"Beyond the GW approximation: a second-order screened exchange correction"

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SELF-ENERGY ASSOCIATED WITH SINGLE EXCITATIONS

The renormalized single excitation (rSE) [1] contribution to the electron correlation energy, and its associated self-energy are presented in terms of Feynman diagrams in Fig. 1(a) and (b), respectively. For convenience we here have used Feynman [2] instead of Goldstone [3] diagrams to represent rSE as was done in Ref. [1]. This implies that the solid arrowed lines in Fig. 1 are time-ordered Green's functions. Each line represents both a propagating particle or hole. Hence a prefactor has to be included in front of each term to remove the redundancy.

With the Feynman-diagram representation, the self-energy can be easily constructed from the total energy in Fig. 1(a) by removing one Green's function from the closed diagrams. The resultant self-energy diagrams are shown in Fig. 1(b). Now the prefactors are cancelled by the number of different ways to remove the Green's function lines. From Fig. 1(b) one can immediately see that these rSE-derived self-energy terms are improper (i.e., reducible), as these diagrams can be broken into two disconnected pieces by cutting a single Green's function line [4].

It should be noted that, in quasiparticle energy calculations, it is the proper, or irreducible, self-energy Σ that enters the Dyson equation [2],

$$G = G^0 + G^0 \Sigma G = G^0 (1 - \Sigma G^0)^{-1} . \tag{1}$$

The improper self-energy, which is usually not needed, can be trivially generated from the corresponding proper one by a simple geometrical expansion,

$$\tilde{\Sigma} = \Sigma + \Sigma G^0 \Sigma + \cdots = \Sigma (1 - G^0 \Sigma)^{-1} . \tag{2}$$

In other words, every improper self-energy has a corresponding irreducible part; that is the proper self-energy. This also holds for the rSE improper self-energy shown in Fig. 1(b). Close inspection reveals that the irreducible part of the diagrams in Fig. 1(b) is nothing but the difference between the non-local exact-exchange self-energy Σ_x

and the local Kohn-Sham exchange-correlation potential v_{xc}^{KS}, as diagrammtically shown in Fig. 1(c).

In usual GW quasiparticle energy calculations, we add the following self-energy term

$$\Delta\Sigma = \Sigma_x - v_{xc}^{\mathrm{KS}} + \Sigma_c^{GW} \tag{3}$$

to the Kohn-Sham orbtial energy. The first two terms are exactly the irreducible self-energy part corresponding to the improper rSE terms in Fig. 1. The rSE self-energy contribution is thus already accounted for in usual GW calculations and no additional rSE self-energy contribution needs to be included.

Without explicitly accounting for the rSE improper self-energy, the rSE correlation energy can be recovered from the normal adiabatic connection procedure. In perturbative calculations, the exchange-correlation energy can be obtained by [5],

$$E_{xc} = \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \mathrm{Tr} \left[G_\lambda \Sigma_\lambda \right] , \tag{4}$$

where G_λ and Σ_λ are the λ-dependent interacting Green function and the irreducible self-energy. In this simple case, we only consider the first-order irreducible self-energy correction $\Delta v = \Sigma_x - v_{xc}^{\mathrm{KS}}$ shown in Fig. 1, then $\Sigma_\lambda = \lambda \Delta v$, and $G_\lambda = \left[G_0^{-1} - \lambda \Delta v \right]^{-1}$. Equation (4) thus becomes

$$\begin{aligned} E_{xc} &= \frac{1}{2} \int_0^1 d\lambda \mathrm{Tr} \left[\frac{G_0 \Delta v}{1 - \lambda G_0 \Delta v} \right] \\ &= \frac{1}{2} \mathrm{Tr} \left[G_0 \Delta v \right] + \frac{1}{4} \mathrm{Tr} \left[(G_0 \Delta v)^2 \right] + \frac{1}{6} \mathrm{Tr} \left[(G_0 \Delta v)^3 \right] + \cdots \\ &= \frac{1}{2} \mathrm{Tr} \left[G_0 \Delta v \right] + E_c^{\mathrm{rSE}} . \end{aligned} \tag{5}$$

Thus the leading term arising from the above integratiaon corresponds to the difference between the exact-exchange energy and the KS exchange-correlation potential energy, and the rest (from the second-order on) terms sum up to the rSE correaltion energy.
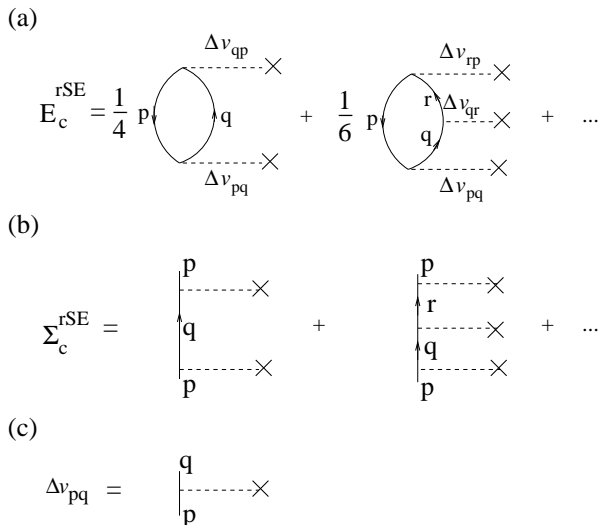
(a)

(b)

(c)

FIG. 1: (a) Feynman diagrams for the rSE contribution to the correlation energy; (b) The (improper) self-energy diagrams corresponding to the rSE correlation energy; (c) Diagrammatic representation for the matrix element of $\Delta v = \Sigma_x - v_{xc}^{\mathrm{KS}}$, i.e., the difference between the non-local exact-exchange and the local Kohn-Sham exchange-correlation potentials. Arrowed solid lines represent the non-interacting Green's function $G_p^0 = 1/(\omega - \epsilon_p)$, and p, q and r are single-particle indices.

BENCHMARK RESULTS FOR VERTICAL IONIZATION ENERGIES

Shown in Tables I and II are vertical ionizaton energies (IEs) for two test sets. These are obtained with G_0W_0 and G_0W_0+SOSEX based on PBE and PBE0 starting points, and compared to CCSD(T) reference values. The first test set consists of 34 closed-shell molecules taken from the G2 test set [6]. The vertical CCSD(T) reference IEs were computed by Bruneval and Marques [7]. All calculations for this test set were done using the Gaussian cc-pVQZ basis set [8].

The second test set consists of 18 atoms from H to Ar, and 8 molecules. These 8 molecules have the feature that the adiabatic and vertical IEs are almost identical (within 0.01 eV) [9]. For atoms these two types of IEs are identical by definition. Hence our computed vertical IE results can be directly compared to the adiabatic CCSD(T) IEs reported in Ref. [10]. An FHI-aims *tier* 4 basis [11] (aug-

mented by diffuse functions from aug-cc-pV5Z [8] ("*tier* 4 + a5Z")) is used for the G_0W_0 and G_0W_0+SOSEX calculations. Our experience indicates that this basis set is very accurate and close to the complete basis set (CBS) limit [12]. The CCSD(T) calculations were done with Gaussian orbitals extrapolated to the CBS limit using two-point fitting.

The comparison to CCSD(T) reproduces the picture gleaned in the main paper from the comparison to the G2 reference numbers. We observe, however, that $(G_0W_0$+SOSEX)@PBE yields noticeably larger errors for open-shell atoms than for closed-shell molecules, as can be seen from Tables I and II. Further explorations into the origin of this behaviour however go beyond the scope of this work.

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TABLE I: The *vertical* IEs (in eV) for 34 molecules (taken from the work of Bruneval and Marques (BM) [Ref. 7]) determined by G_0W_0 and G_0W_0+SOSEX on top of PBE and PBE0 references respectively, compared to the CCSD(T) results.[7] The columns of G_0W_0(BM) correspond to G_0W_0 results reported in Ref. 7. The Gaussian cc-pVQZ basis set [8] is used for all calculations. At the bottom of the table the mean error (ME) and mean absolute error (MAE) with respect to the CCSD(T) results are shown.

Molecule	G_0W_0(BM)	G_0W_0	(G_0W_0+SOSEX)@	G_0W_0(BM)	G_0W_0	(G_0W_0+SOSEX)	CCSD(T)
	@PBE			@PBE0			
LiH	6.50^a	6.50	7.03	7.66	7.50	8.06	7.94
Li$_2$	4.98^a	5.03	5.48	5.29	5.23	5.45	5.17
LiF	9.93^a	9.94	11.13	10.93	10.82	11.77	11.51
Na$_2$	4.89	4.81	5.13	4.97	4.93	5.08	4.82
NaCl	8.00^a	8.00	8.37	8.82	8.74	9.15	9.13
CO	13.55	13.46	14.20	14.00	13.96	14.46	14.05
CO$_2$	13.32	13.22	13.80	13.68	13.63	14.05	13.78
CS	10.93	10.83	11.64	11.43	11.39	11.85	11.45
C$_2$H$_2$	11.08	11.01	11.27	11.27	11.25	11.38	11.42
C$_2$H$_4$	10.37	10.34	10.58	10.53	10.51	10.62	10.69
CH$_4$	14.03	13.93	14.28	14.30	14.26	14.47	14.40
CH$_3$Cl	10.98	10.95	11.33	11.21	11.20	11.47	11.41
CH$_3$OH	10.64	10.54	11.17	10.97	10.94	11.37	11.08
CH$_3$SH	9.17	9.10	9.45	9.36	9.31	9.55	9.49
Cl$_2$	11.16	11.13	11.52	11.42	11.41	11.67	11.62
ClF	12.33	12.29	12.81	12.61	12.59	12.95	12.82
F$_2$	15.19	15.08	16.06	15.66	15.62	16.34	15.85
HOCl	10.85	10.78	11.33	11.14	11.11	11.49	11.30
HCl	12.35	12.25	12.72	12.54	12.48	12.82	12.74
H$_2$O$_2$	11.02	10.92	11.67	11.38	11.34	11.91	11.49
H$_2$CO	10.51	10.35	11.08	10.87	10.81	11.24	10.95
HCN	13.20	13.12	13.42	13.44	13.41	13.57	13.64
HF	15.51	15.40	16.30	15.81	15.77	16.49	16.09
H$_2$O	12.15	12.25	12.82	12.44	12.41	13.02	12.64
NH$_3$	10.50	10.43	11.13	10.78	10.76	11.26	10.92
N$_2$	14.98	14.88	15.66	15.45	15.40	15.96	15.49
N$_2$H$_4$	9.87	9.80	10.36	10.15	10.13	10.51	10.24
SH$_2$	10.10	10.03	10.45	10.27	10.22	10.51	10.43
SO$_2$	11.83	11.71	12.34	12.23	12.19	12.57	12.41
PH$_3$	10.21	10.16	10.49	10.39	10.36	10.55	10.49
P$_2$	10.12	10.09	10.37	10.27	10.25	10.40	10.76
SiH$_4$	12.40	12.29	12.68	12.72	12.68	12.90	12.82
Si$_2$H$_6$	10.38	10.29	10.53	10.62	10.56	10.69	10.69
SiO	11.03	10.90	11.51	11.34	11.29	11.63	11.55
ME	-0.46	-0.57	-0.03	-0.16	-0.20	0.17	
MAE	0.46	0.57	0.18	0.17	0.21	0.20	

^{a}Ref. 13

TABLE II: The *vertical* IEs (in eV) for 18 atoms (H-Ar) and 8 molecules determined by G_0W_0 and G_0W_0+SOSEX based on PBE and PBE0 references respectively, compared to the CCSD(T) results reported in Ref. [10]. The composite "*tier* 4 + a5Z" [12] basis set is used for G_0W_0 and G_0W_0+SOSEX calculations, and Gaussian orbitals are used for CCSD(T) calculations extrapolated to the CBS limit. The core correlation contribution is added to the CCSD(T) numbers (cf Table VI in Ref. [10]). The ME and MAE are taken with respect to the CCSD(T) results.

Molecule	G_0W_0@		$(G_0W_0$+SOSEX)@		CCSD(T)
	PBE	PBE0	PBE	PBE0	
H	12.52	13.04	13.80	13.77	13.61
He	23.59	24.01	24.37	24.65	24.59
Li	5.67	5.84	5.91	5.55	5.39
Be	9.03	9.26	9.48	9.34	9.32
B	7.65	8.11	9.03	8.55	8.28
C	10.47	10.93	11.96	11.51	11.25
N	13.51	14.06	14.52	14.82	14.55
O	13.04	13.37	13.28	13.82	13.60
F	16.71	17.07	17.19	17.59	17.43
Ne	20.54	21.10	21.22	21.49	21.61
Na	5.45	5.47	5.44	5.33	5.12
Mg	7.71	7.64	7.88	7.72	7.62
Al	5.64	5.94	6.34	6.06	5.96
Si	7.76	8.01	8.61	8.22	8.15
P	10.11	10.25	10.50	10.61	10.52
S	9.94	10.24	11.01	10.45	10.33
Cl	12.51	12.83	12.5	12.79	12.98
Ar	15.21	15.51	15.58	15.74	15.84
OH	12.41	12.79	12.92	13.96	13.05
CO	13.30	13.78	14.06	14.32	14.02
N_2	14.86	15.45	15.56	16.04	15.64
Cl_2	11.04	11.49	11.41	11.64	11.56
CO_2	13.21	13.68	13.77	14.07	13.92
CH_3	9.24	9.59	9.44	10.07	9.80
C_6H_6	9.00	9.20	9.30	9.42	9.32
CH_3SH	9.06	9.31	9.40	9.53	9.50
ME	-0.51	-0.18	0.06	0.15	
MAE	0.56	0.25	0.27	0.18	