



Comparing Many-Body approaches on **Real Exact Solutions:** Helium atom Excitations



Valerio Olevano
CNRS and UGA, Grenoble, France

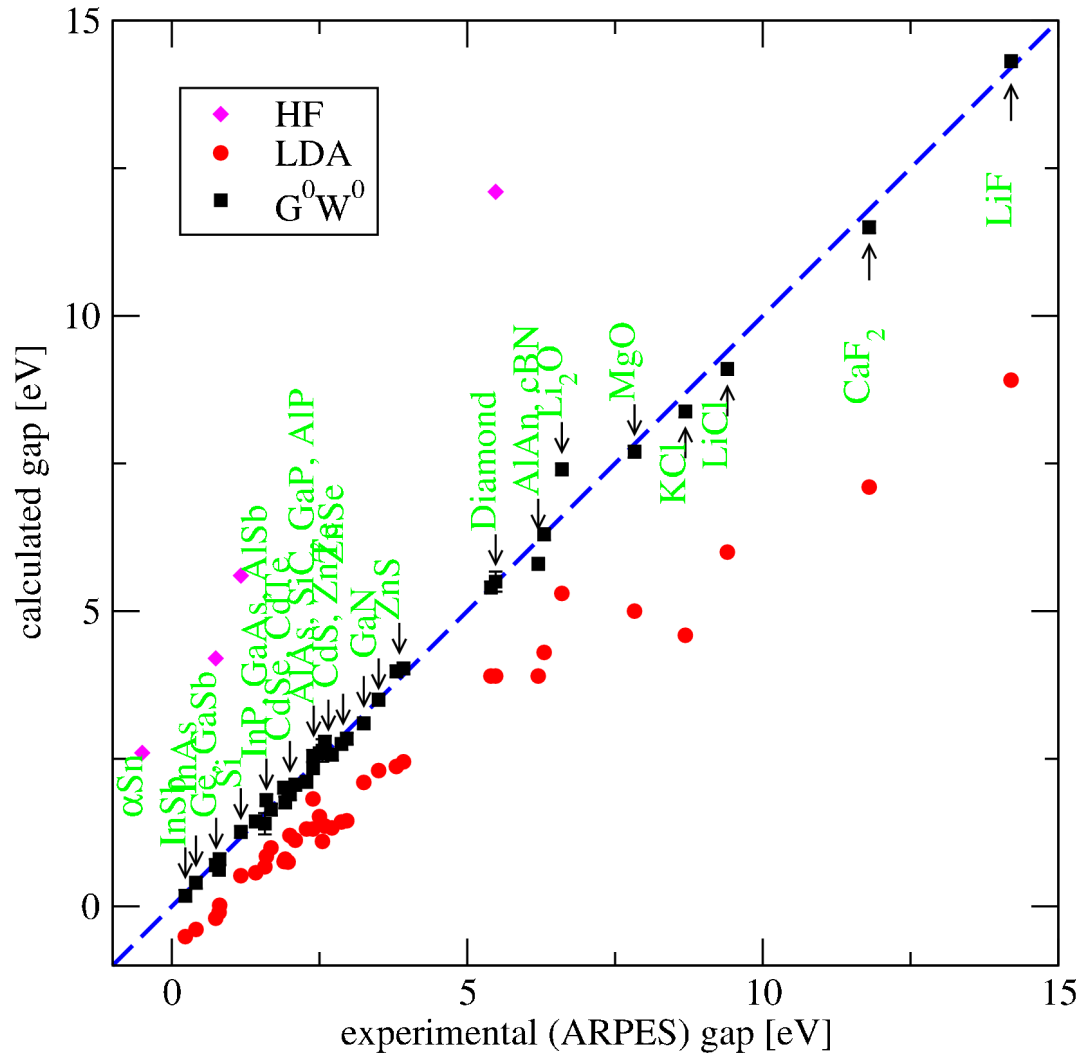


Résumé

- Motivation
- He atom excitations
- Exact Hylleraas solution
- QMC, full-CI, are they really exact?
- HF, Exact-DFT, DFT-LDA
- Exact-DFT+TDLDA, DFT-LDA+TDLDA
- GW+BSE vs TDHF (nuclear-RPA)
- beyond nuclear RPA: SC-RPA

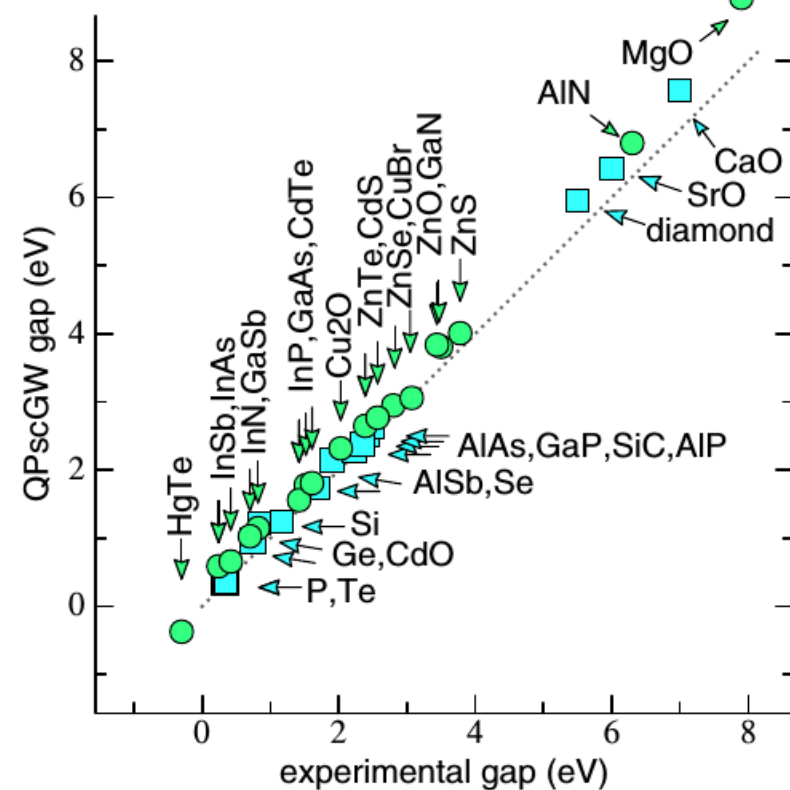
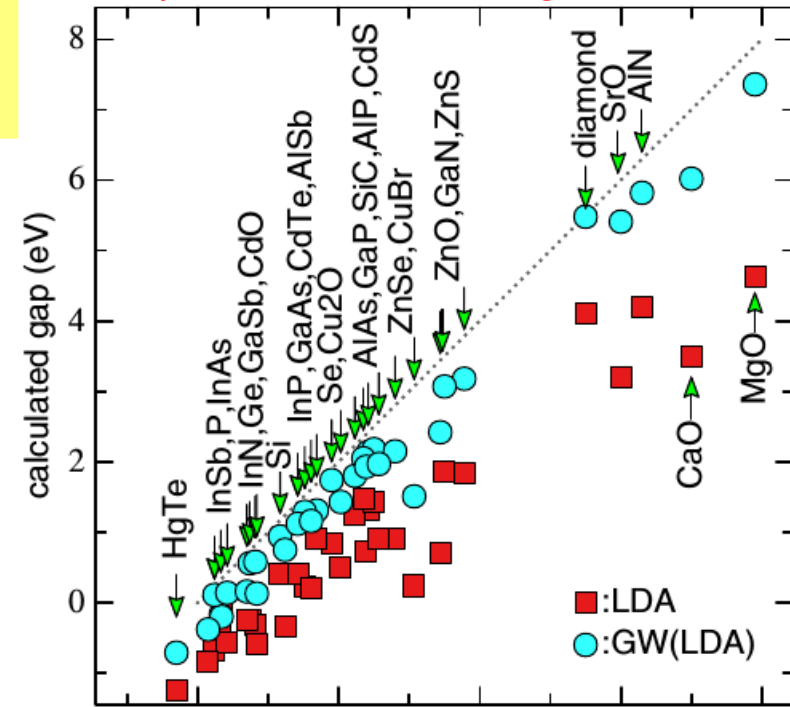
Motivation

- Is a comparison to the Experiment really meaningful?

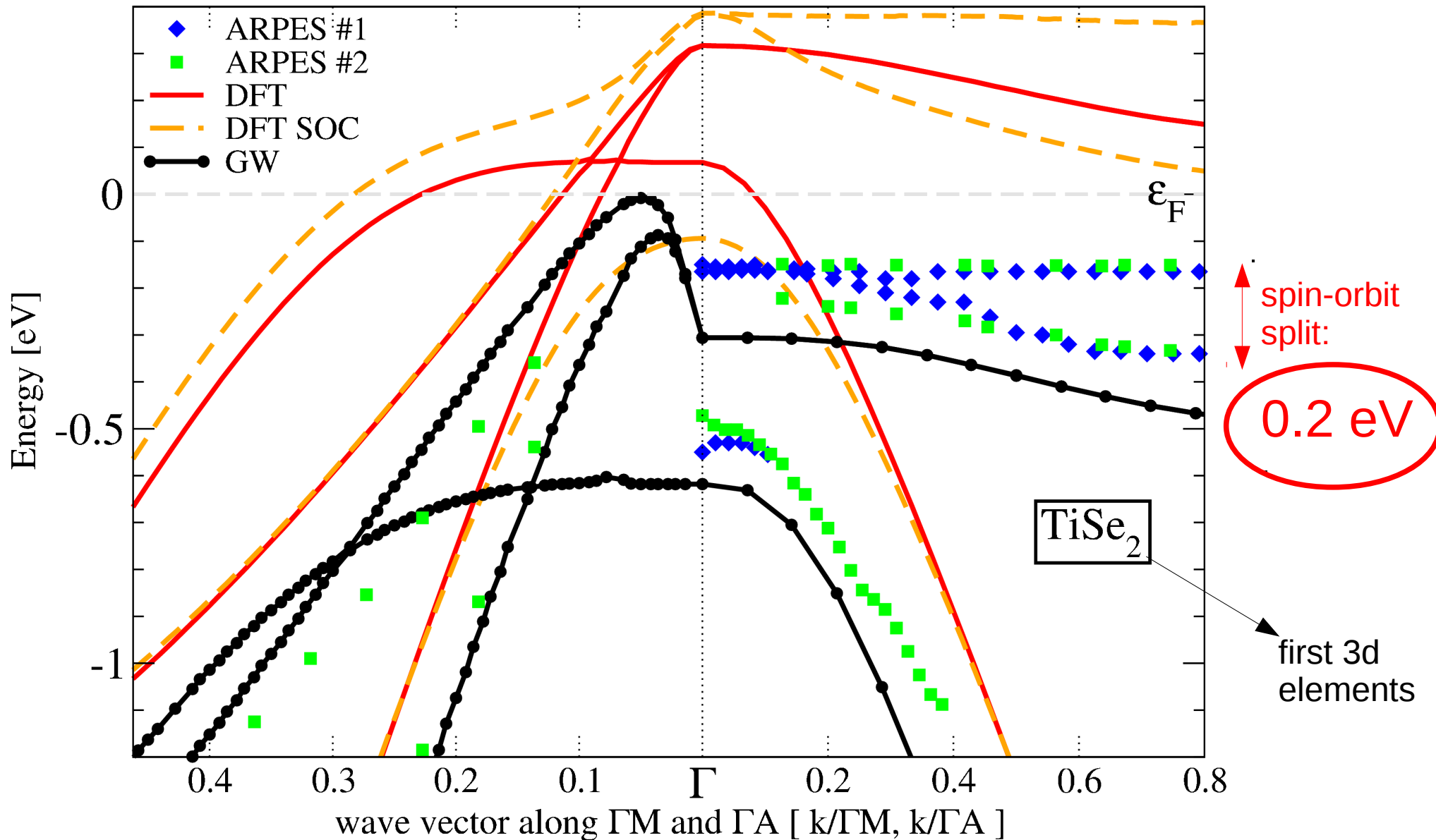


A statistics taking data from the literature.

Adapted from van Schilfgaarde et al.:



What about Relativistic Effects?



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

5

Computational Materials Science 83 (2014) 341–348



Contents lists available at ScienceDirect

Computational Materials Science

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

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



S. Poncé^{a,*}, G. Antonius^b, P. Boulanger^c, E. Cannuccia^d, A. Marini^e, M. Côté^b, X. Gonze^a

^a Université catholique de Louvain, Institute of Condensed Matter and Nanosciences, NAPS Chemin des étoiles 8, bte L07.03.01, B-1348 Louvain-la-neuve, Belgium

^b Département de Physique, Université de Montreal, C.P. 6128, Succursale Centre-Ville, Montreal H3C 3J7, Canada

^c Institut Néel, 25 Avenue des Martyrs, BP 166, 38042 Grenoble cedex 9, France

^d Institut Laue Langevin, BP 156, 38042 Grenoble, France

^e Consiglio Nazionale delle Ricerche (CNR), Via Salaria Km 29.3, CP 10, 00016 Monterotondo Stazione, Italy

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).



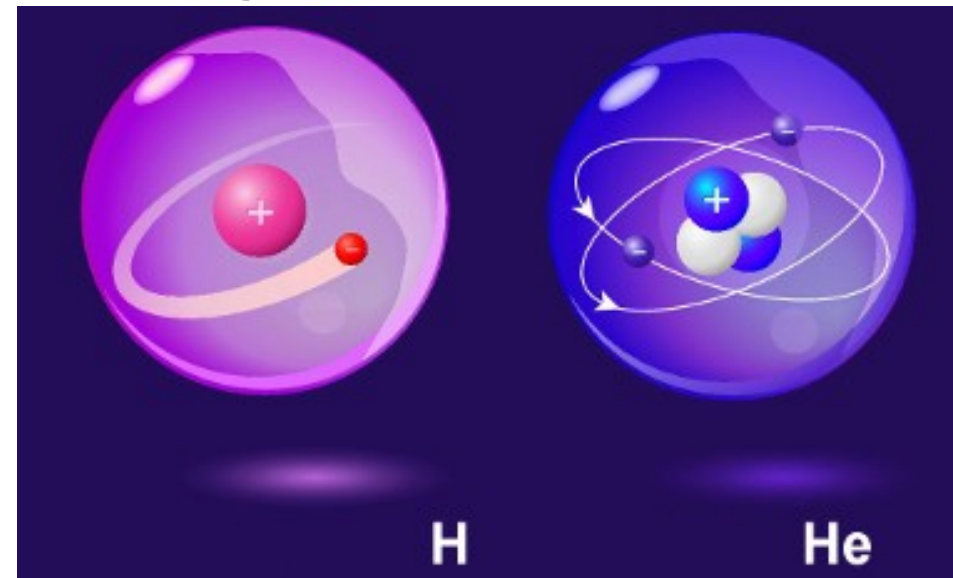
Motivation

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

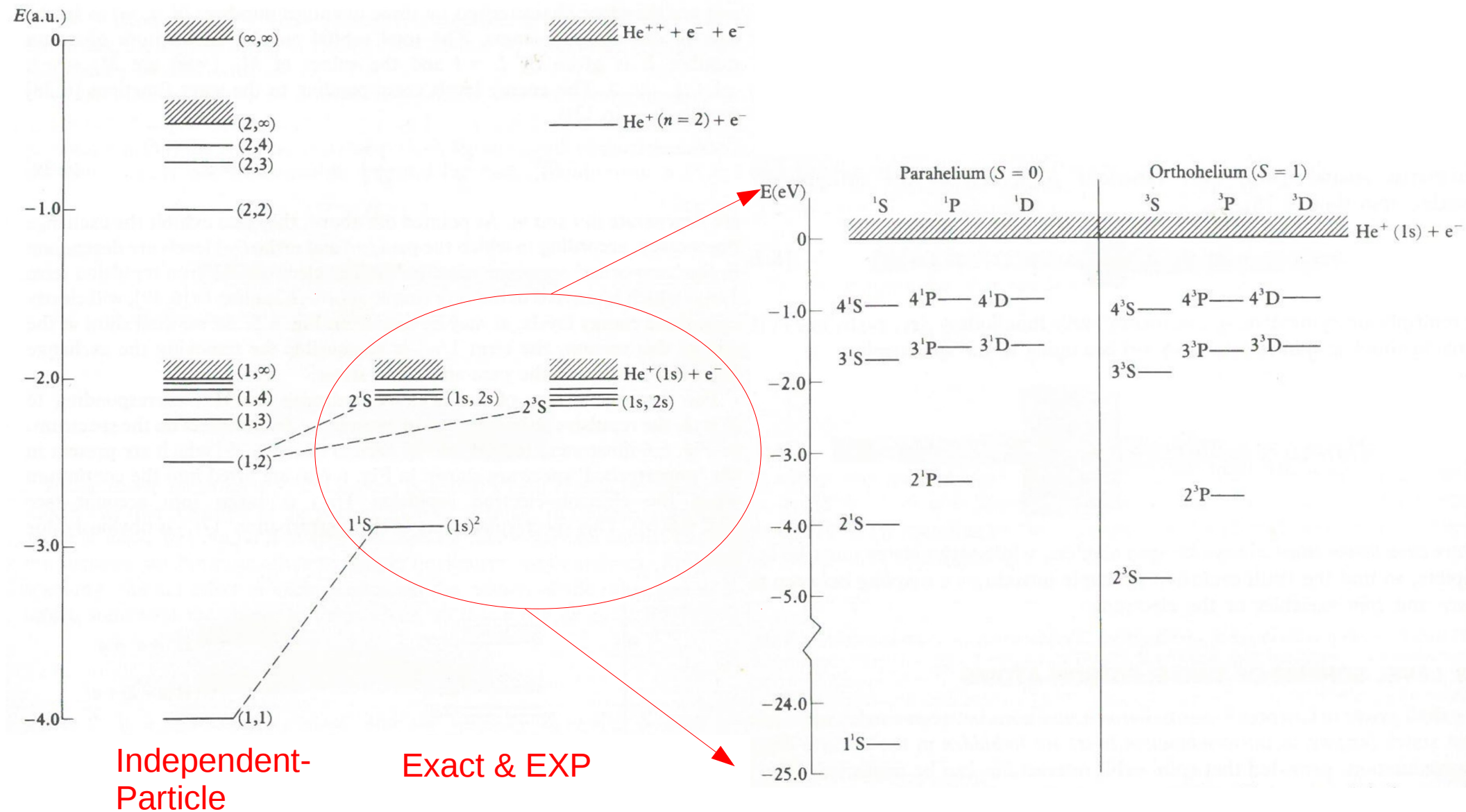
He atom

- **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!**

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



Helium atom electronic structure



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

Hylleraas 1929 exact calculation

$$s = r_1 + r_2$$

$$t = r_1 - r_2$$

$$u = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

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)

$$E_{1^1S} = -2.90324 \pm 0.00048 \quad (\pm 0.013 \text{ eV}) \quad \text{Ground state energy}$$

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	-2.903 724 377 034 114 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 <i>et al.</i>	-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^{-7} Ha

$$\Phi(s, t, u) = e^{-ks} \sum_{l,m,n,i,j} c_{l,m,n,i,j} s^l t^m u^n (s^2 + t^2)^{i/2} (\ln s)^j \quad \text{Frankowski \& Pekeris 1966}$$

$$\Phi(s, t, u) = e^{-ks} \sum_{l,m,n,j} c_{l,m,n,j} s^l (t/s)^m (u/s)^n (\ln s)^j \quad \text{Schwartz 2006}$$

- The Hylleraas calculation of He excitations seems today a problem analogous to providing, e.g., $\arctan(x)$ to the machine precision.

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	198310.82 ± 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)

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

He atom Ground State

Ground State Energy	HF	Exact	DFT-LDA
1^1S	-2.8616 Ha	-2.9037 Ha	-2.8348 Ha
1^1S	-77.868 eV	-79.014 eV	-77.139 eV

- Expected performances of both:
 - HF error: 1.1 eV = correlation energy
 - DFT-LDA error: 1.9 eV (error of LDA, not of DFT)

He atom and Exact-DFT

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

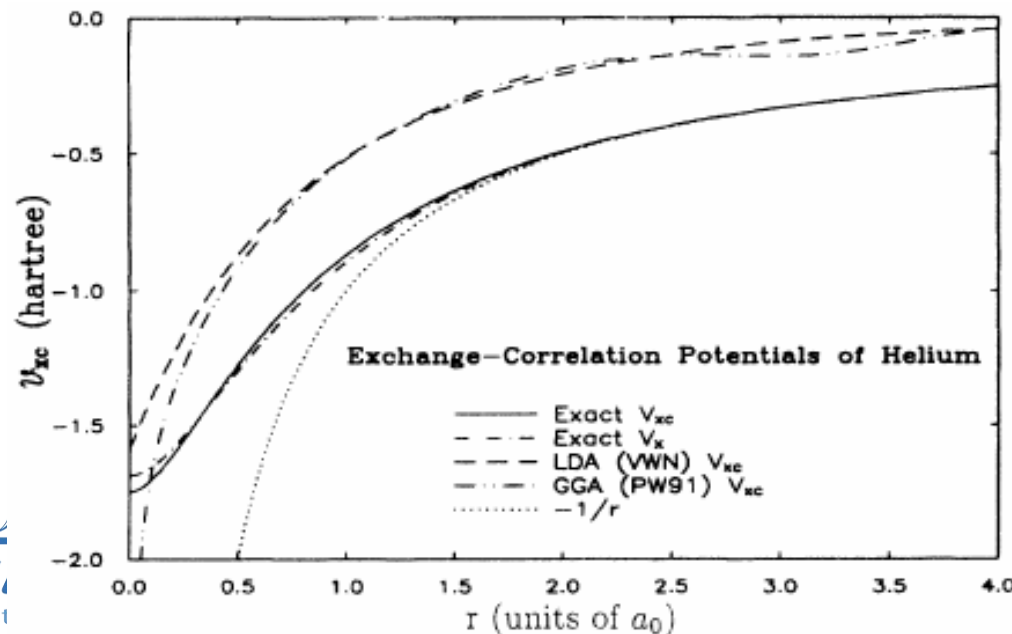
$$\Psi^{\text{exact}}(r_1, r_2) \rightarrow \rho^{\text{exact}}(r) \rightarrow \phi_{\text{HOMO}}^{\text{exact-KS}}(r) = \sqrt{\frac{\rho^{\text{exact}}(r)}{2}} \rightarrow v_{xc}^{\text{exact-DFT}}(r)$$

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

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

Exact xc potential by inversion
the Kohn-Sham equation

Umrigar, and Gonze (1994)

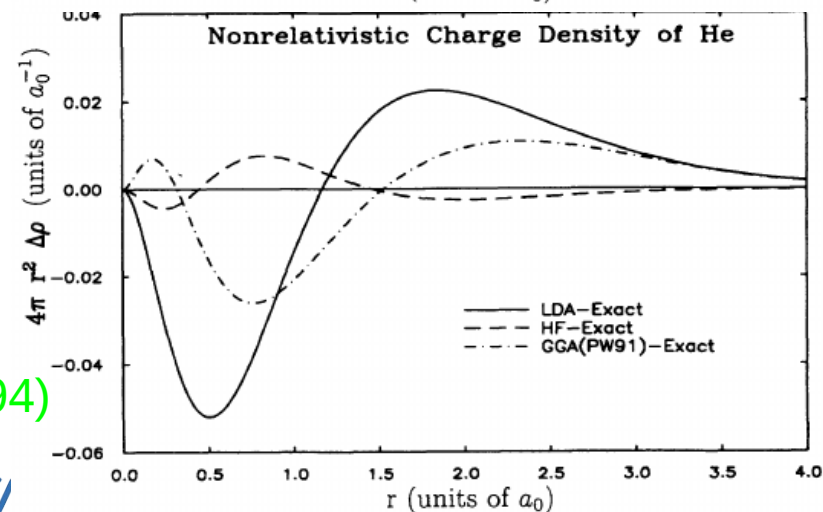
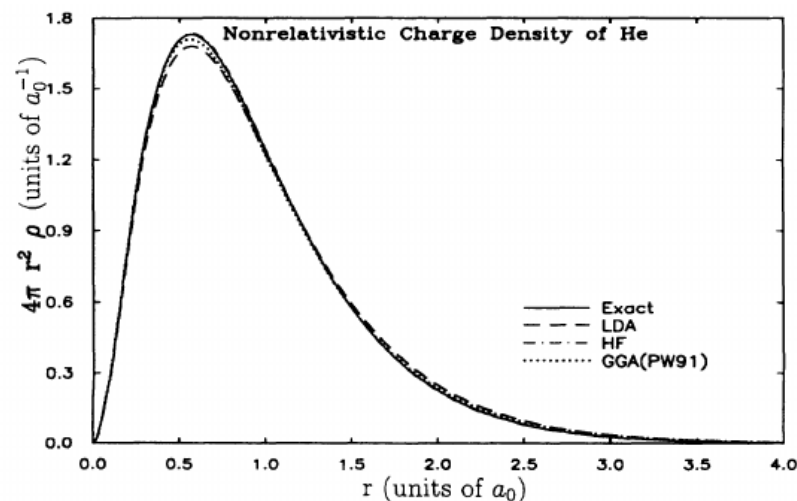


He atom Ground State

Ground State Energy	HF	Exact	Exact-DFT	DFT-LDA
1^1S	-2.8616 Ha	-2.9037 Ha	-2.9037 Ha	-2.8348 Ha
1^1S	-77.868 eV	-79.014 eV	-79.014 eV	-77.139 eV

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

Umrigar, and Gonze (1994)



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 <i>et al.</i>	-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: $7 * 10^{-7}$ Ha

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

Hylleraas → Kinoshita 1957

$$\Phi(s, t, u) = e^{-ks} \sum_{l,m,n,i,j} c_{l,m,n,i,j} s^l t^m u^n (s^2 + t^2)^{i/2} (\ln s)^j$$

Frankowski & Pekeris 1966

$$E^{\text{DMC}} = -2.903 724 6(9)$$

Neil Drummond, private communication (2017)
CASINO, Jastrow wavefunction,
CPU time: 32h (VMC) + 121h (DMC)

DMC: $\Delta E / 10 \rightarrow \text{CPU} * 100 \rightarrow \text{N \& N accuracy: } 10^{68}\text{h}$

(age of the universe = 10^{14}h)

He atom Excitations

- Check of GW+BSE, RPA and beyond, TDDFT, etc. against the Hylleraas Exact solution.
- Is the way to correlation beyond HF of GW and BSE, based on the concept of screening, valid also in an only 2 electrons system, far to be an infinite solid?
- **Validity of the BSE two-particle electron-hole propagator in a system where the hole is dug in a Fermi sea of only 2 electrons.**
- Are self-interaction/screening problems, achieving their maximum criticality in a 2 electrons system, limiting the validity of GW+BSE?

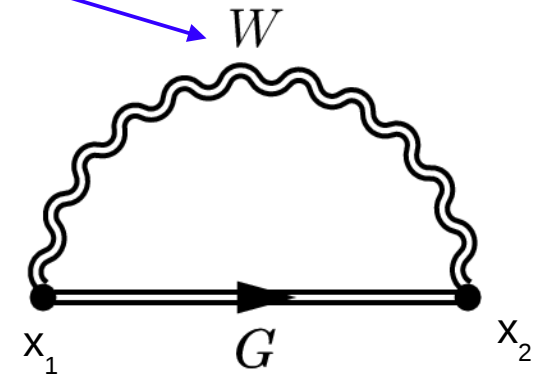
GW approximation to the Self-Energy

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

Dynamical Screened Interaction W (in RPA approx.)

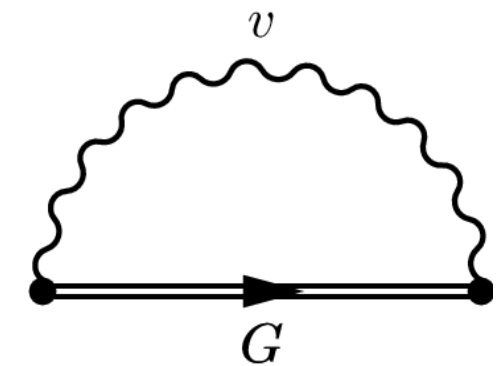
GW Self-Energy

$$\Sigma^{GW}(x_1, x_2) = i G(x_1, x_2) W(x_1, x_2)$$



Hartree-Fock Self-Energy

$$\Sigma_x(x_1, x_2) = i G(x_1, x_2) v(x_1, x_2)$$



Bare Coulombian Potential v

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

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

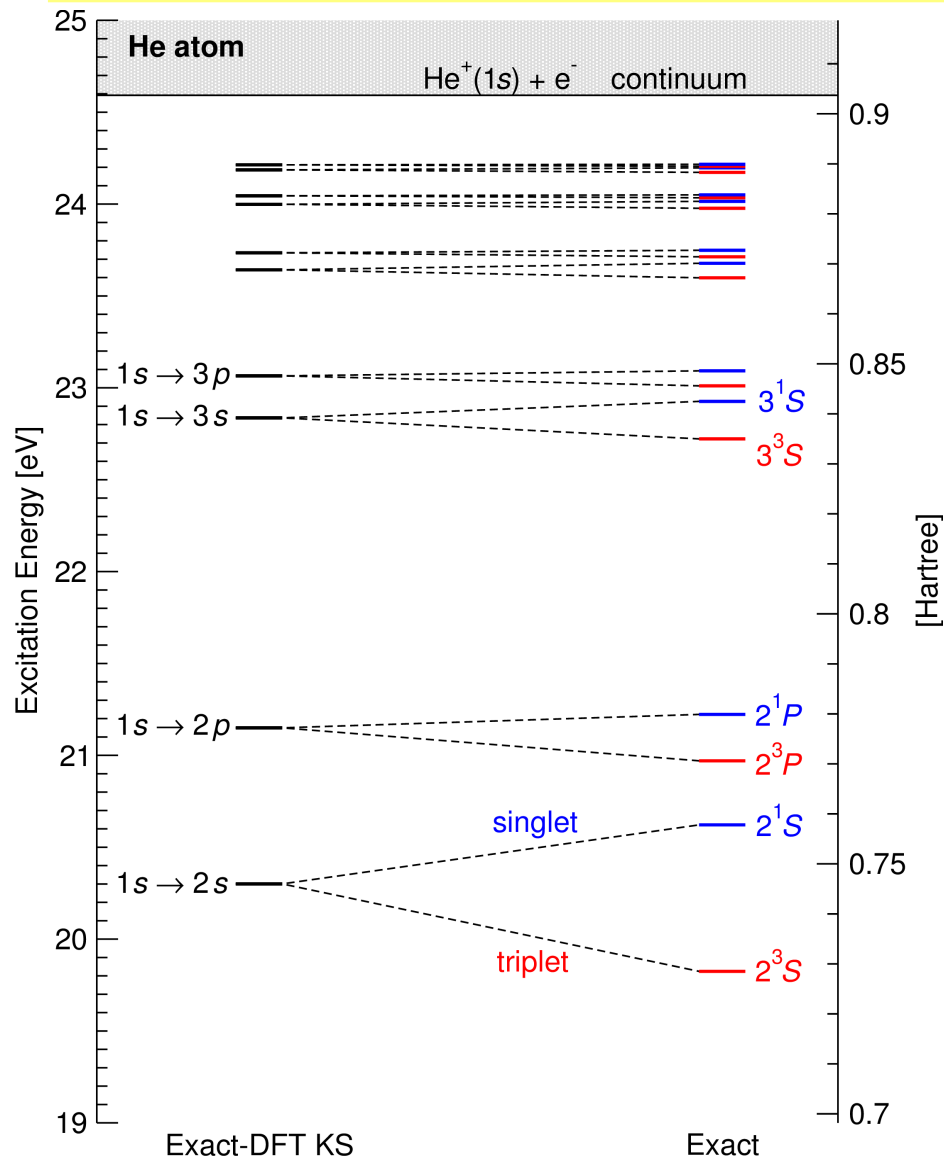
HOMO-LUMO gap

[eV]	HF	GW	EXP	Exact-DFT	DFT-LDA
1s → 2s	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!
 - Any search for a DFT functional overperforming Exact-DFT on the LUMO and the HOMO-LUMO gap is discutable.

From Quasiparticle Charged Excitations to Optical Neutral Excitations

He Neutral Excitations: Exact-DFT KS energy-differences



- Exact-DFT Kohn-Sham energy-differences are 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)

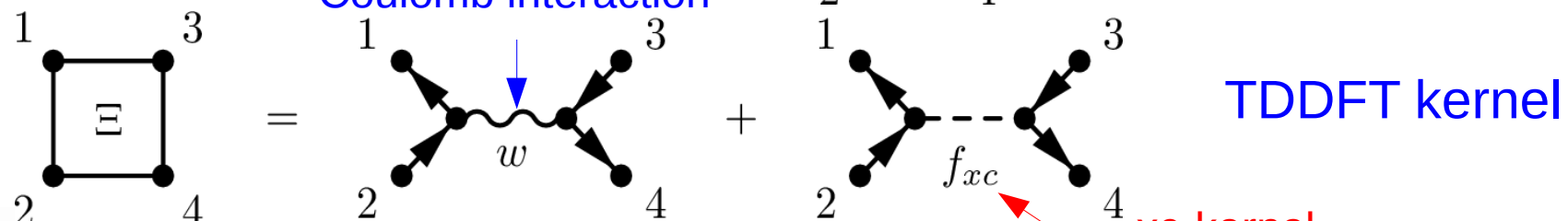
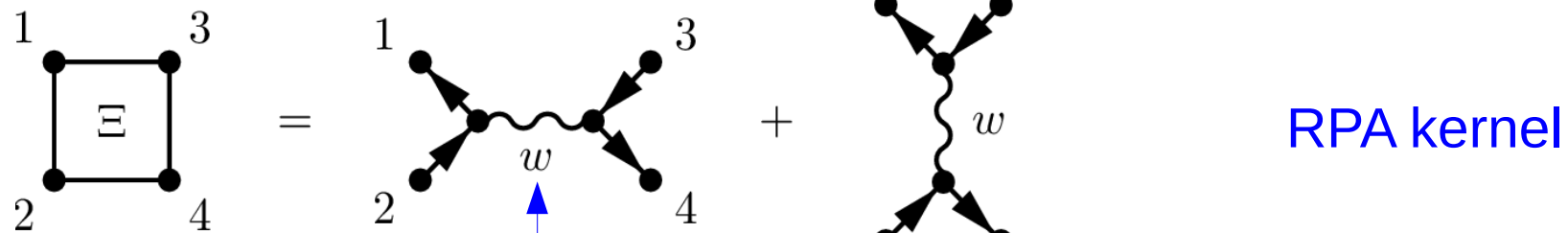
DFT → TDDFT: short intro for nuclear physicists

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} \quad \text{same equation as RPA}$$

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

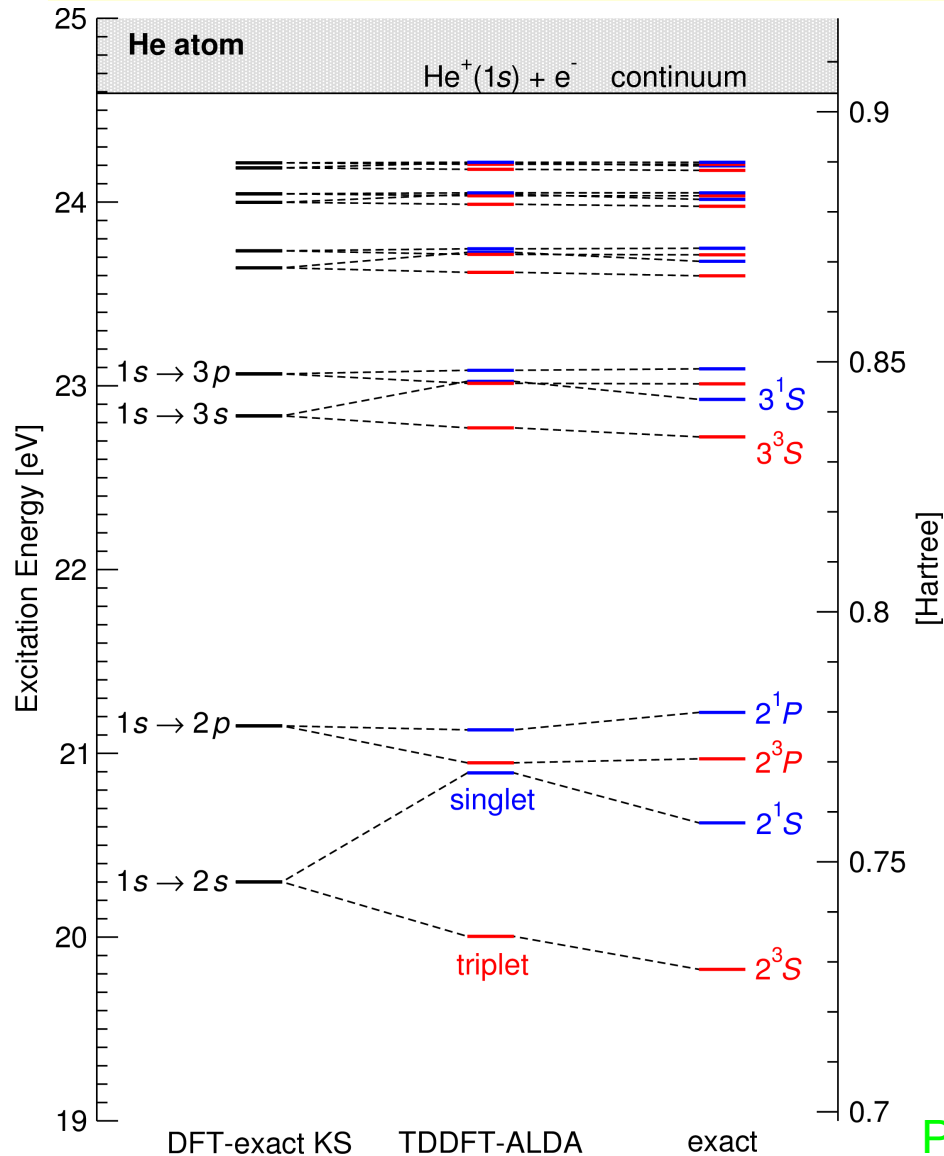
$$B_{ph,h'p'} = i\Xi_{ph,h'p'}$$

Kohn-Sham energies
instead than Hartree-Fock



xc-kernel
(must be approximated:
Adiabatic LDA)

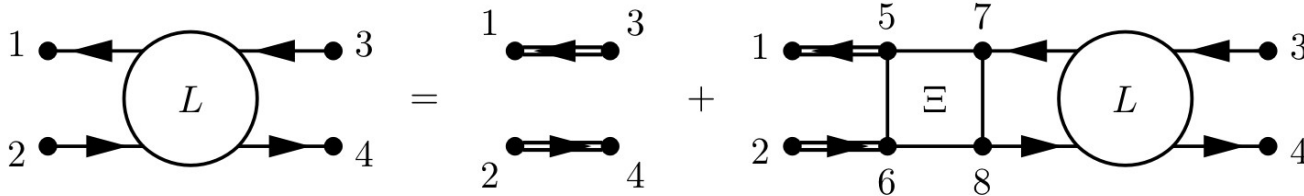
He Neutral Excitations: Exact-DFT+TDLDA



- Exact-DFT+Exact-TDDFT must of course reproduce the Exact result.
- **Approximated TDLDA on top of Exact-DFT introduces the right singlet-triplet exchange splitting and performs reasonably well.**
- **TDLDA performance: 0.2 eV error.**
- The scenario is completely different in DFT-LDA+TDLDA

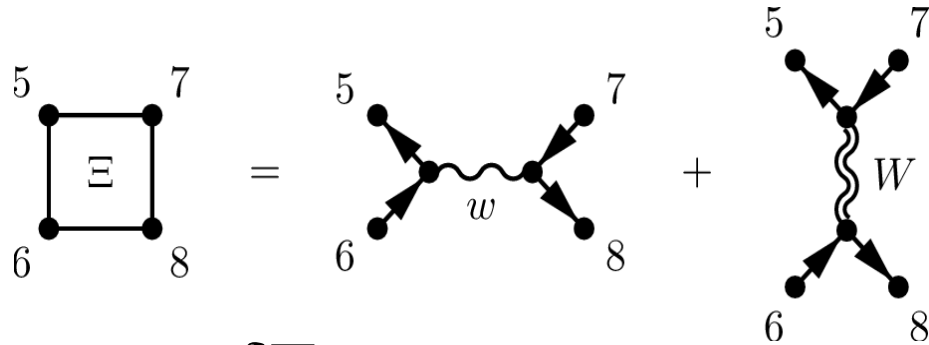
Petersilka, Gross and Burke (2000)

Bethe-Salpeter Equation



$$L = GG + GG\xi L$$

Bethe-Salpeter Equation

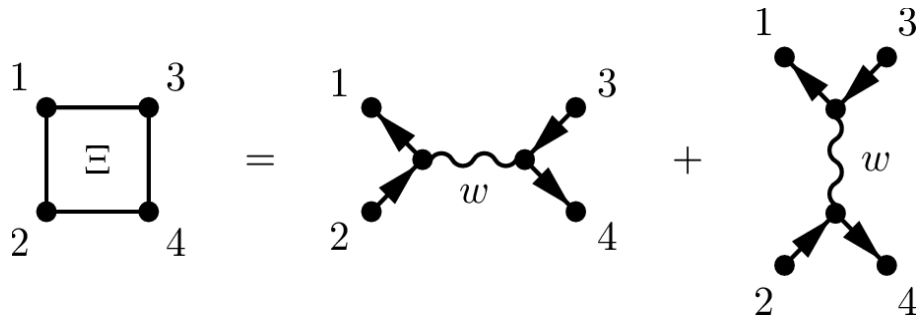


$$\xi = \frac{\delta \Sigma}{\delta G} \simeq -iw + iW$$

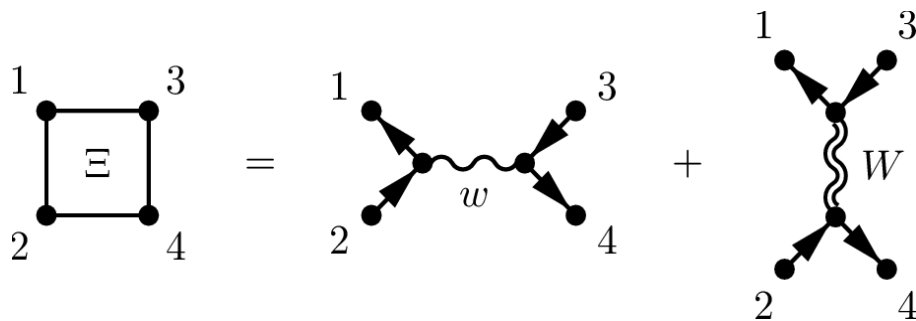
Interaction Kernel

$W = e-h$ Screened Interaction

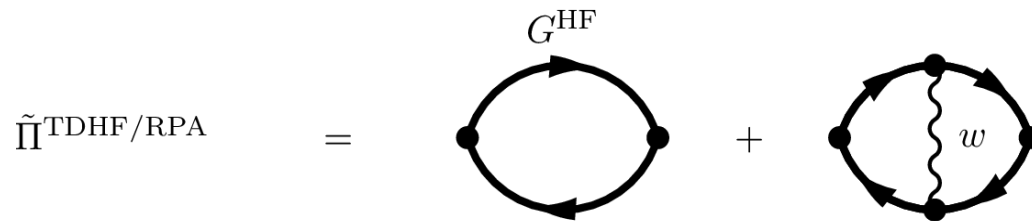
BSE vs TDHF=RPA(nuclear physics)



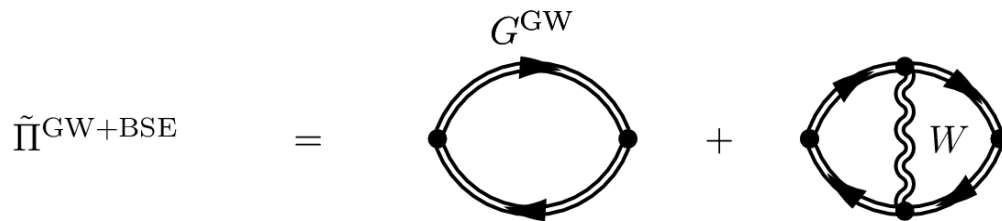
RPA (nuclear physics)



BSE



- Screening is the GW+BSE way to correlations!



BSE vs TDHF=RPA(nuclear physics)

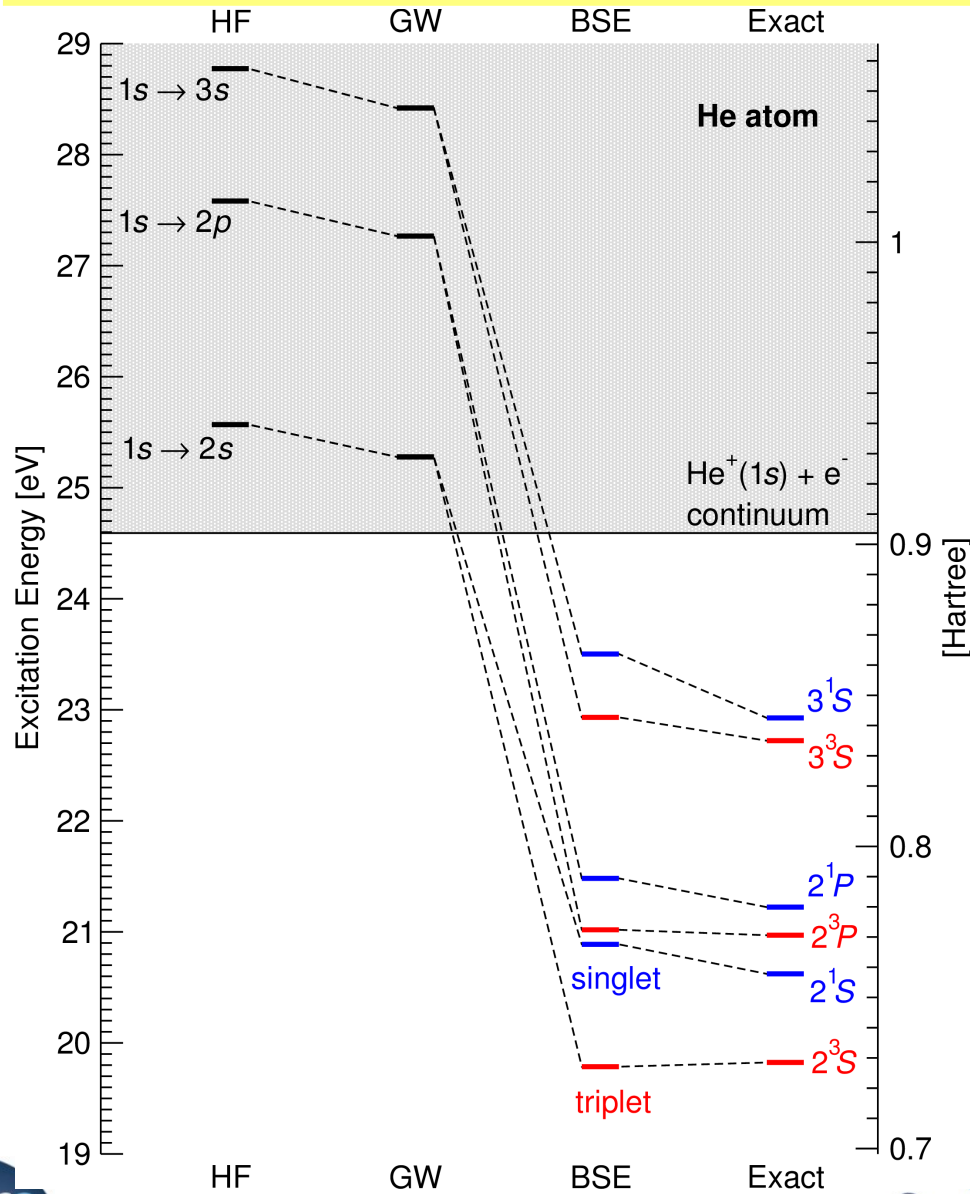
$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix} = E_\lambda \begin{pmatrix} X_\lambda \\ Y_\lambda \end{pmatrix}$$

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

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

GW quasiparticle energies
instead than 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, lie in the continuum, **as they must.**
- In contrast to the TDDFT kernel, the BSE kernel has a hard task to accomplish:
 - Bring excitations 5 eV down from the continuum
 - Exchange-split singlet-triplet states
- **GW+BSE error: < 0.1 eV**

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

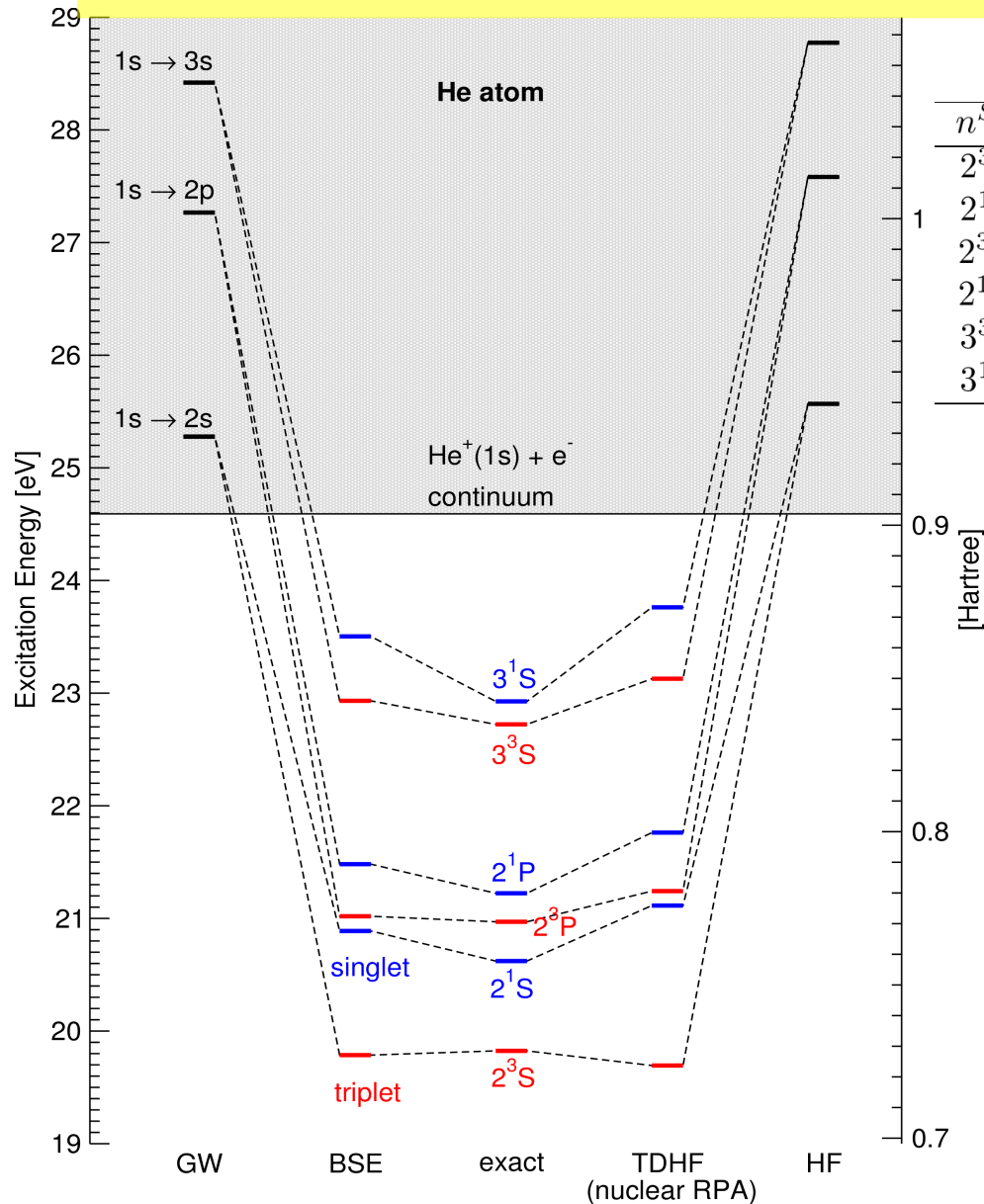
Gaussian basis set convergence

	cc-pV5Z	aug-cc-pV5Z	d-aug-cc-pV5Z	Exact
ϵ_{1s}	-0.9066	-0.9076	-0.9075	-0.9037
E_{2^3S}	0.8538	0.7284	0.7271	0.7285
E_{2^1P}	1.3345	0.8684	0.7894	0.7799
E_{3^1S}	2.6041	1.1952	0.8637	0.8425

- *d-aug-cc-pV5Z: non plus ultra!*
- And we achieved safe convergence only for the HOMO, the LUMO and the LUMO+1 (probably also the LUMO+2 is converged, but we cannot verify)!
- How can a gaussian full CI calculation be better?

- GW+BSE error: **< 0.1 eV** on the lowest (converged) lying states
- Achieves 0.6 eV on the highest, but for merely basis set (gaussians) incompleteness.

GW+BSE vs TDHF (nuclear RPA)



$n^S L$	HF	G_0W_0	GW	BSE _{TDA}	BSE	Exact	TDHF
2 ³ S				19.832	19.786	19.824	19.692
2 ¹ S	25.569	25.298	25.276	20.923	20.888	20.621	21.115
2 ³ P				21.029	21.018	20.969	21.242
2 ¹ P	27.581	27.288	27.266	21.489	21.480	21.222	21.762
3 ³ S				22.945	22.930	22.722	23.128
3 ¹ S	28.773	28.444	28.421	23.532	23.502	22.926	23.762

- TDHF (nuclear RPA): **twice the GW-BSE error!**
- TDA and G_0W_0 errors < than the quoted 0.1 eV error
- **Self-interaction/screening problems not really affecting**
 - or for < 0.1 eV
 - see also “GW on H atom”, Nelson, Bokes, Rinke, Godby 2007)

Hylleraas exact calculation

$$s = r_1 + r_2$$

$$t = r_1 - r_2$$

$$u = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

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)

$$E_{1^1S} = -2.90324 \pm 0.00048 \quad (\pm 0.013 \text{ eV}) \quad \text{Hylleraas (1929)}$$

$$\begin{aligned} \text{N} = 0 \rightarrow \Phi(r_1, r_2) &= \psi_{1s}^{Z_e}(r_1) \psi_{1s}^{Z_e}(r_2) \\ \psi_{1s}^{Z_e}(r) &= \sqrt{\frac{Z_e^3}{\pi}} e^{-Z_e r} \end{aligned} \quad \rightarrow \quad Z_e = Z - 5/16$$

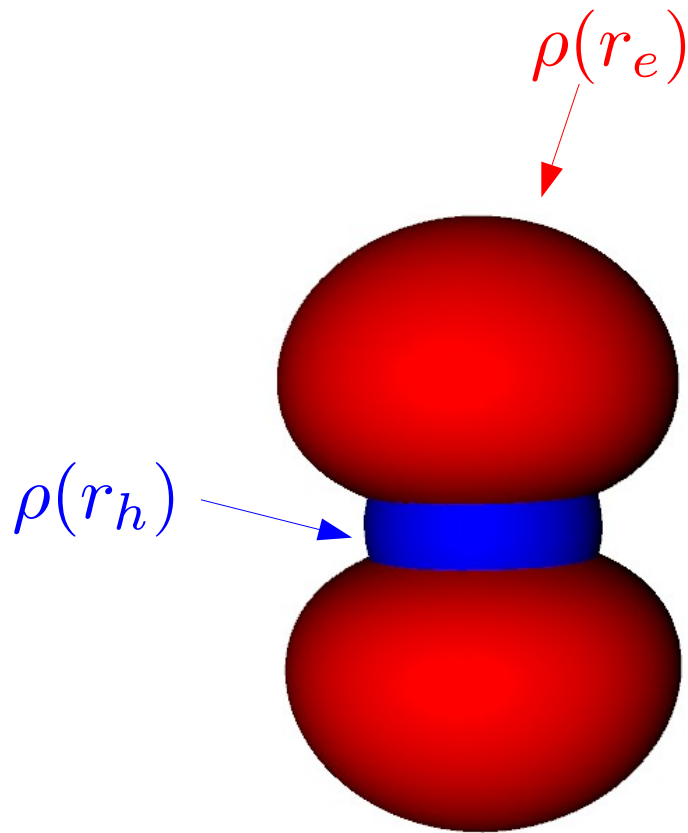
effective charge
(screening)

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

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

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

BSE Excitonic Wavefunction



Electron hole-averaged and
hole electron-averaged
distribution probabilities

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

Excitonic Wavefunction

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 sensitive 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)

Towards SC-RPA: Improved RPA

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

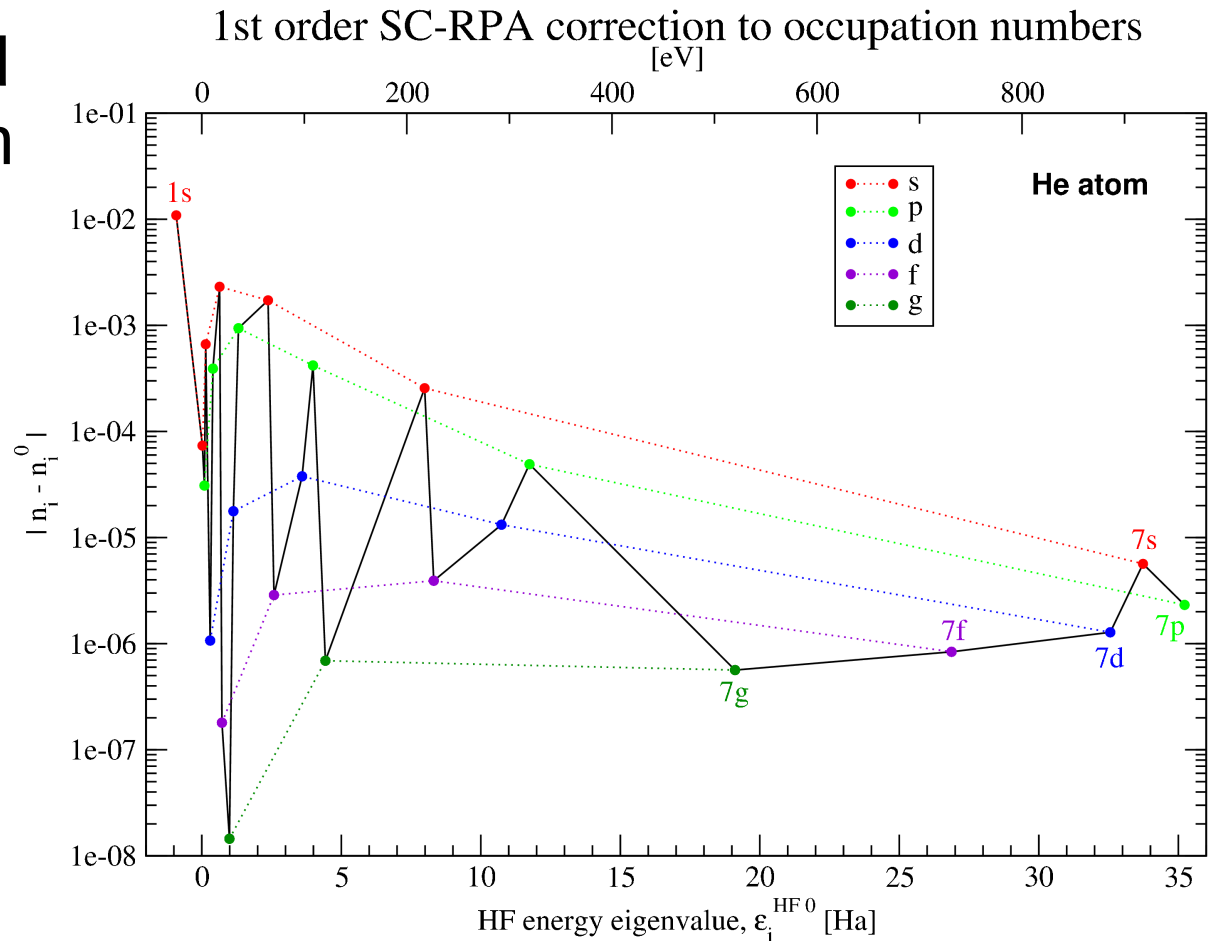
Catara et al. 1996, Rowe 1968, correct to $O(|Y|^2)$:

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

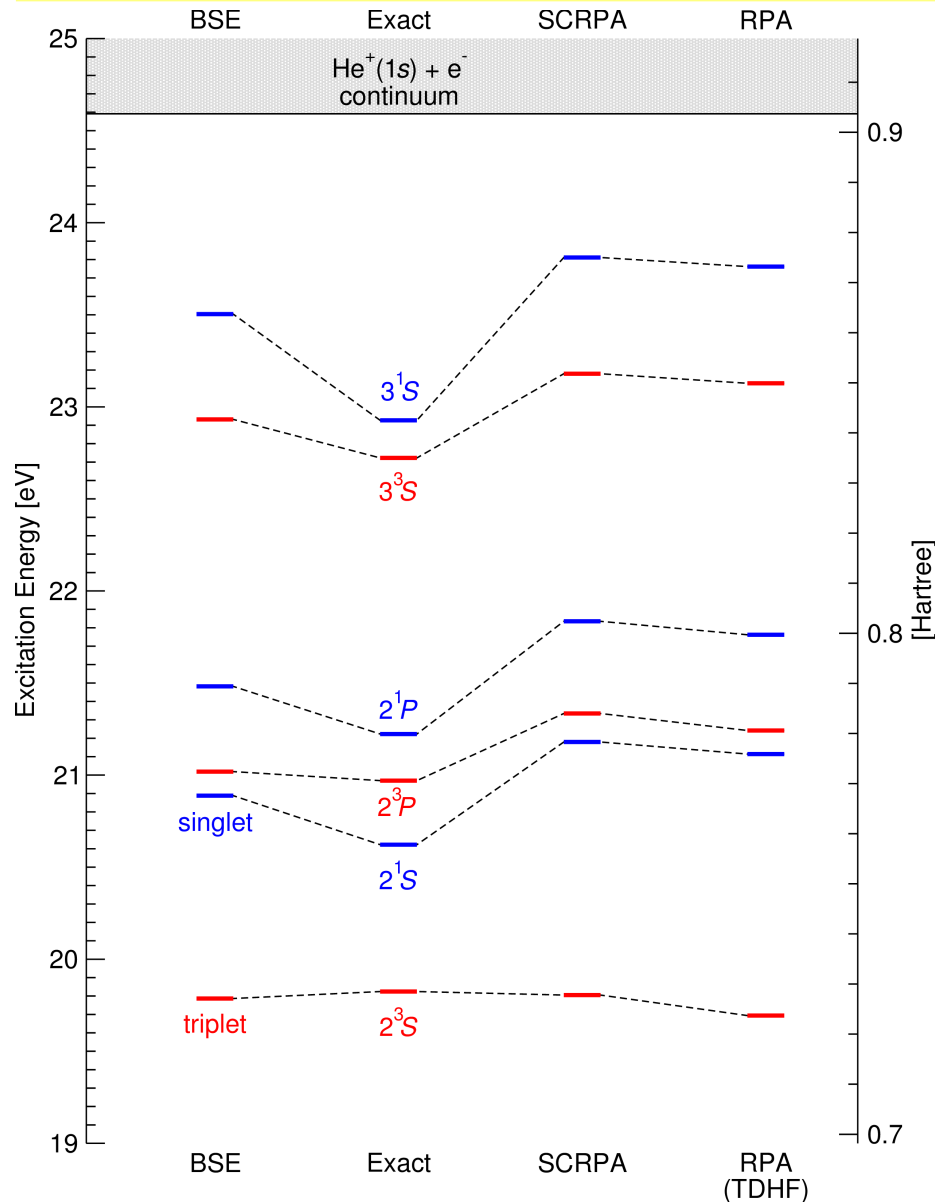
$$n_p = +\frac{1}{2} \sum_{\lambda h} |Y_{\lambda}^{ph}|^2$$

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

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



Towards SC-RPA: Improved RPA



- I-RPA improves RPA on 1st excitation (and probably the ground-state), where is better than GW+BSE.
- **Not on further excitations**

$n^S L$	HF	RPA	1 st it	SC-RPA	SC-RPA	exact	BSE
2 ³ S	25.569	19.692	19.810	19.805	19.824	19.786	
2 ¹ S		21.115	21.180	21.178	20.621	20.888	
2 ³ P	27.581	21.242	21.337	21.333	20.969	21.018	
2 ¹ P		21.762	21.837	21.835	21.222	21.480	
3 ³ S	28.773	23.128	23.181	23.179	22.722	22.930	
3 ¹ S		23.762	23.813	23.811	22.926	23.502	

	RPA	SC-RPA	exact	HF
$f_{1^1S \rightarrow 2^1P}$	0.2916	0.2889	0.27616	0.2009
$f_{1s \rightarrow 2p}$				

V. Olevano and P. Schuck, preliminary data.

Conclusions

- Many-body approaches should be benchmarked against safe exact solutions, possibly in real systems: He atom.
- **GW+BSE performs unexpectedly well on the He atom, not sensibly affected by self-interaction/screening errors.**
- The GW+BSE error is half the TDHF/RPA error.
- 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 does not catch the Rydberg series.
- Nuclear physics SC-RPA improves upon RPA only on the 1st excitation (and probably the ground-state: ongoing work) but goes in the wrong direction for the rest of the excitations.



Acknowledgements

Jing Li, Xavier Blase
CNRS Institut Neel Grenoble

Ivan Duchemin
CEA L_Sim Grenoble

Neil Drummond
University of Lancaster

Markus Holzmann, Peter Schuck
CNRS LPMMC, Grenoble

