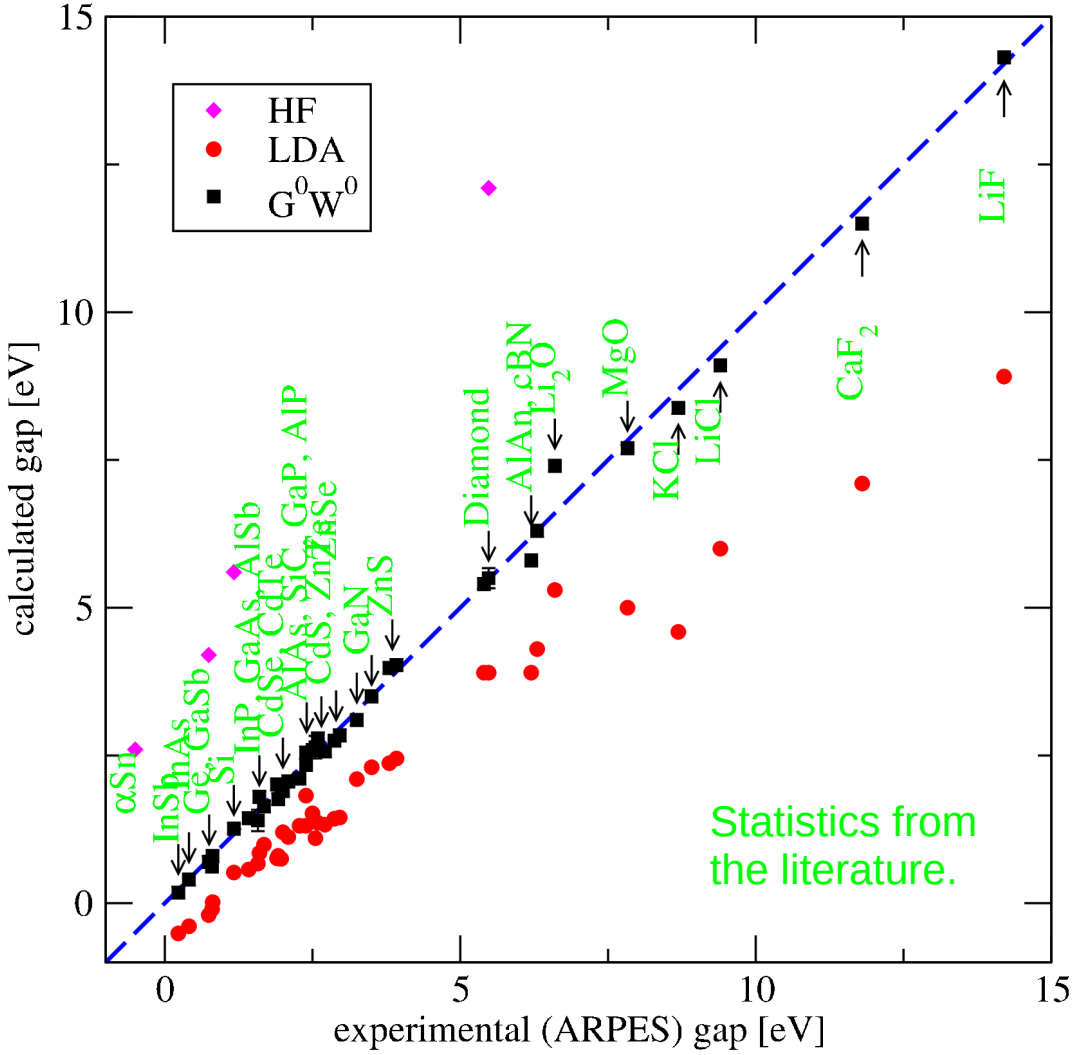
Keywords:
Density functional perturbation theory
Electron–phonon coupling
Temperature dependence
Verification
Allen–Heine–Cardona theory
Zero-point motion renormalization
Diamond

ABSTRACT

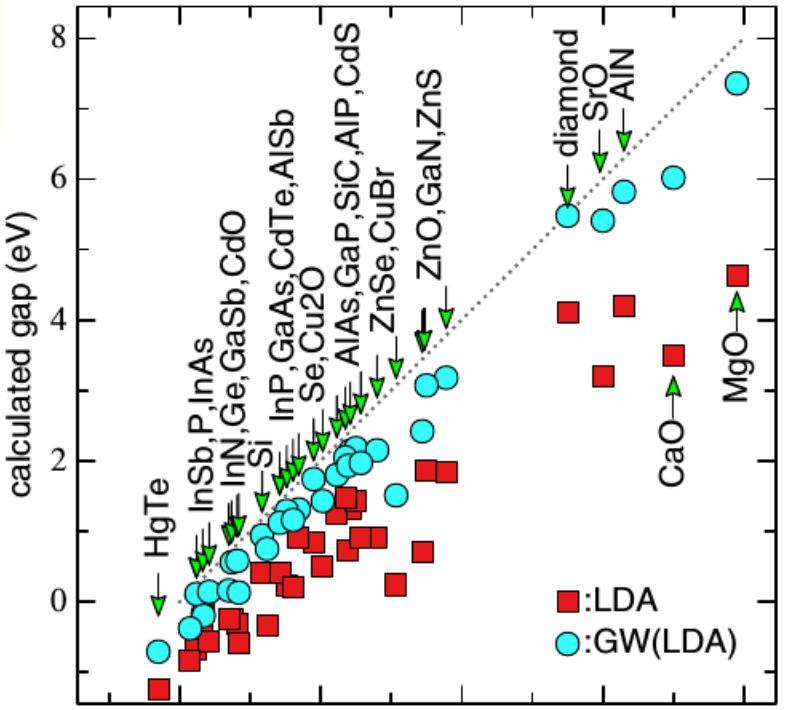
With the ever-increasing sophistication of codes, the verification of the implementation of advanced theoretical formalisms becomes critical. In particular, cross comparison between different codes provides a strong hint in favor of the correctness of the implementations, and a measure of the (hopefully small) possible numerical differences. We lead a rigorous and careful study of the quantities that enter in the calculation of the zero-point motion renormalization of the direct band gap of diamond due to electron–phonon coupling, starting from the total energy, and going through the computation of phonon frequencies and electron–phonon matrix elements. We rely on two independent implementations: Quantum Espresso + Yambo and ABINIT. We provide the order of magnitude of the numerical discrepancies between the codes, that are present for the different quantities: less than 10^{-5} Ha per atom on the total energy (−5.722 Ha/at), less than 0.07 cm^{-1} on the Γ, L, X phonon frequencies (555–1330 cm^{-1}), less than 0.5% on the square of the electron–phonon matrix elements and less than 4 meV on the zero-point motion renormalization of each eigenenergies (44–264 meV). Within our approximations, the DFT converged direct band gap renormalization in diamond due to the electron–phonon coupling is −0.409 eV (reduction of the band gap).

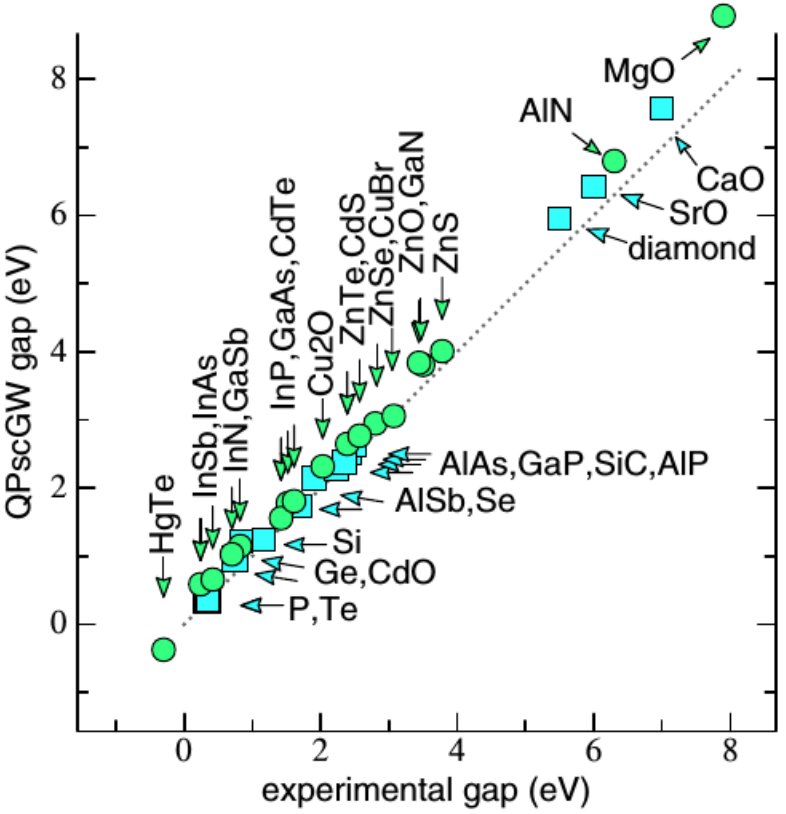
Background

- Is a comparison to the Experiment really meaningful?



Adapted from van Schilfgaarde et al.:





Background

- We must check our many-body approaches against **Exact Solution benchmarks!**
- Getting rid of:
  - mass corrections
  - electron-phonon
  - relativistic effects
  - QED
  - …
- which mask real many-body performances.

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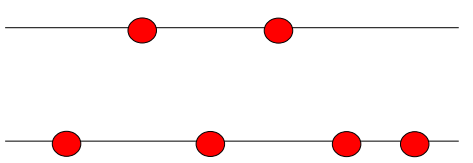
Peter's proposal: Lipkin model

$$H = \epsilon J_z + \frac{V}{2}(J_+ J_+ + J_- J_-)$$

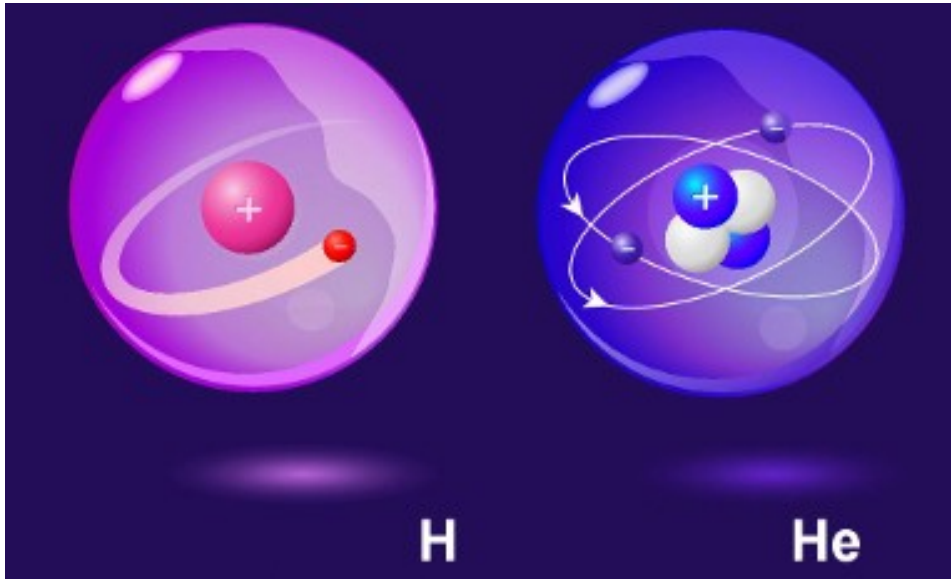


- Only two levels (p=N degenerate) model.
- Exact solution available.
- My criticism: Too far from reality?

He atom

- **Exact solution** (Hylleraas) available! for both ground and excited states.
- The simplest many-body system (although here many=2)
- Not a model, but even a **Real System**!

$$H = -\frac{\partial_{r_1}^2}{2} - \frac{\partial_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_2 - r_1|}$$



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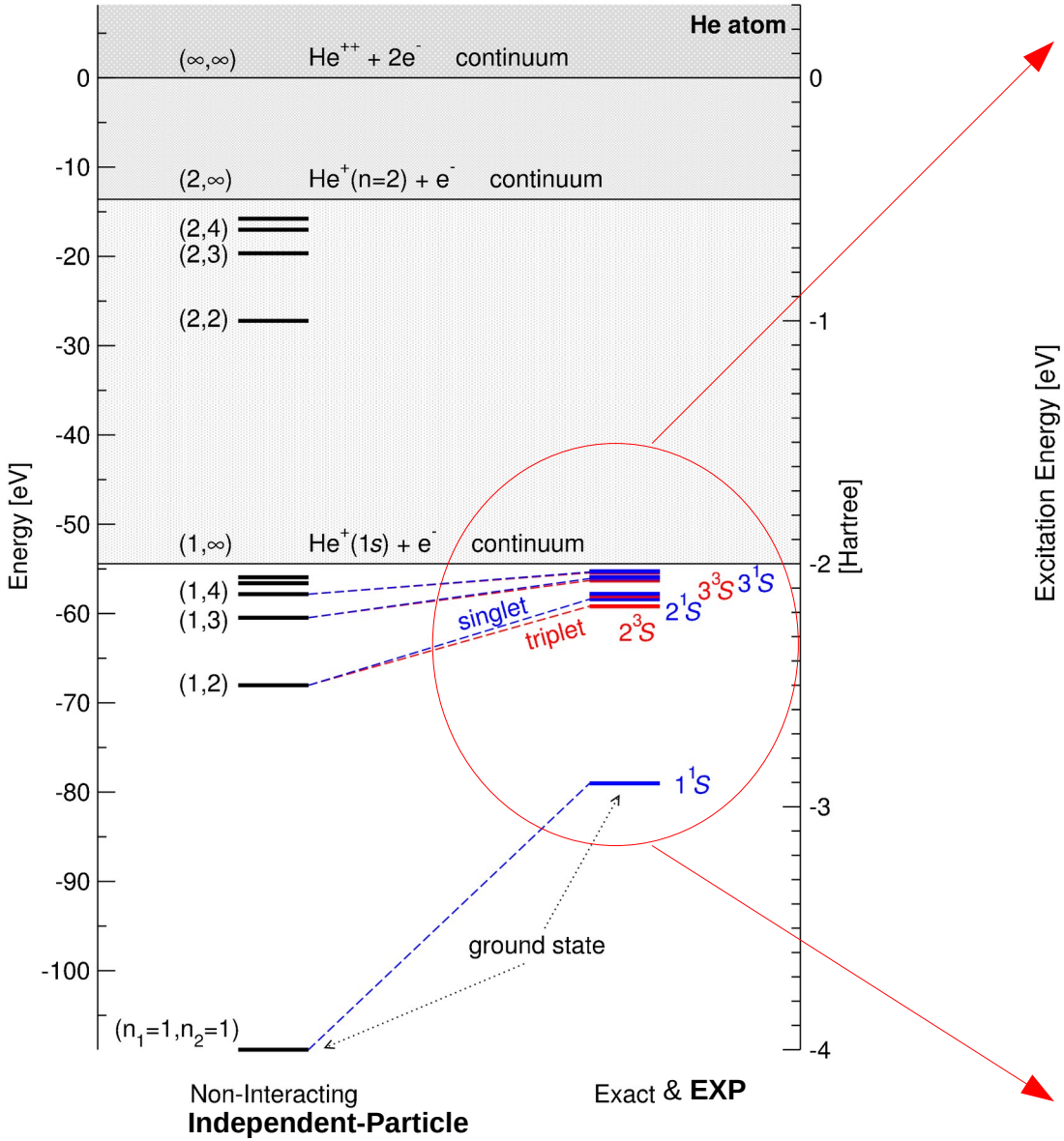
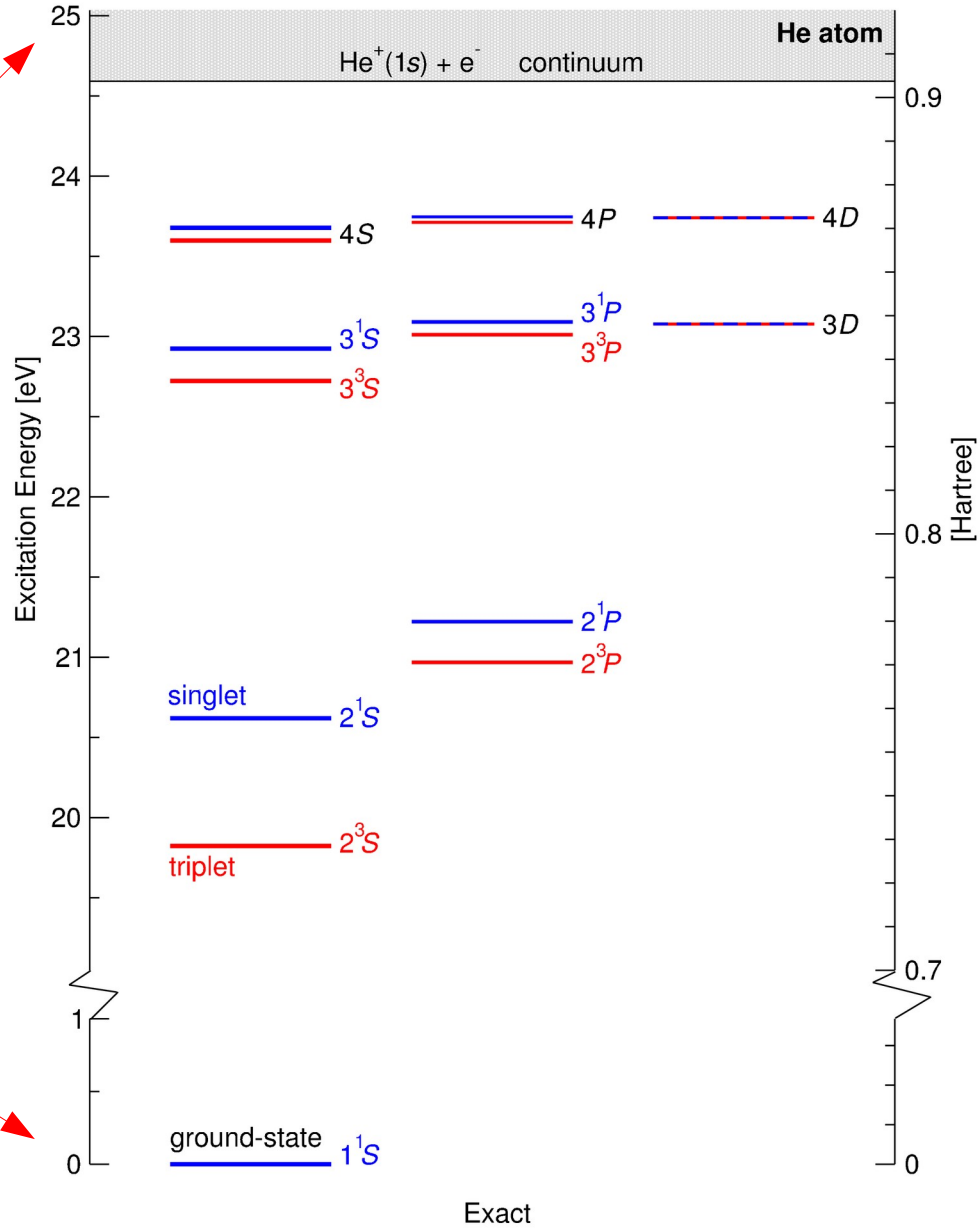
Helium atom electronic structure





$$E^0_{n_1 n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

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Hylleraas 1929 exact calculation

$$
\begin{aligned}
s &= r_1 + r_2 \\
t &= r_1 - r_2 \\
u &= r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|
\end{aligned}
$$

Hylleraas coordinates
(3 scalars instead than 6)

Formal Solution to the He S.E.
in a **Mathematical** sense

$$\Phi(s,t,u) = e^{-ks} \sum_{l,m,n} c_{lmn}\, s^l t^m u^n$$

Hylleraas functions

(for singlets → space-symmetric even function of *t*
→ *m = 0, 2, 4, … even*)

$$E_{1^1S} = -2.90324 \pm 0.00048 \quad (\pm 0.013\,\mathrm{eV})$$

Ground state energy

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Hylleraas: a really EXACT solution

Year	Reference	Helium atom 1^1S ground state energy [Ha]
1929	Hylleraas	**-2.903** 24
1957	Kinoshita	**-2.903 722** 5
1966	Frankowski & Pekeris	**-2.903 724 377 032** 6
1994	Thakka & Koga	**-2.903 724 377 034 11**4 4
1998	Goldman	**-2.903 724 377 034 119 59**4
1999	Drake	**-2.903 724 377 034 119 59**6
2002	Sims & Hagstrom	**-2.903 724 377 034 119 598 299** 9
2002	Drake *et al.*	**-2.903 724 377 034 119 598 30**5
2002	Korobov	**-2.903 724 377 034 119 598 311 158** 7
2006	Schwartz	**-2.903 724 377 034 119 598 311 159 245 194 404** 440 049 5
2007	Nakashima & Nakatsuji	**-2.903 724 377 034 119 598 311 159 245 194 404 446 696** 905 37

EXP accuracy: 10^{-9} Ha

- Numerically exact solution fulfilling the Numerical Analysis mathematical definition
- E_0^{He} became for physicists the mathematicians π

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Helium atom: a triumph of Quantum Mechanics!

Ionisation Potential [cm^{-1}]

	non-relativistic Hylleraas	reduced-mass correction	mass-polarization	relativistic corrections	QED radiative corrections	THEORY	EXPERIMENT
H^-	6090.644289	3.315791	3.928	0.304	0.0037	6083.092	6100 ± 100
He	198344.58014348	27.192711	4.785	0.562	1.341	198310.699	198 310.82 ± 0.15
Li^+	610120.4882	47.7689	4.960	−19.69	7.83	610079.62	610079 ± 25
Be^{2+}	1241253.351	75.681	5.619	−114.52	27.1	1241259.5	1241225 ± 100
B^{3+}	2091806.533	104.436	6.046	−372.88	65.7	2092003.2	2091960 ± 200
C^{4+}	3161805.752	144.864	6.878	−919.00	132	3162441	3162450 ± 300

0.02 meV

Pekeris PR (1958)

$$H = -\frac{\partial_{r_1}^2}{2} - \frac{\partial_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_2 - r_1|}$$

Today Experiment for IP and E

$198310.6664 \pm 2 \cdot 10^{-4} \mathrm{cm}^{-1}$

$2.903569880 \pm 10^{-9} \mathrm{Ha}$

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Outline

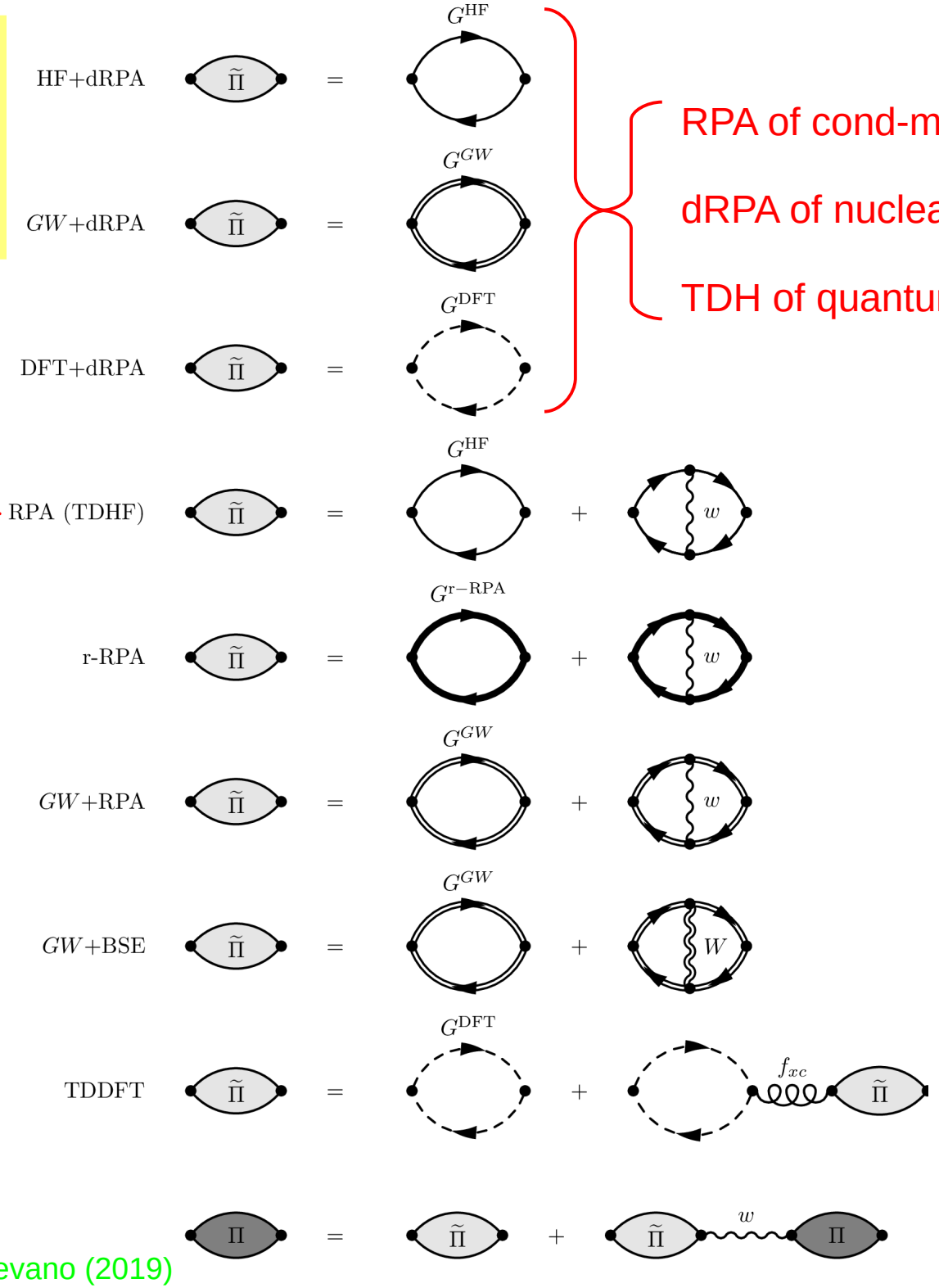
Comparing **many-body** approaches:

- HF and post-HF
- QMC
- DFT / TDDFT
- GW / BSE
- RPA and post-RPA

On the **He atom exact solution** for the:

- Ground state
- Quasiparticle charged excitations
- Optical neutral excitations

RPA-ology: Polarizability



He atom Ground State

He atom Ground State

Method	Energy [Ha]	[eV]
Noninteracting	-4	
Hartree	-1.9517	
HF	-2.8616	77.868
DFT-LDA	-2.8348	77.139
DFT-GGA	-2.8929	78.720
Exact-DFT [62]	-2.903724377034118	
Exact [10]	$-2.903724377034119598311159245194404$	79.014

$$E^0_{n_1 n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$$

- Errors:
  - HF: 1.1 eV = correlation energy
  - DFT-LDA: 1.9 eV (error of LDA, not of DFT)
  - DFT-GGA: 0.3 eV

He atom and Exact-DFT

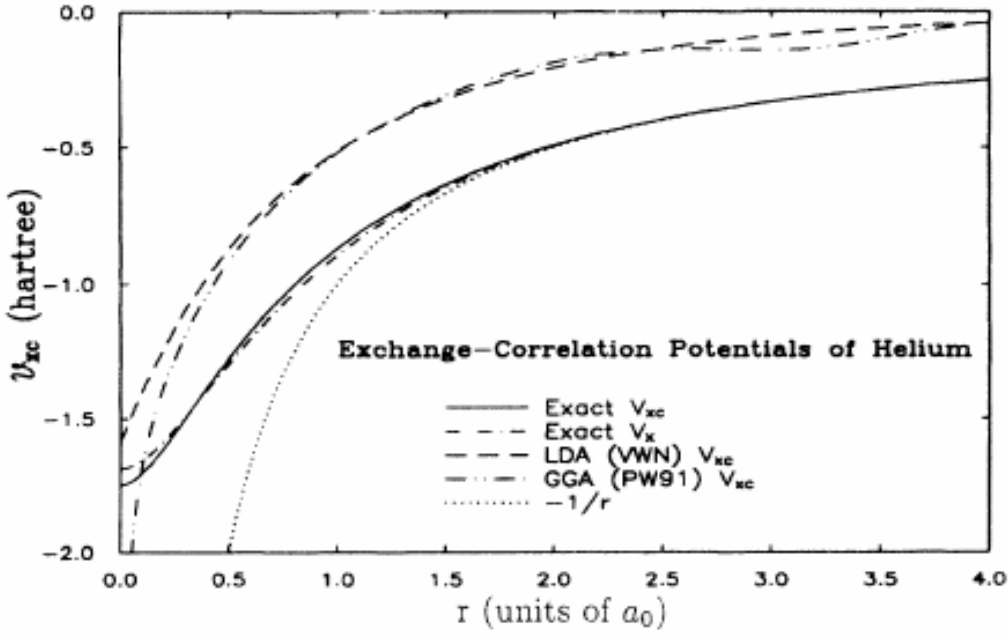
- Thank to the Hylleraas Exact solution, we have the **Exact-DFT exchange-correlation!**

$$\Psi^{\text{exact}}(r_1, r_2) \rightarrow \rho^{\text{exact}}(r) \rightarrow \phi^{\text{exact-KS}}_{\text{HOMO}}(r) = \sqrt{\frac{\rho^{\text{exact}}(r)}{2}} \rightarrow v_{xc}^{\text{exact-DFT}}(r)$$

$$\left[-\frac{\partial_r^2}{2} - \frac{Z}{r} + v_H[\rho^{\text{exact}}](r) + v_{xc}^{\text{exact-DFT}}(r)\right] \phi^{\text{exact-KS}}_{\text{HOMO}}(r) = \epsilon^{\text{exact}}_{\text{HOMO}} \phi^{\text{exact-KS}}_{\text{HOMO}}(r)$$ Kohn-Sham equation

$$v_{xc}^{\text{exact-DFT}}(r) = \epsilon^{\text{exact}}_{\text{HOMO}} + \frac{1}{2}\frac{\partial_r^2 \phi^{\text{exact-KS}}_{\text{HOMO}}(r)}{\phi^{\text{exact-KS}}_{\text{HOMO}}(r)} + \frac{Z}{r} - v_H[\rho^{\text{exact}}](r)$$

Exact xc potential by inversion the Kohn-Sham equation



Umrigar, and Gonze (1994)

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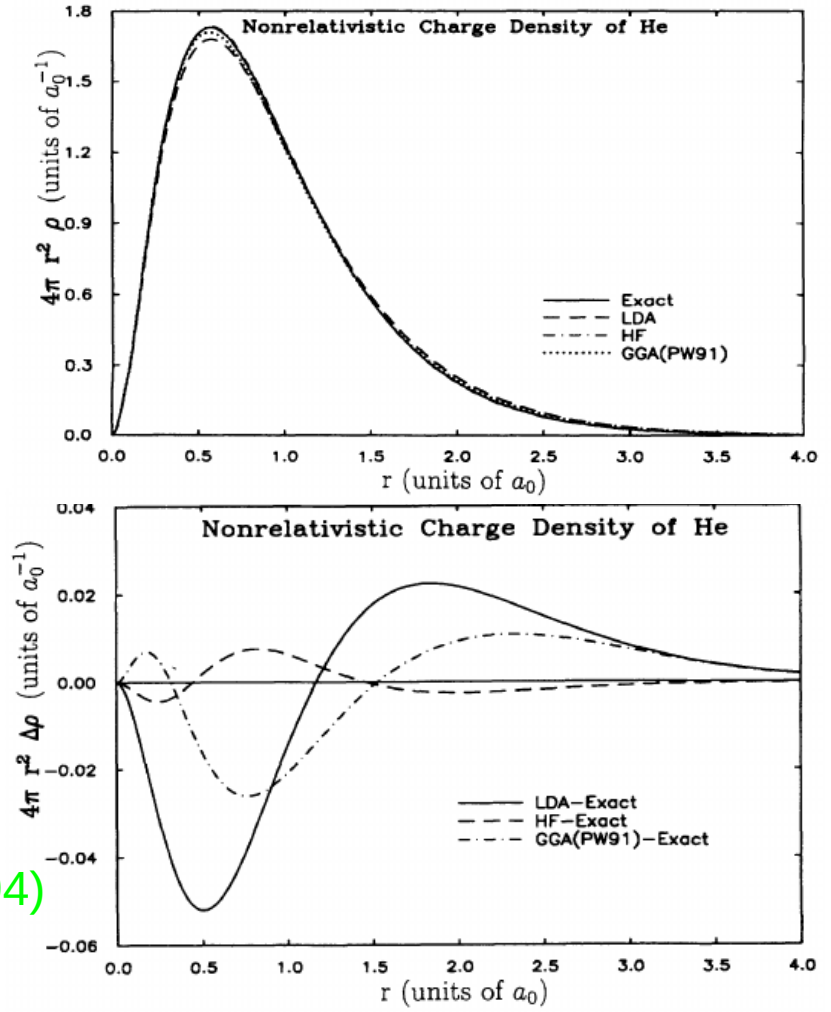
He atom Ground State

- Good HF wavefunction, much better than expected!
- but LDA and GGA wavefunctions also better than expected.



Umrigar, and Gonze (1994)

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EXACT vs exact: QMC

Year	Reference	Helium atom 1^1S ground state energy [Ha]
1929	Hylleraas	**-2.903** 24
1957	Kinoshita	**-2.903 722** 5
1966	Frankowski & Pekeris	**-2.903 724 377 032** 6
1994	Thakka & Koga	**-2.903 724 377 034 114** 4
1998	Goldman	**-2.903 724 377 034 119 594**
1999	Drake	**-2.903 724 377 034 119 596**
2002	Sims & Hagstrom	**-2.903 724 377 034 119 598 299** 9
2002	Drake *et al.*	**-2.903 724 377 034 119 598 305**
2002	Korobov	**-2.903 724 377 034 119 598 311 158** 7
2006	Schwartz	**-2.903 724 377 034 119 598 311 159 245 194 404** 440 049 5
2007	Nakashima & Nakatsuji	**-2.903 724 377 034 119 598 311 159 245 194 404 446 696** 905 37

EXP accuracy: 10^{-9} Ha

$$E^{\mathrm{DMC}} = -\mathbf{2.903\,724}\,6(9)$$

CASINO, Jastrow wavefunction,
CPU time: 32h (VMC) + 121h (DMC)

However:
- He ground state nodeless wavefunction: no sign problem
- statistical error: not a numerical analysis exact solution
- DMC: ΔE / 10 → CPU * 100 → N & N accuracy: 10^{68}h (age of the universe = 10^{14}h)

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Li, Drummond, Schuck and Olevano (2019)

EXACT vs exact: CI

Year	Reference	Helium atom 1^1S ground state energy [Ha]
1929	Hylleraas	**-2.903** 24
1957	Kinoshita	**-2.903 722** 5
1966	Frankowski & Pekeris	**-2.903 724 377** 032 6
1994	Thakka & Koga	**-2.903 724 377 034** 114 4
1998	Goldman	**-2.903 724 377 034 119** 594
1999	Drake	**-2.903 724 377 034 119** 596
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2002	Drake *et al.*	**-2.903 724 377 034 119 598** 305
2002	Korobov	**-2.903 724 377 034 119 598 311 158** 7
2006	Schwartz	**-2.903 724 377 034 119 598 311 159 245 194 404** 440 049 5
2007	Nakashima & Nakatsuji	**-2.903 724 377 034 119 598 311 159 245 194 404 446 696** 905 37

EXP accuracy: 10^{-9} Ha

He

$E^{\mathrm{CI}} = -\mathbf{2.900}$ full-CI cc-pVTZ ORCA calculation

$E^{\mathrm{CI}} = -\mathbf{2.903}\,2$ *d-aug*-cc-pV5Z: ***non plus ultra!***

Chemical Accuracy: 1 kcal/mol ~ 0.001 Ha

Impossible to provide an error bar: not a Numerical Analysis exact solution

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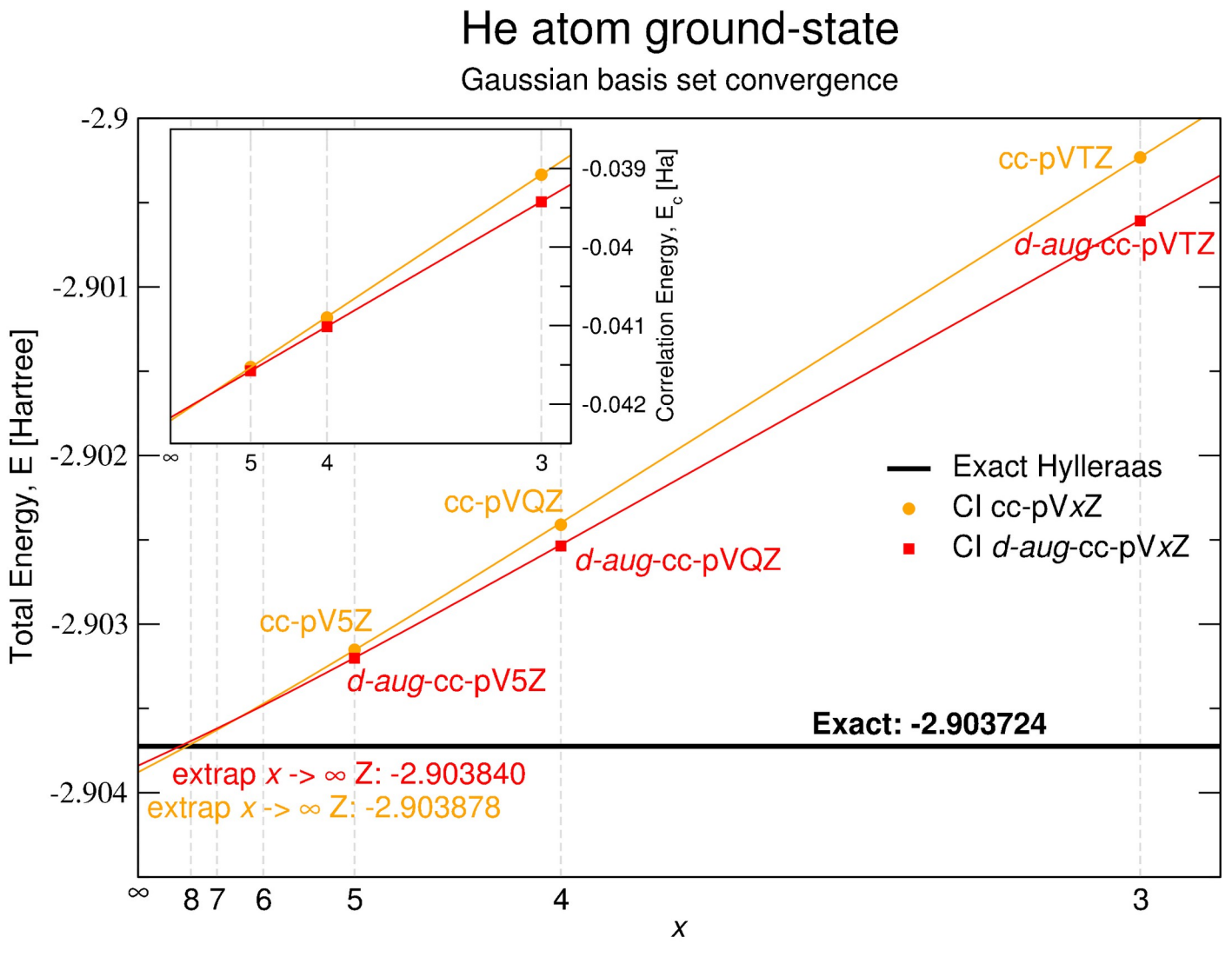
Full-CI extrapolation



Li, Drummond, Schuck and Olevano (2019)

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He atom Ground State

Method	Energy [Ha]
Noninteracting	-4
Hartree	-1.9517
HF	-2.8616
DFT-LDA	-2.8348
DFT-GGA	-2.8929
Exact-DFT [62]	-2.903724377034118
RPA (TDHF)	-2.9097
r-RPA	-2.9085
GW+BSE	-2.9080
CI	-2.9032
QMC-VMC (SJ)	$-2.90372220(7)$
QMC-DMC	$-2.9037246(9)$
Exact [10]	$-2.903724377034119598311159245194404$

towards SCRPA

Li, Drummond, Schuck and Olevano (2019)

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He atom Ground State

Energy contribution	HF	Exact-DFT	VMC
Kinetic	+2.8615	+2.867082	+2.90377(6)
External (e-N)	−6.7489	−6.753267	−6.75332(6)
Hartree	+2.0515	+2.049137	
Exchange	−1.0257		
Exchange-Correlation		−1.066676	
Many-body (e-e)			+0.94585(5)
Total	−2.8616	−2.903724	−2.90372220(7)
Correlation	−0.0421		
Exact [6]	**−2.903724377**		

Li, Drummond, Schuck and Olevano (2019)

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He atom Charged Excitations

GW approximation to the Self-Energy

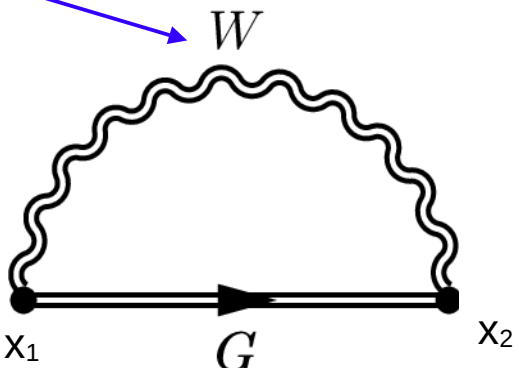
$$W(r,r',\omega)=\epsilon^{-1}(r,r',\omega)\frac{1}{|r-r'|}$$

$v(r,r')$

Dynamical Screened Interaction W (in RPA approx.)

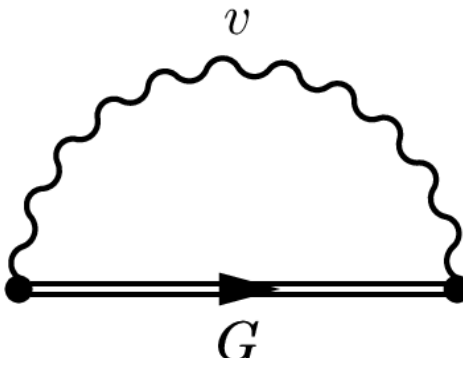
GW Self-Energy

$$\Sigma^{GW}(x_1,x_2)=iG(x_1,x_2)W(x_1,x_2) \quad =$$



Hartree-Fock Self-Energy

$$\Sigma_x(x_1,x_2)=iG(x_1,x_2)v(x_1,x_2) \quad =$$



Bare Coulombian Potential v

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He Quasiparticle states: Ionisation Potential (IP) Electron Affinity (EA)

QPstate [eV]	HF	GW	**Exact &EXP**	Exact-DFT	DFT-LDA
1*s* (= - IP)	-24.979	-24.696	**-24.591**	-24.591	-15.522
2*s* (= - EA)	0.590	0.580	**>0**	-4.291	0.331
2*p*	2.603	2.570		-3.445	1.841
3*s*	3.794	3.725		-1.755	2.692

- HF error on IP: 0.4 eV
- GW error on IP improves to: 0.1 eV
- The Exact-DFT HOMO KS eigenvalue provides the Exact IP.
- The EXP indicates a negative EA (unbound state):
  - like in HF and GW and unlike Exact-DFT
- The Exact-DFT LUMO KS eigenvalue **has nothing to see** with the real EA!

He

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HOMO-LUMO gap

[eV]	HF	GW	**EXP**	Exact-DFT	DFT-LDA
1*s* → 2*s*	25.569	25.276	**>24.591**	20.300	15.853

- Qualitatively correct HOMO-LUMO gap in both HF and GW
- Usual 30~40% DFT-LDA underestimation
- The Exact-DFT HOMO-LUMO gap has **nothing to see** with the real HOMO-LUMO gap!
  - Useless to struggle searching for a DFT functional overperforming Exact-DFT on the HOMO-LUMO gap.

He atom Neutral Excitations

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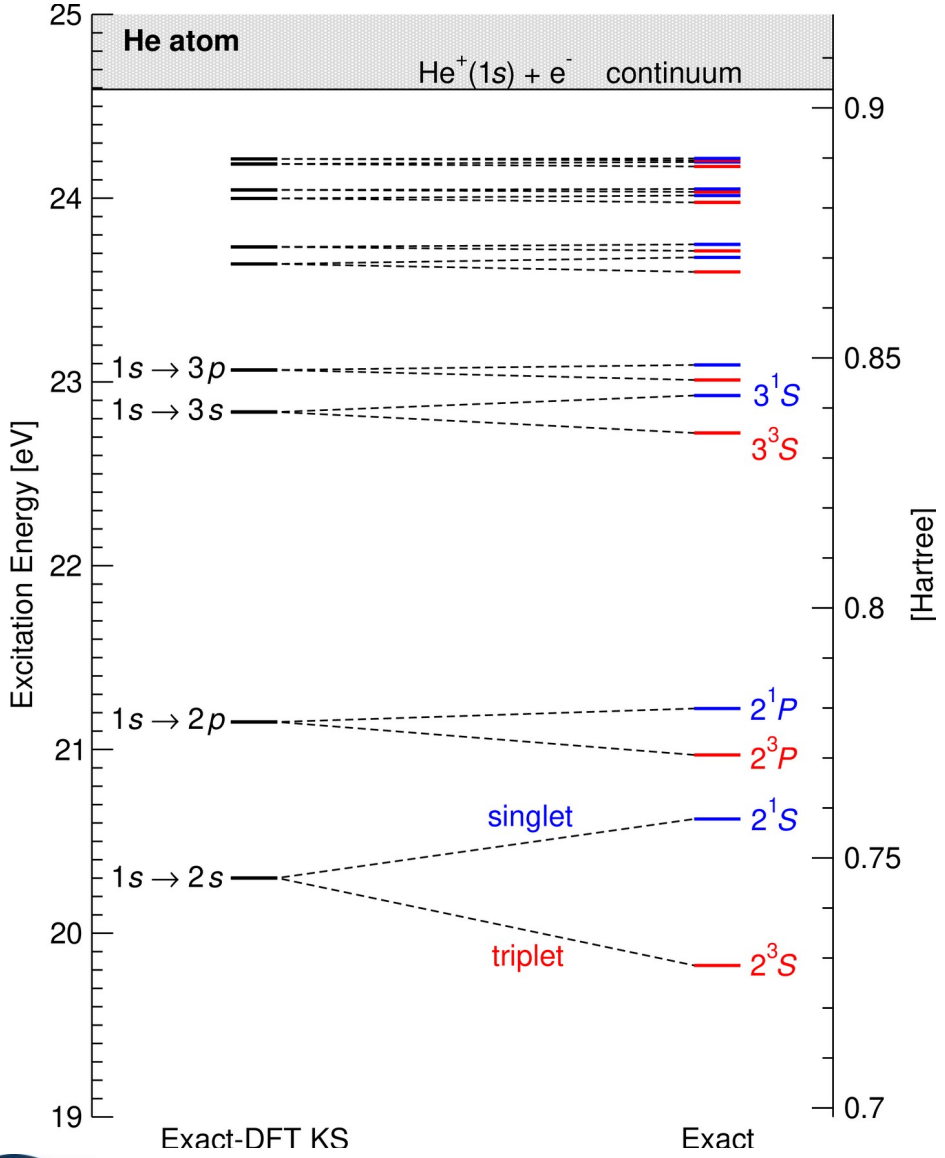
He Neutral Excitations: Exact-DFT KS energy-differences



- Exact-DFT Kohn-Sham energy-differences already in **surprising good agreement** with Exact neutral excitations!
- Exact-DFT KS energy-differences reproduce the correct Rydberg series (highest lying states) → correct **1/r behaviour** of the **Exact-DFT exchange-correlation potential**!

Savin, Umrigar and Gonze (1998)

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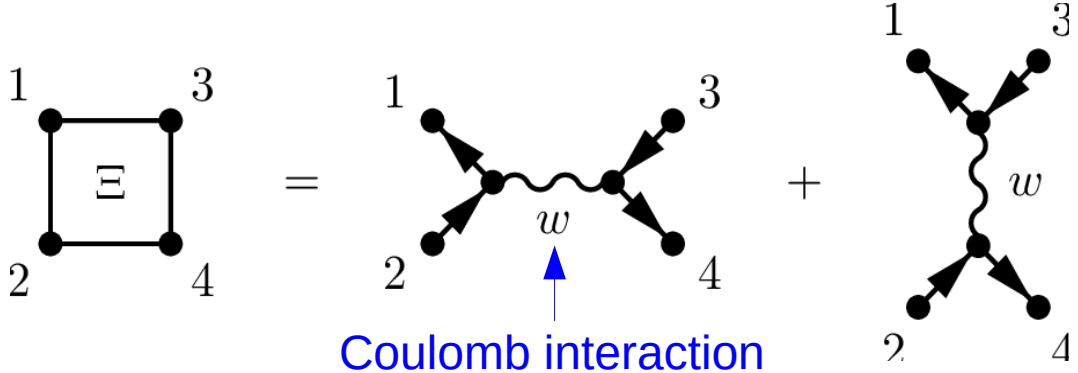
DFT → TDDFT

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

same equation as
RPA of nuclear physics

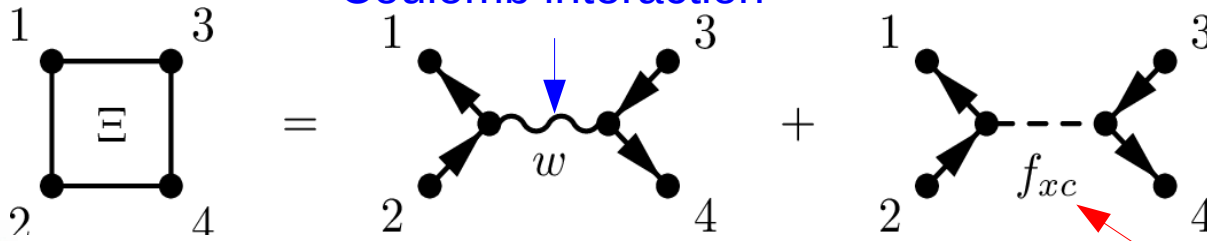
$$A_{ph,p'h'} = i\Xi_{ph,p'h'} + (\varepsilon_p - \varepsilon_h)\delta_{pp'}\delta_{hh'}$$
$$B_{ph,h'p'} = i\Xi_{ph,h'p'}$$

Kohn-Sham energies
instead of Hartree-Fock



TDHF (RPA) kernel

Coulomb interaction



TDDFT kernel

xc-kernel
(must be approximated:
Adiabatic LDA)

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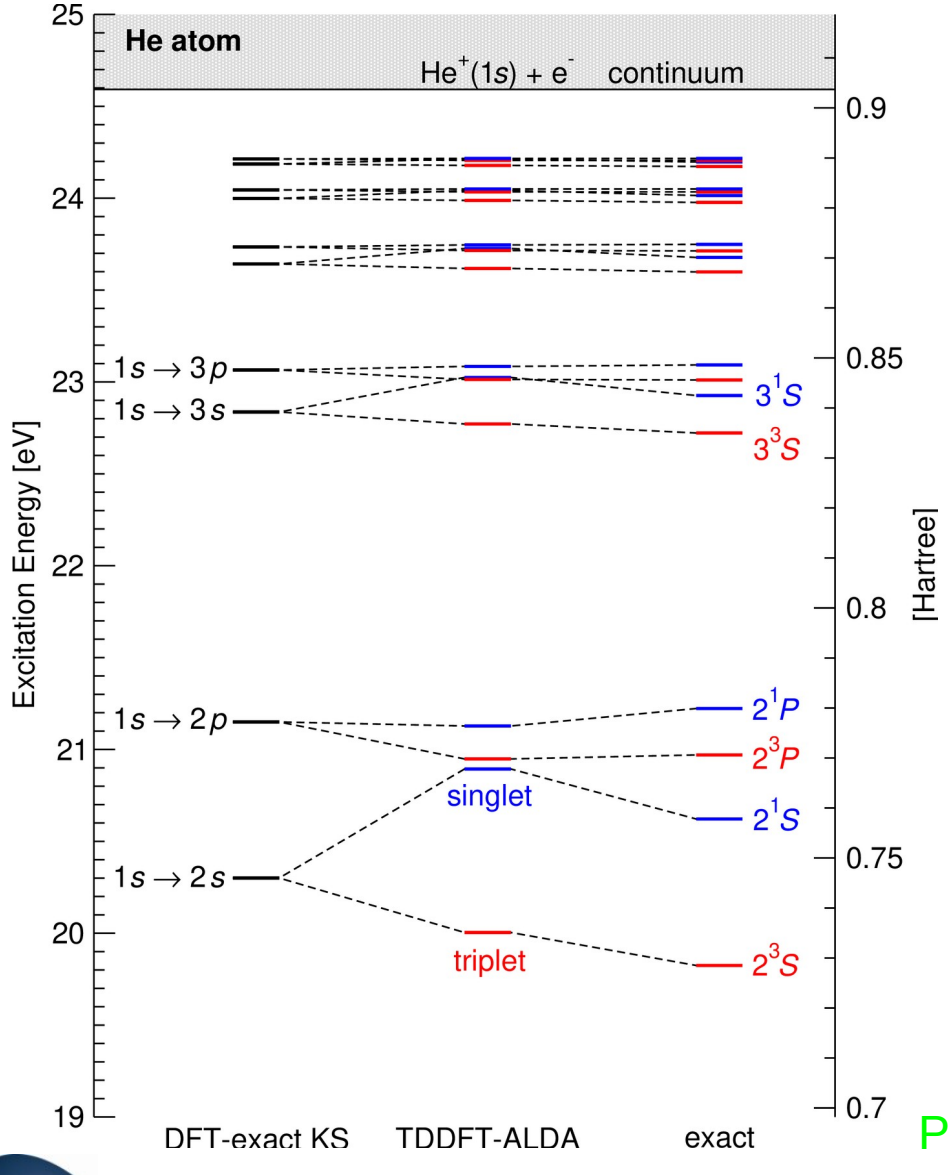
He Neutral Excitations: Exact-DFT+TDLDA



- Exact-DFT+Exact-TDDFT must of course reproduce the Exact result.
- Approximated TDLDA on top of Exact-DFT introduces the right singlet-triplet exchange split (but thank to the v term) and performs reasonably well.
- TDLDA performance: 0.2 eV error.

Petersilka, Gross and Burke (2000)

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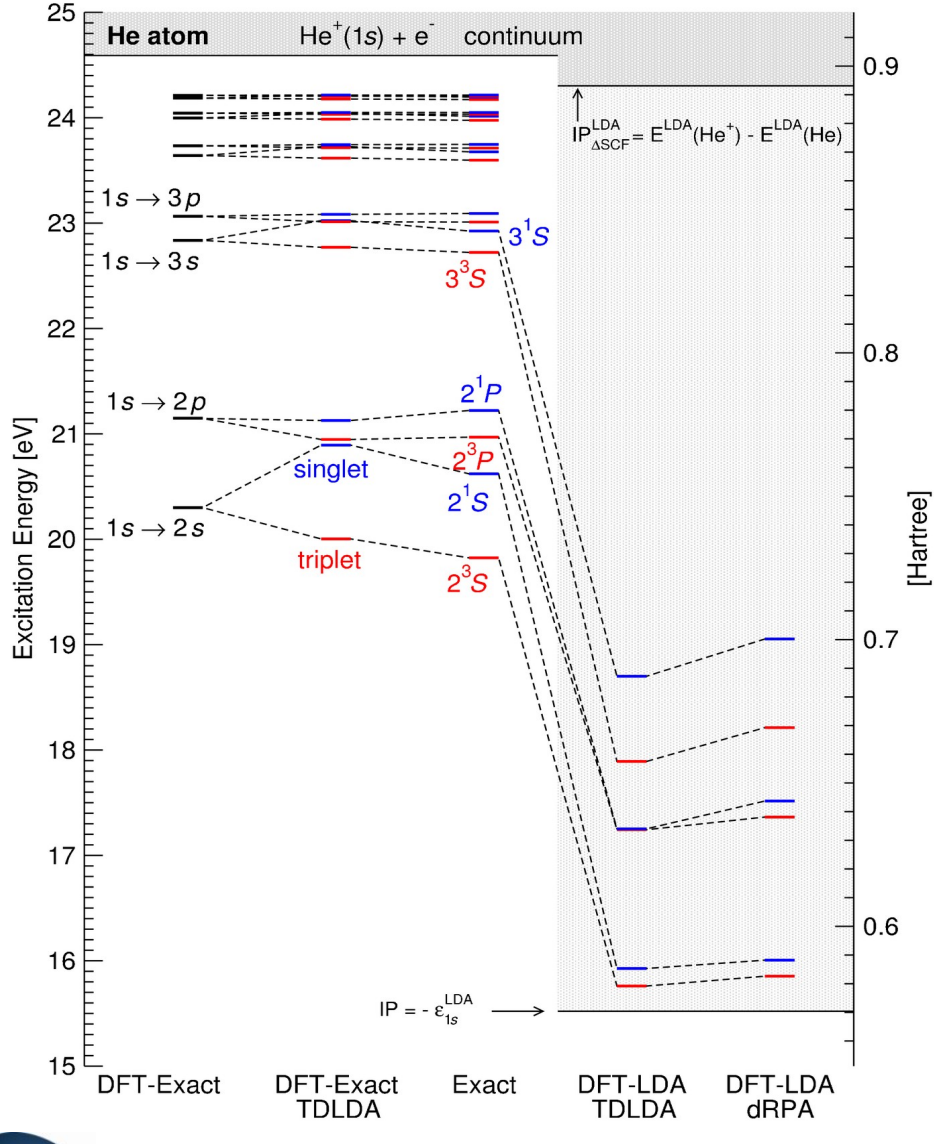
He Neutral Excitations: DFT-LDA+TDLDA



- DFT-LDA+TDLDA strongly red-shifted
- Usually believed that the DFT-LDA+TDLDA spectrum is unbound, but it depends on how the IP is calculated:
  - 1st KS energy?
  - or DeltaSCF method?

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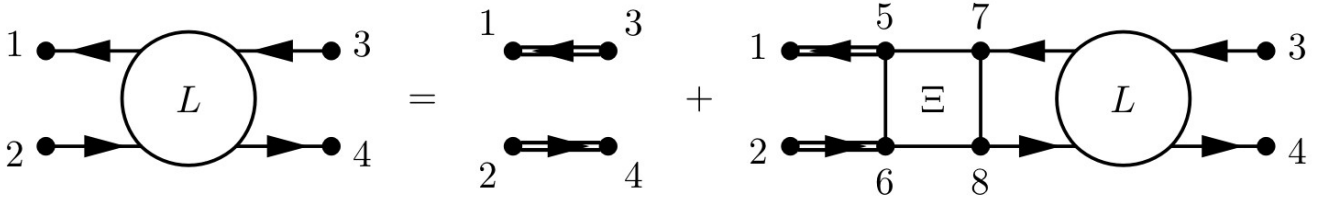
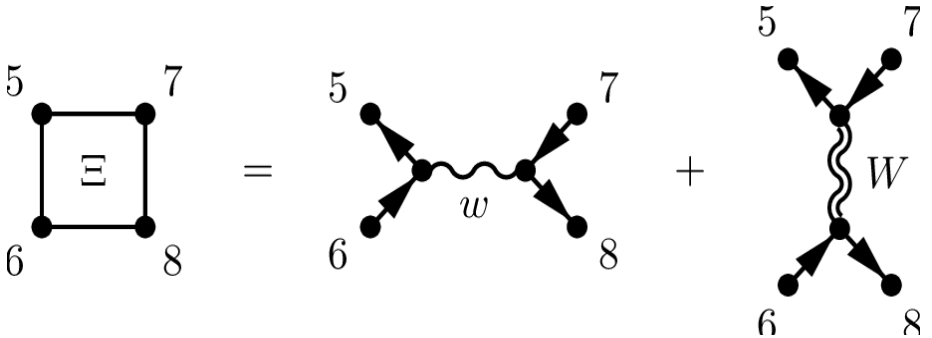
Bethe-Salpeter Equation



$$L = GG + GG\Xi L$$

Bethe-Salpeter Equation



$$\Xi = \frac{\delta\Sigma}{\delta G} \simeq -iw + iW$$

Interaction Kernel

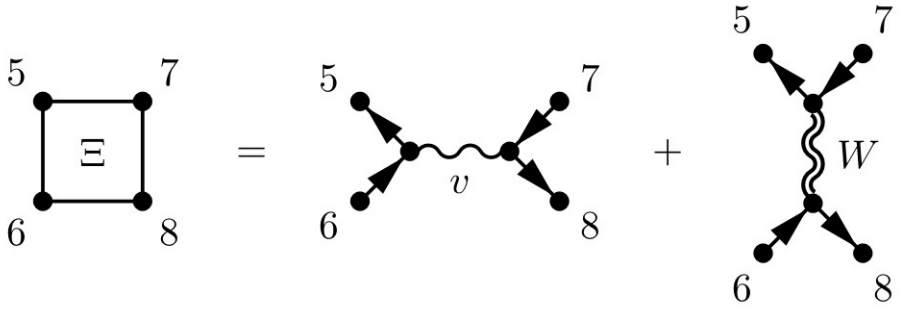
W = e-h Screened Interaction

BSE kernel: approximations

1st approx: GW approx on the Self-Energy $\Sigma = iGW\Gamma$

2nd approx: neglect dW / dG $\frac{\delta\Sigma}{\delta G} = iW + iG\frac{\delta W}{\delta G}$

3rd approx: neglect frequency dependence in $W(\omega) = W(0)$

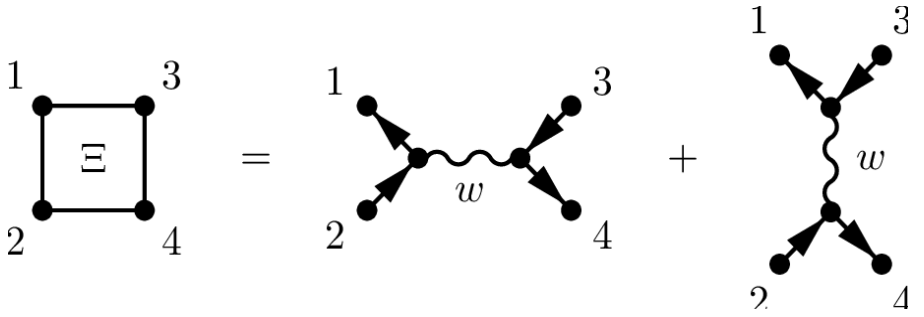


$$\Xi = \frac{\delta\Sigma}{\delta G} \simeq -iv + iW$$

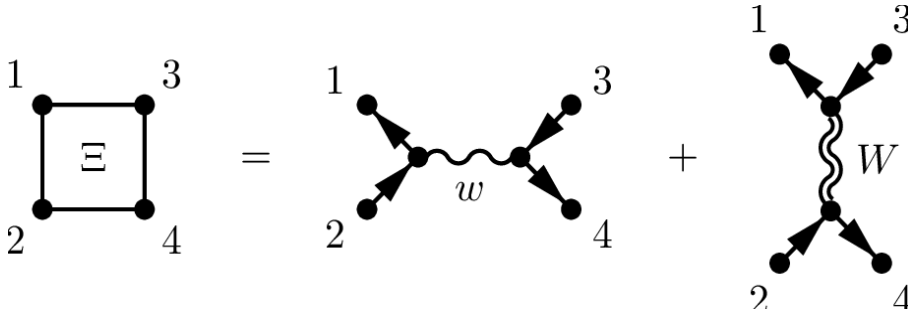
Interaction Kernel

W = e-h Screened Interaction

BSE vs TDHF=RPA(nuclear physics)

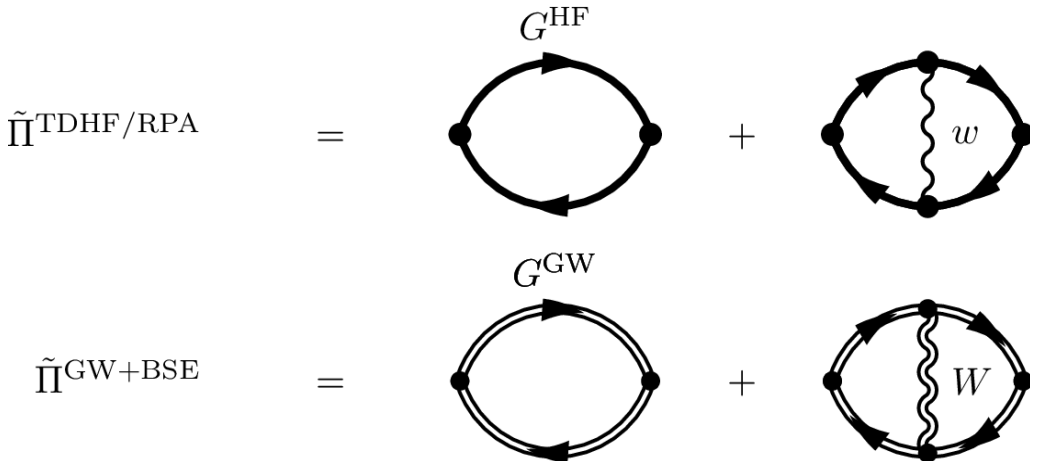


TDHF / RPA (nuclear physics)



BSE

- Screening is the GW+BSE way to correlations!



BSE vs TDHF=RPA(nuclear physics)

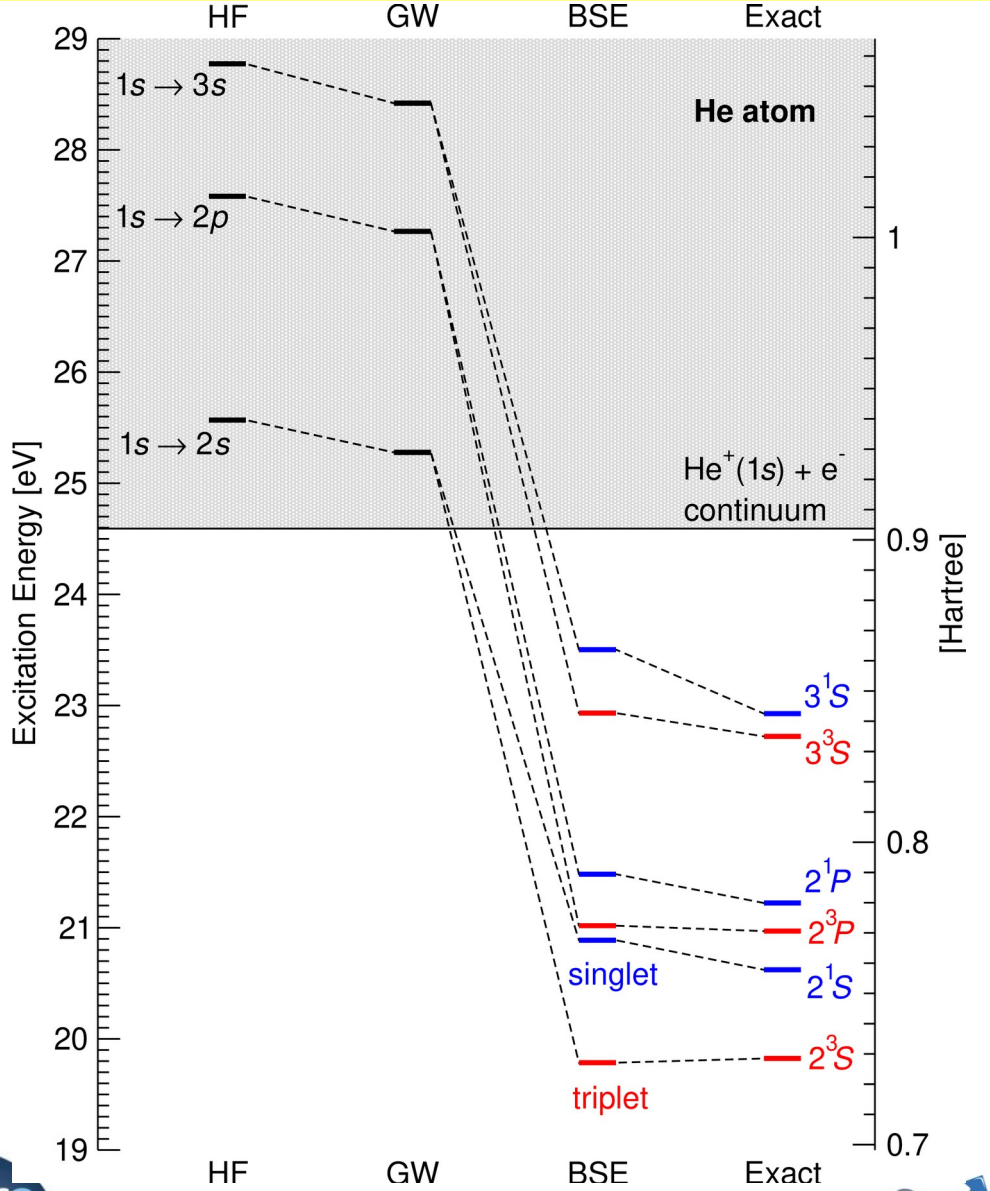
$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

$$A_{ph,p'h'} = i\Xi_{ph,p'h'} + (\varepsilon_p - \varepsilon_h)\delta_{pp'}\delta_{hh'}$$

$$B_{ph,h'p'} = i\Xi_{ph,h'p'}$$

GW quasiparticle energies instead of Hartree-Fock (we start from a ground state which already contains some correlation)

He Neutral Excitations: GW+BSE



- HF and GW quasiparticle energy-differences, unlike Exact-DFT KS, lye in the continuum, **as they must**.
- In contrast to TDDFT, the BSE kernel has the **hard task** to bring excitations 5 eV down from the continuum.

Li, Holzmann, Duchemin, Blase, Olevano (2017)

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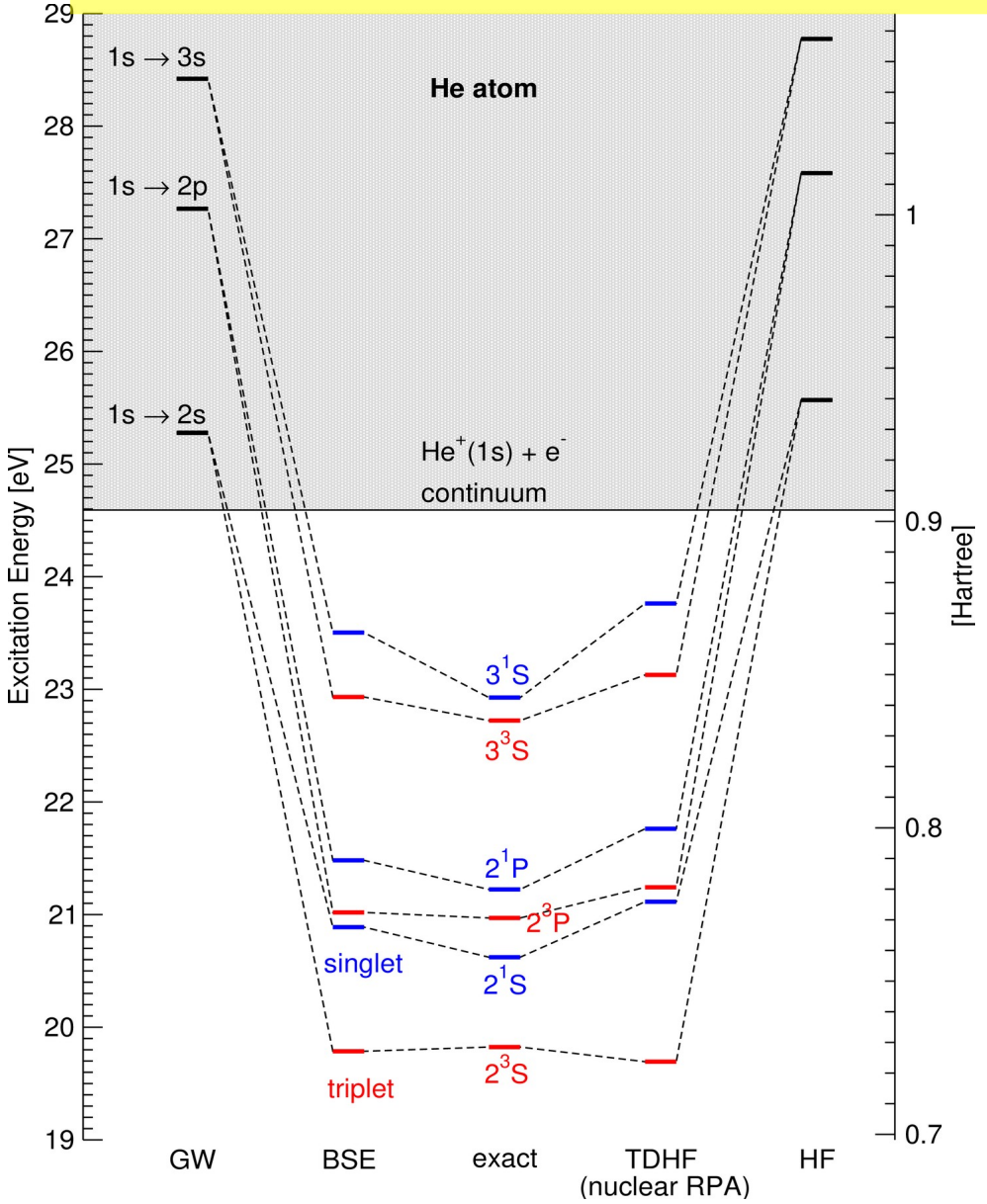
GW+BSE vs nuclear RPA (TDHF)



- nuclear RPA (TDHF): **twice the GW-BSE error**!
- **Self-interaction/screening** problems not really affecting
  - or for < 0.1 eV
  - see also “GW on H atom”, Nelson, Bokes, Rinke, Godby 2007)

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Hylleraas exact calculation

$$
\begin{aligned}
s &= r_1 + r_2 \\
t &= r_1 - r_2 \\
u &= r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|
\end{aligned}
$$

Hylleraas coordinates
(3 scalars instead than 6)

$$\Phi(s,t,u) = e^{-ks} \sum_{l,m,n=0}^{N} c_{l,2m,n} s^l t^{2m} u^n$$

Hylleraas functions

(for singlets → space-symmetric even function of *t*)

$$E_{1^1S} = -2.90324 \pm 0.00048 \quad (\pm 0.013\,\mathrm{eV})$$

Hylleraas (1929)

N = 0 →

$$\Phi(r_1, r_2) = \psi_{1s}^{Z_e}(r_1)\psi_{1s}^{Z_e}(r_2)$$

$$\psi_{1s}^{Z_e}(r) = \sqrt{\frac{Z_e^3}{\pi}} e^{-Z_e r} \quad \rightarrow \quad Z_e = Z - 5/16$$

effective charge
(screening)

$$E_{1^1S}^{\mathrm{scr}} = -2.848 \pm 0.056 \quad (\pm 1.5\,\mathrm{eV})$$

$$E_{1^1S}^{0} = -4.0$$

- It is not that strange that screening capture most of correlations even in 2-electrons He atom

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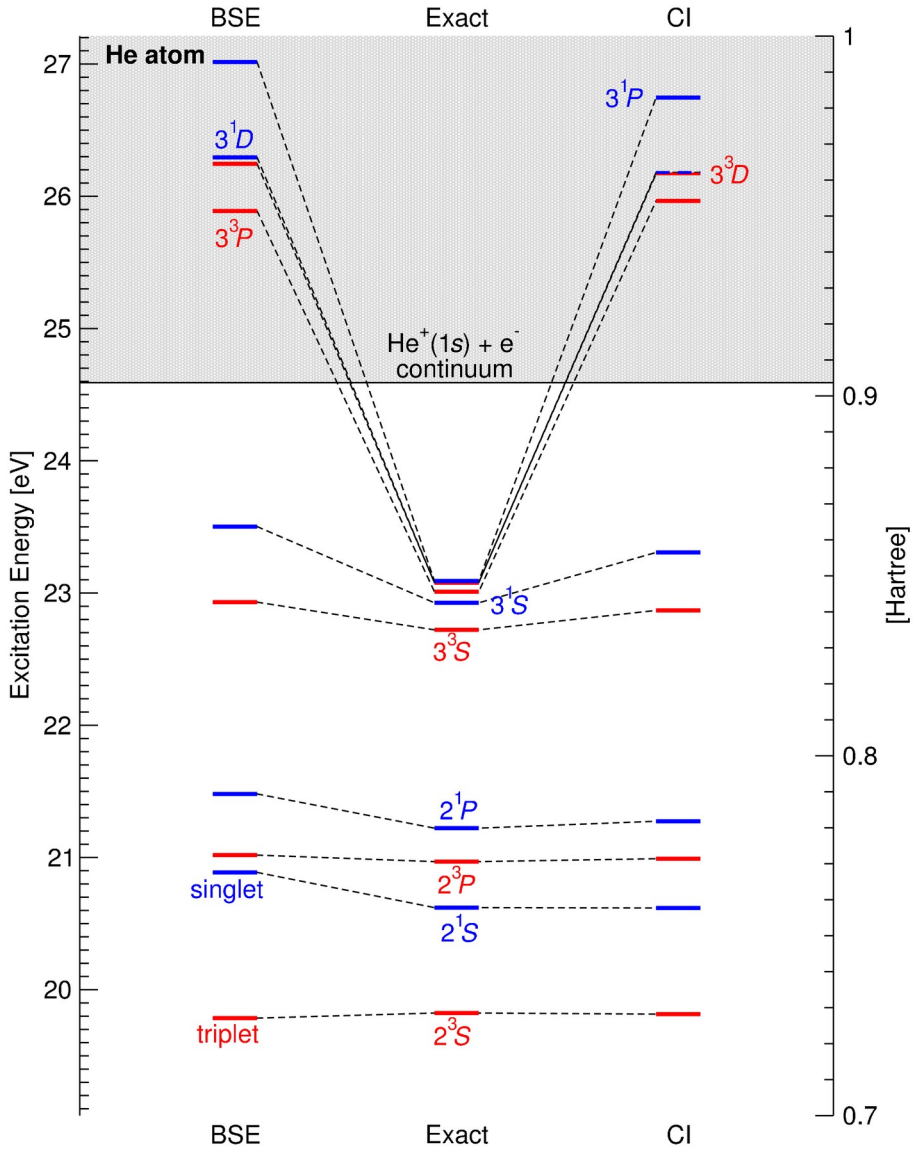
GW+BSE vs full CI

- Gaussian basis set convergence: *d-aug*-cc-pV5Z: ***non plus ultra!*** and only converged 2S, 2P, 3S
- 2^3S GW+BSE error: **< 0.1 eV**



Chemical Accuracy: 1 kcal/mol = 0.04 eV

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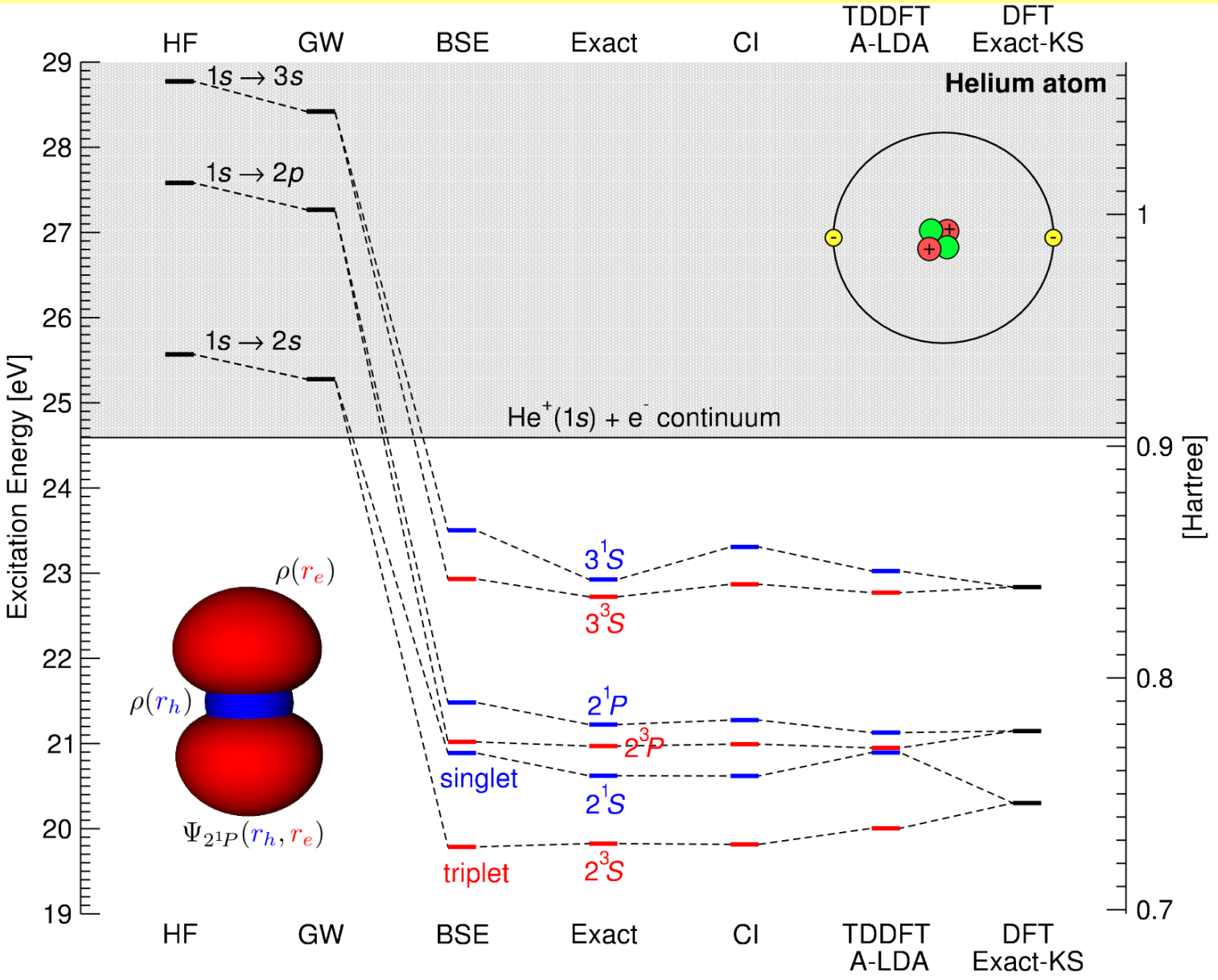
CI vs Exact-DFT+TDLDA



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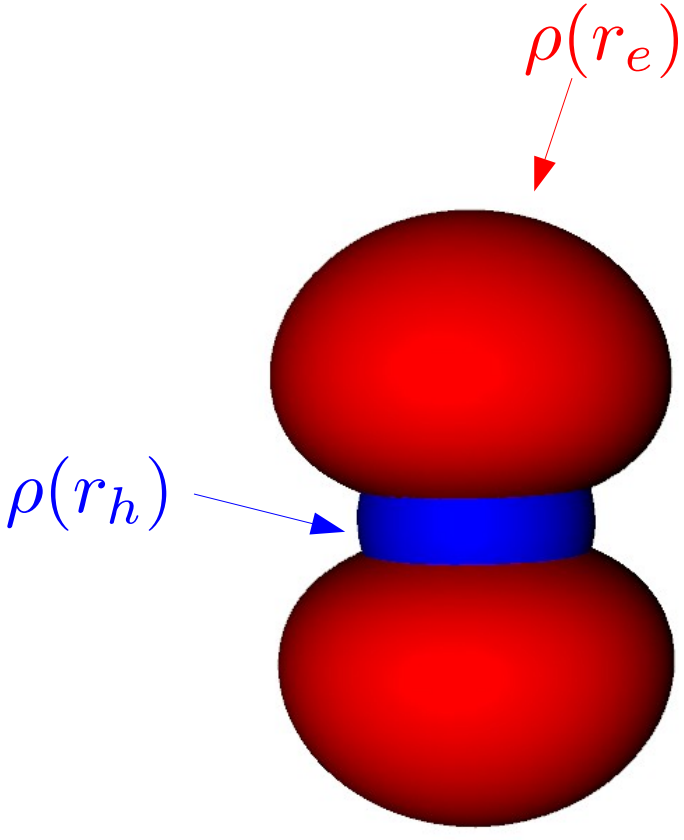
Oscillator Strengths

	BSE	**Exact**	TDHF	HF	Exact-DFT	
$f_{1^1S\rightarrow 2^1P}$	0.2763	**0.27616**	0.2916	0.2009	0.3243	$f_{1s\rightarrow 2p}$
		Kono, Hattori (1984)			Appel, Gross, Burke (2003)	

- Oscillator Strengths are sensistive to both QP and Excitonic wavefunctions (independently from energies).
- Surprising **excellent agreement** on the first dipole allowed Oscillator Strength!

Li, Holzmann, Duchemin, Blase, Olevano (2017)

He atom: BSE Excitonic Wavefunction



Electron hole-averaged and
hole electron-averaged
distribution proabilities

$\Psi_{2^1P}(r_h, r_e)$

Excitonic Wavefunction

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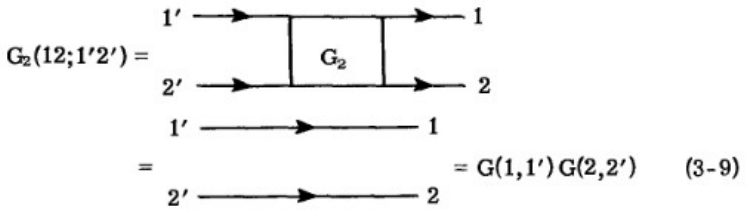
Beyond RPA: SC-RPA

- Any approximation to the 2-particle G has a corresponding approximation on the self-energy, and so on the 1-particle G, the ground state etc.

Hartree approximation:



(3-9)

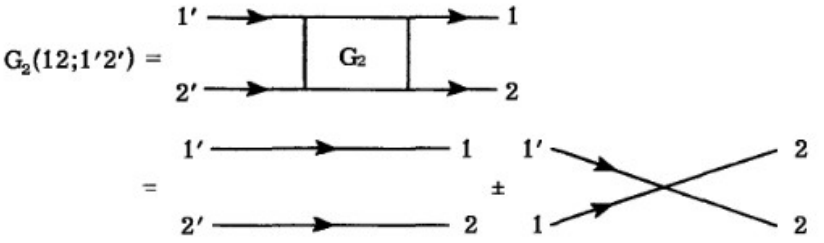
If we then substitute (3-9) into the equation of motion (3-2a), we obtain the approximate equation for G:

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} \mp i\int dr_2\, v(r_1 - r_2)\,G(2,2^+)\right] G(1,1')$$

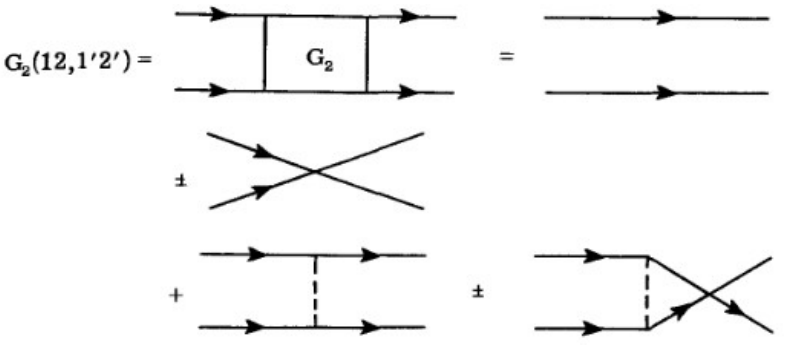
$$= \left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - \int dr_2\, v(r_1 - r_2)\,\langle n(r_2)\rangle\right] G(1,1')$$

$$= \delta(1 - 1') \qquad (3\text{-}10)$$

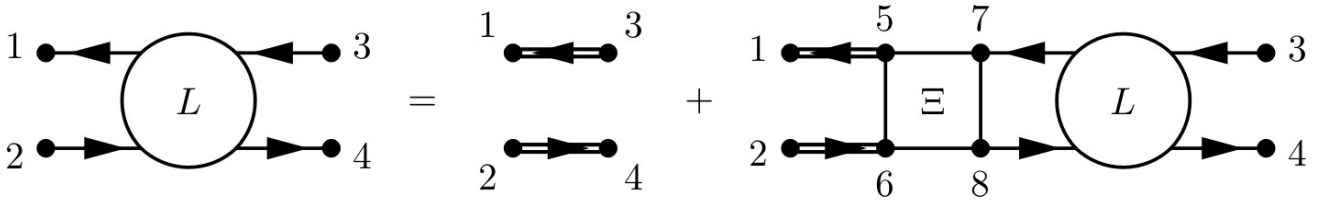
Hartree-Fock:



Born approximation:



Beyond RPA: SC-RPA



- Introducing correlations in the single-particle G (and in the ground-state) at the same level of the 2-particle G, self-consistently.

Towards SC-RPA: r-RPA

- From HF uncorrelated 0,1 integer occupation numbers, to fractional correlated ones:

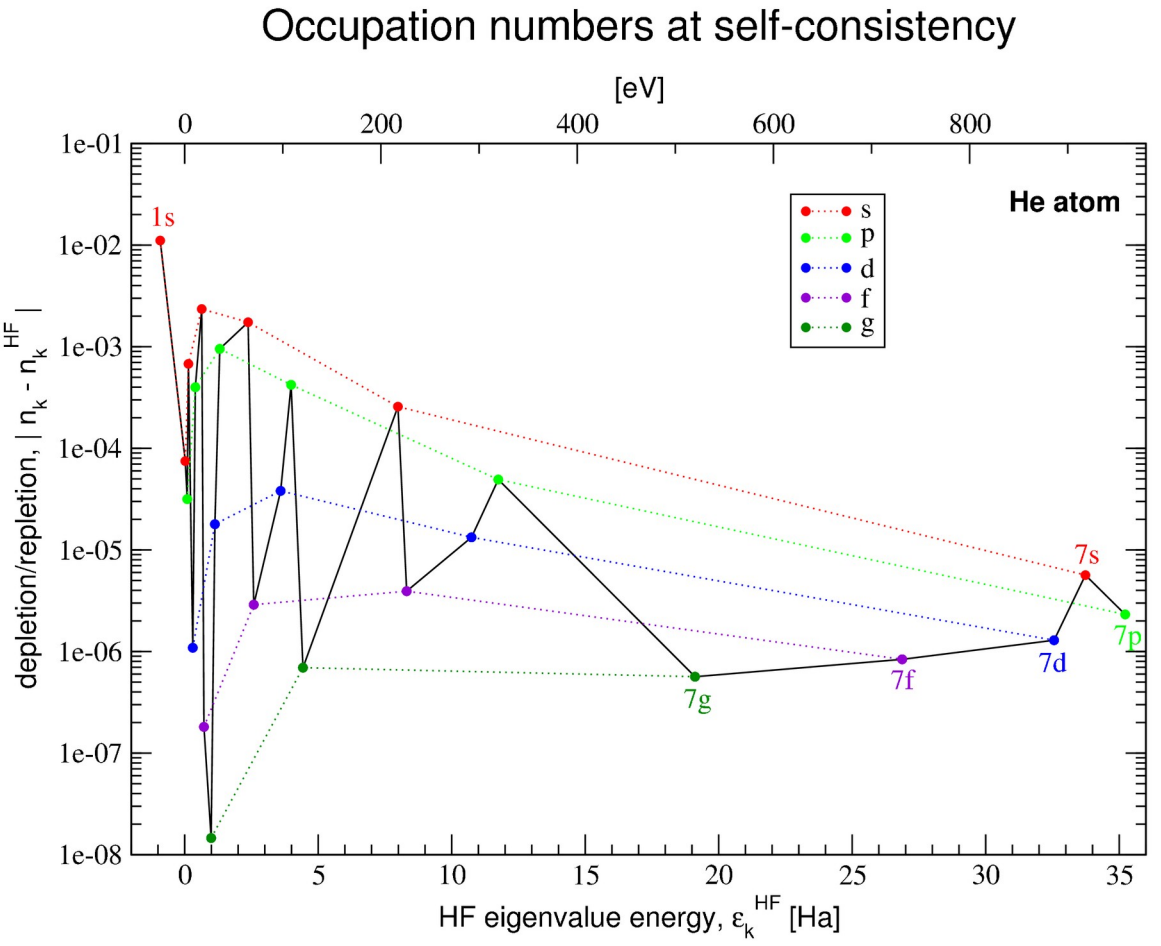
Catara et al. 1996, Rowe 1968, correct to O(|Y|²):

$$n_h = n_h^0 - \frac{1}{2}\sum_{\lambda p} |Y_\lambda^{ph}|^2$$

$$n_p = +\frac{1}{2}\sum_{\lambda h} |Y_\lambda^{ph}|^2$$

$$N = \sum_h n_h + \sum_p n_p$$

Luttinger Theorem (checked up to 10^{-18})



nl	HF	GW	Exact	r-RPA
$1s$ $(= -\text{IP})$	-0.9179	-0.9075	-0.9037	-0.9123
$2s$ $(= -\text{EA})$	$+0.0217$	$+0.0213$	> 0	$+0.0202$
$2p$	$+0.0956$	$+0.0944$		$+0.0935$
$3s$	$+0.1394$	$+0.1369$		$+0.1370$

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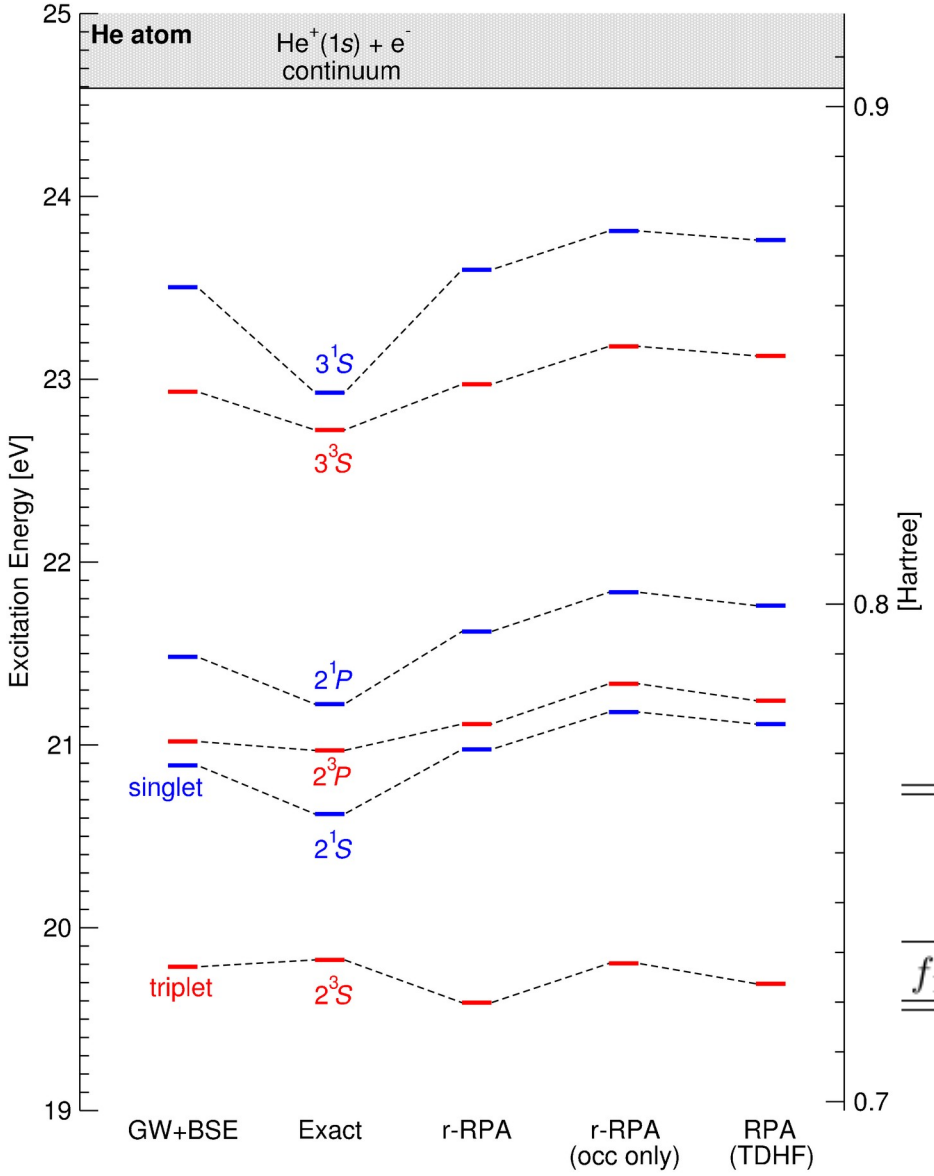
Towards SC-RPA: r-RPA



- Importance to include also corrections to QP energies beyond occupations only.
- Problem on the 1st excited state: importance of screening that should be contained in the neglected SC-RPA terms.

	RPA (TDHF)	r-RPA occ. only	r-RPA occ. & ene.	**Exact**	*GW* + RPA	*GW* + BSE
$f_{1^1S\to 2^1P}$	0.2916	0.2889	0.2877	**0.27616**	0.2946	0.2763

Li, Drummond, Schuck and Olevano (2019)

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Conclusions

- Many-body approaches should be benchmarked against safe exact solutions, possibly in real systems: He atom Hylleraas.
- On the ground-state energy: remarkable performances of DMC; SJ-VMC shows its bias, but the Gaussian full-CI error is larger.
- The unphysical Exact-DFT KS energy differences have in fact nothing to see with the exact HOMO-LUMO (Band) gap, but are surprisingly close to Optical gaps and excitations.
- GW+BSE performs unexpectedly well on the He atom, not sensibly affected by self-interaction/screening errors.
- TDLDA performs also reasonably well, but must be done on top of an Exact-DFT or an xc-potential with a 1/r asymptotic correct behaviour. DFT-LDA+TDLDA severely red-shifted.
- r-RPA towards SC-RPA improves on RPA, but consistent improvements require modifications of the kernel.

Acknowledgements

Jing Li, Ivan Duchemin
LETI CEA Grenoble

Xavier Blase
CNRS Institut Neel Grenoble

Neil Drummond
University of Lancaster

Markus Holzmann, Peter Schuck
CNRS LPMMC, Grenoble