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SPECIAL ISSUE IN HONOUR OF NICHOLAS C. HANDY

Coupled-cluster reference values for the GW27 and GW100 test sets for the assessment of GW methods

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The vertical ionisation energies of the molecules of the GW27 (27 molecules) and GW100 (100 molecules) test sets are computed in a polarised triple-zeta-valence basis set in the framework of coupled-cluster theory with single, double, and non-iterative triple substitutions. The molecular geometries were kept fixed to those of the two test sets. To demonstrate the usefulness of the coupled-cluster reference values, they are compared with quasi-particle energies obtained in the G_0W_0 approximation for functionals commonly used in Kohn–Sham density-functional theory (DFT). Furthermore, an approximation is assessed, in which only exchange contributions are added to the DFT orbital energies.

Keywords: density-functional theory; exchange potential; response theory; random-phase approximation; G_0W_0 approximation

1. Introduction

It is well known that in Kohn–Sham density-functional theory (DFT) using conventional approximations such as the generalised gradient approximation (GGA), the eigenvalue of the highest occupied molecular orbital (HOMO) is a rather poor approximation to the ionisation energy (IE) of the system under study. HOMO eigenvalues lie well above the negative of the IE when GGA functionals are used. Among others, Tozer and Handy have pointed out [1] that the Kohn–Sham eigenvalues depend critically on the exchange–correlation potential and that it is essential to understand the behaviour of this potential. They also emphasised the importance of the integer discontinuity in the exchange–correlation potential in view of their asymptotic-correction scheme [2]. This discontinuity has been known since 1982, when Perdew *et al.* [3] investigated the behaviour of the exchange–correlation potential for non-integer number of electrons N . They showed that when N increases through an integer, the derivative of the energy with respect to N jumps discontinuously from $-I$ to A , where I is the IE and A is the electron affinity of the system. GGAs are continuum functionals whose potentials $V_{XC}(\mathbf{r})$ do not exhibit a discontinuity as N increases through an integer. Consequently, they should exhibit a non-zero asymptotic value $V_{XC}(\infty)$, which is related to the IE and the HOMO eigenvalue [2],

$$V_{XC}(\infty) = \varepsilon_{\text{HOMO}} + I. \quad (1)$$

In the asymptotic-correction scheme, the GGA potential is replaced by

$$\lim_{r \rightarrow \infty} V_{XC}(\mathbf{r}) = -\frac{1}{r} + \varepsilon_{\text{HOMO}} + I \quad (2)$$

in the asymptotic region while an interpolation is performed in the intermediate region between the inner and asymptotic regions.

In the many-body Green's function GW formalism, the IE is computed as the negative of an eigenvalue in a quasi-particle (QP) framework, and recent work has been concerned with applying the GW formalism to molecular systems (as opposed to solids). Refs. [4–10] represent examples of such works.

Our article is motivated by the work done by van Setten *et al.* [7], who implemented the G_0W_0 approximation in the TURBOMOLE program package [11,12]. In Ref. [7], van Setten *et al.* assessed their implementation by comparing computed vertical IEs with experimental values for a test set consisting of 27 closed-shell molecules (GW27 test set). More recently, these authors have designed a larger test set comprising 100 closed-shell atoms and molecules (GW100 test set) [13].

However, a comparison with experimental IEs is problematic, which, for example, has been noted by Caruso *et al.* [6]. They noted that ‘for an unbiased assessment, it would be desirable to benchmark GW against higher-level theories, since in experiment the distinction between vertical

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and adiabatic ionisation energies is difficult and vibrational effects are always present.’ Therefore, we decided to perform high-level coupled-cluster calculations for all atoms and molecules of the GW27 and GW100 test sets at exactly the same molecular geometries and in exactly the same basis as chosen by van Setten and co-workers in their works [7,13]. Such calculations will provide purely electronic vertical ionisation energies (VIEs) that can be used in a straightforward manner to assess GW methods, because also the QP HOMO eigenvalues refer to VIEs.

We have performed coupled-cluster calculations in the CCSD(T) approximation [14]; that is, coupled-cluster theory with single and double substitutions plus a perturbation-theory correction for connected triple substitutions. To illustrate the use of the CCSD(T) reference values, we have computed G_0W_0 VIEs using three different DFT functionals: an ‘exchange-only’ GGA functional (OPTX [15–17]), an exchange–correlation GGA functional (PBE [18]), and a hybrid exchange–correlation functional containing some amount of Hartree–Fock exchange (PBE0 [19–21]). Furthermore, we assess a very simple empirical G_0W_0 method in which only the exchange parts of the self-energy and the Kohn–Sham potential are evaluated. We call this method x_α - G_0W_0 , because the G_0W_0 correction to the Kohn–Sham eigenvalues is scaled with an empirical parameter α .

This article is organised as follows: the notation and definitions of the G_0W_0 implementation in TURBOMOLE are given in Section 2. This section also gives details on the x_α - G_0W_0 method. Computational details with respect to all calculations (CCSD(T) as well as G_0W_0) are given in Section 3. The results are discussed in Section 4 and Section 5 concludes the article.

2. G_0W_0 theory

In the G_0W_0 method, we aim at computing the QP energies

$$\varepsilon_p^{\text{QP}} = \varepsilon_p + Z_p \langle \varphi_p | \Sigma_X + \Sigma_C(\varepsilon_p) - V_{\text{XC}} | \varphi_p \rangle, \quad (3)$$

where φ_p is a Kohn–Sham spin orbital (which is assumed to be real) and ε_p is its corresponding orbital energy. Equation (3) is obtained from a first-order Taylor expansion about the Kohn–Sham solution, with

$$Z_p = \{1 - \langle \varphi_p | (\partial \Sigma_C(\varepsilon) / \partial \varepsilon)_{\varepsilon=\varepsilon_p} | \varphi_p \rangle\}^{-1}. \quad (4)$$

The correction due to Σ_X is simply the expectation value of the Hartree–Fock exchange operator (computed with Kohn–Sham orbitals, however),

$$\langle \varphi_p | \Sigma_X | \varphi_p \rangle = - \sum_i (p_i | i p). \quad (5)$$

Here and in the following, we use the indices i, j, k, \dots for occupied, a, b, c, \dots for unoccupied (virtual), and

p, q, r, \dots for arbitrary spin orbitals. We use Mulliken’s notation for two-electron integrals,

$$(pq|rs) = \iint \varphi_p(\mathbf{x}) \varphi_r(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varphi_q(\mathbf{x}) \varphi_s(\mathbf{x}') d\mathbf{x} d\mathbf{x}'. \quad (6)$$

The correlation part of the self-energy is computed as

$$\begin{aligned} \langle \varphi_p | \Sigma_C(\varepsilon_p) | \varphi_p \rangle &= \sum_k \sum_{ai} \frac{|(pk|\rho_{ai})|^2}{\varepsilon_p - \varepsilon_k + \omega_{ai} - i\delta} \\ &+ \sum_c \sum_{ai} \frac{|(pc|\rho_{ai})|^2}{\varepsilon_p - \varepsilon_c - \omega_{ai} + i\delta}, \end{aligned} \quad (7)$$

where

$$(pk|\rho_{ai}) = \sum_{bj} (pk|bj)(X_{bj,ai} + Y_{bj,ai}). \quad (8)$$

Similarly,

$$\begin{aligned} \langle \varphi_p | (\partial \Sigma_C(\varepsilon) / \partial \varepsilon)_{\varepsilon=\varepsilon_p} | \varphi_p \rangle &= - \sum_k \sum_{ai} \frac{|(pk|\rho_{ai})|^2}{(\varepsilon_p - \varepsilon_k + \omega_{ai} - i\delta)^2} \\ &- \sum_c \sum_{ai} \frac{|(pc|\rho_{ai})|^2}{(\varepsilon_p - \varepsilon_c - \omega_{ai} + i\delta)^2}. \end{aligned} \quad (9)$$

The sums run over all excitation energies ω_{ai} . $X_{ai,bj}$ and $Y_{ai,bj}$ are matrix elements of the matrices X and Y of the non-Hermitian eigenvalue problem

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X & Y \\ Y & X \end{pmatrix} = \begin{pmatrix} X & Y \\ Y & X \end{pmatrix} \begin{pmatrix} \Omega & 0 \\ 0 & -\Omega \end{pmatrix}, \quad (10)$$

with $\Omega_{ai,bj} = \delta_{ij} \delta_{ab} \omega_{ai}$. In the random-phase approximation (RPA), the orbital-rotation Hessians are defined as

$$A_{ai,bj} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ai|bj), \quad (11a)$$

$$B_{ai,bj} = (ai|bj). \quad (11b)$$

(This approximation is sometimes referred to as ‘direct’ random-phase approximation, dRPA [22].) From the non-Hermitian RPA eigenvalue problem, we obtain the following symmetric eigenvalue problem of reduced dimension for the squared excitation energies in the usual manner:

$$\mathbf{M}\mathbf{Z} = \mathbf{Z}\mathbf{\Omega}^2, \quad (12)$$

with

$$\mathbf{M} = (\mathbf{A} - \mathbf{B})^{1/2} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{1/2}. \quad (13)$$

The required (de)excitation vectors are obtained as

$$\mathbf{X} + \mathbf{Y} = (\mathbf{A} - \mathbf{B})^{1/2} \mathbf{Z} \boldsymbol{\Omega}^{-1/2}. \quad (14)$$

In the present work, we are concerned with a very simple approximation to the full G_0W_0 approach, denoted x_α - G_0W_0 . In this approach, the QP energies are computed as

$$\varepsilon_p^{\text{QP}}(x_\alpha\text{-}G_0W_0) = \varepsilon_p + \alpha \langle \varphi_p | \Sigma_X - V_X | \varphi_p \rangle; \quad (15)$$

that is, the only correction to the orbital energies of DFT is the difference between the orbital expectation values of the exchange self-energy and the exchange potential. This difference is scaled with an empirical parameter α .

Finally, in the tda- G_0W_0 approach, the matrices \mathbf{X} and \mathbf{Y} are computed employing the Tamm–Dancoff approximation, in which the orbital-rotation Hessians take the form $\mathbf{A}^{\text{TDA}} = \mathbf{A}$ and $\mathbf{B}^{\text{TDA}} = \mathbf{0}$. We denote this approach as tda- G_0W_0 while the full G_0W_0 approach will be denoted as rpa- G_0W_0 .

3. Computational details

The data reported in this article as well as in its supplemental content were all obtained from computations with the TURBOMOLE program package using the modules DSCF, RICC2 and ESCF [11, 12]. Concerning the latter, version number 101014 was used for the G_0W_0 part, which is a revised version of the implementation reported in Ref. [7]. As a check on the coupled-cluster results obtained with TURBOMOLE, the corresponding Hartree–Fock and CCSD(T) energies were computed with the CFOUR program package [23] as well. The computations were run in parallel on up to 16 cores [24–26].

For all of the calculations, the def2-TVZPP basis set [27] was used as obtained from the basis-set library of TURBOMOLE V6.6. For the atoms Rb, Ag, I, Cs and Au, the $[\text{Ar}]3d^{10}$ (Rb, Ag, I), $[\text{Kr}]4d^{10}$ (Cs) and $[\text{Kr}]4d^{10}4f^{14}$ (Au) cores were treated with the pseudopotentials [28–30] that come with the def2-TVZPP basis sets in TURBOMOLE V6.6. We want to stress that it is crucial to use the same geometries and basis sets for all assessments in order to obtain deviations which are purely due to differences in methodology. For example, an extrapolation to the complete-basis-set limit of CCSD(T) theory would not be beneficial, because then also the corresponding GW computation should be carried out in a nearly complete basis or extrapolated to the basis-set limit.

Concerning the Hartree–Fock, DFT and G_0W_0 computations with DSCF and ESCF, no approximations were made to the two-electron electron-repulsion integrals (ERIs), and tight convergence criteria were used (`scfconv=9`). TURBOMOLE’s grid 5 was used for numerical integration [12]. All possible singly substituted states were taken into account in the G_0W_0 computations, which were done in the

RPA – see Equation (11). The damping parameter was set to zero in all calculations – $\delta = 0$ in Equations (7) and (9). For example, for naphthacene (CAS number 92-24-0) with 60 doubly occupied spatial orbitals and 666 virtual spatial orbitals, the ESCF calculation comprised 39,960 singly substituted states. Note that the GW27 and GW100 test sets only contain closed-shell molecules and that the Kohn–Sham spin orbitals needed for the G_0W_0 calculations were obtained from *restricted* Kohn–Sham theory. The functionals investigated were OPTX [15–17], PBE [18] and PBE0 [19–21]. For OPTX, we used the XCFUN library of Ekström *et al.* [31].

The CCSD(T) computations were performed after checking for Hartree–Fock instabilities. Accordingly, many CCSD(T) computations had to be carried out with respect to an *unrestricted* Hartree–Fock reference and without imposing any symmetry restrictions (e.g., by using the keywords `SYMMETRY=OFF` and `HFSTABILITY=FOLLOW` for the computations with CFOUR). No approximations were made to the ERIs of CFOUR, but a resolution-of-the-identity (RI) approximation was invoked in the computations with RICC2. For this RI approximation, the default auxiliary basis sets of TURBOMOLE’s basis-set library were used (`cbas=def2-TZVPP`) [32,33]. All of the CCSD(T) computations were performed in the frozen-core approximation; that is, inner core orbitals were not included in the correlation treatment. The number of neglected core orbitals (doubly occupied) is given in Tables 4 and 5. Default convergence thresholds were used for the coupled-cluster computation as well as the underlying Hartree–Fock computation.

4. Results and discussion

In Tables 1–3, we report x_α - G_0W_0 , tda- G_0W_0 and rpa- G_0W_0 QP energies of the Li atom as obtained in the def2-TVZPP basis, for three different functionals: OPTX

Table 1. OPTX quasi-particle energies (in eV) of the Li atom in the def2-TVZPP basis, with damping parameter $\delta = 0$ and empirical parameter $\alpha = 0.75$.

	OPTX	x_α - G_0W_0	tda- G_0W_0	rpa- G_0W_0
α spin				
1s	−50.93	−63.51	−60.05	−60.88
2s	−2.98	−4.76	−5.60	−5.49
2p	−0.85	0.92	0.88	0.98
3s	1.67	3.07	3.12	3.15
β spin				
1s	−50.74	−63.07	−59.95	−60.75
2s	−0.46	0.65	−0.49	−0.20
2p	1.60	2.71	1.32	1.52
3s	3.13	4.17	3.57	3.68

Table 2. PBE quasi-particle energies (in eV) of the Li atom in the def2-TZVPP basis, with damping parameter $\delta = 0$ and empirical parameter $\alpha = 0.75$.

	OPTX	x_α -G ₀ W ₀	tda-G ₀ W ₀	rpa-G ₀ W ₀
α spin				
1s	-51.71	-64.30	-60.07	-60.90
2s	-3.22	-5.03	-5.64	-5.52
2p	-1.12	0.70	0.89	0.99
3s	1.43	2.94	3.06	3.09
β spin				
1s	-51.48	-63.90	-59.97	-60.78
2s	-0.36	0.70	-0.26	0.06
2p	1.82	2.85	1.47	1.65
3s	3.23	3.89	3.51	3.59

Table 3. PBE0 quasi-particle energies (in eV) of the Li atom in the def2-TZVPP basis, with damping parameter $\delta = 0$ and empirical parameter $\alpha = 0.75$.

	OPTX	x_α -G ₀ W ₀	tda-G ₀ W ₀	rpa-G ₀ W ₀
α spin				
1s	-55.86	-65.33	-62.38	-62.94
2s	-3.83	-5.18	-5.72	-5.62
2p	-0.52	0.82	1.02	1.08
3s	1.93	3.07	3.27	3.31
β spin				
1s	-55.57	-64.91	-62.16	-62.70
2s	0.09	0.78	-0.11	0.09
2p	2.27	2.95	1.86	2.04
3s	3.51	4.05	3.82	3.88

(Table 1), PBE (Table 2) and PBE0 (Table 3). The purpose of these tables is to provide data that can be reproduced easily by any computer program that uses atom-centred Gaussian basis functions. Lithium was chosen as it represents the simplest many-electron open-shell system. An unrestricted Kohn–Sham reference was used. Concerning the x_α -G₀W₀ method in conjunction with the PBE and PBE0 functionals, it is important to note that only the exchange potential V_X enters Equation (15). Hence, only the exchange

contributions to the PBE and PBE0 exchange–correlation potentials must be computed to obtain the x_α -G₀W₀ correction. In Tables 1–3, the parameter α was set equal to 0.75. As we will see later, test sets can be used to optimise an empirical parameter such as α for a given exchange–correlation functional, but the value of 0.75 is just a crude estimate based on a few preliminary computations. When comparing the three functionals OPTX, PBE and PBE0, it appears that the Kohn–Sham eigenvalues show much larger

Table 4. Vertical ionisation energies (VIEs, in eV) of the GW27 test set as obtained at the Δ CCSD(T)/def2-TZVPP level. The CCSD(T)/def2-TZVPP energies of the neutral molecules and their cations are given in E_h . The last column gives the number of doubly occupied core orbitals, which are excluded from the correlation treatment.

CAS Nr.	Compound	VIE	Neutral	Cation	Core
106-97-8	Butane	11.580	-158.15593	-157.73036	4
107-02-8	2-Propenal	10.197	-191.58718	-191.21244	4
120-12-7	Anthracene	7.014	-538.49711	-538.23935	14
12184-83-7	Cesium dimer	3.578	-40.03785	-39.90636	0
12187-09-6	Gold dimer	9.095	-270.70784	-270.37362	2
124236-18-6	Au4	7.671	-541.46477	-541.18286	4
124-38-9	Carbon dioxide	13.671	-188.33369	-187.83129	3
1333-74-0	Hydrogen	16.213	-1.17195	-0.57613	0
13768-60-0	Boron fluoride	11.135	-124.50573	-124.09652	2
14452-59-6	Lithium dimer	5.195	-14.97157	-14.78065	0
25681-79-2	Disodium	4.918	-324.07265	-323.89193	2
67-64-1	Acetone	9.706	-192.83888	-192.48221	4
71-43-2	Benzene	9.340	-231.80776	-231.46454	6
74-82-8	Methane	14.359	-40.43859	-39.91091	1
74-84-0	Ethane	13.118	-79.67545	-79.19335	2
74-85-1	Ethylene	10.698	-78.43988	-78.04673	2
74-98-6	Propane	12.132	-118.91407	-118.46825	3
75-28-5	Isobutane	11.682	-158.15828	-157.72898	4
7580-67-8	Lithium hydride	7.930	-8.05638	-7.76494	0
7664-41-7	Ammonia	10.853	-56.47585	-56.07701	1
7727-37-9	Nitrogen	15.541	-109.37721	-108.80609	2
7732-18-5	Water	12.611	-76.33668	-75.87322	1
7782-41-4	Fluorine	15.461	-199.30086	-198.73268	2
7783-60-0	Sulfur tetrafluoride	12.624	-796.63971	-796.17578	9
7803-62-5	Silane	12.703	-291.43474	-290.96793	5
91-20-3	Naphthalene	8.042	-385.15892	-384.86337	10
92-24-0	Naphthalene	6.434	-691.83764	-691.60118	18

Table 5. Vertical ionisation energies (VIEs, in eV) of the GW100 test set as obtained at the $\Delta\text{CCSD(T)/def2-TZVPP}$ level. The CCSD(T)/def2-TZVPP energies of the neutral molecules and their cations are given in E_h . The last column gives the number of doubly occupied core orbitals, which are excluded from the correlation treatment.

CAS Nr.	Compound	VIE	Neutral	Cation	Core
10028-15-6	Ozone	12.547	-225.13195	-224.67084	3
100-41-4	Ethylbenzene	8.852	-310.29199	-309.96669	8
10043-11-5	Boron nitride	11.890	-79.25773	-78.82078	2
106-97-8	Butane	11.567	-158.15571	-157.73064	4
108-88-3	Toluene	8.899	-271.04816	-270.72115	7
108-95-2	Phenol	8.702	-306.93323	-306.61345	7
110-86-1	Pyridine	9.659	-247.83460	-247.47964	6
12184-80-4	Tetracarbon	11.260	-151.78993	-151.37614	4
12184-83-7	Cesium dimer	3.642	-40.03729	-39.90347	0
12185-09-0	Phosphorus dimer	10.468	-681.79533	-681.41064	10
12187-06-3	Silver dimer	7.494	-293.45658	-293.18118	2
12190-70-4	Copper dimer	7.566	-3278.78349	-3278.50546	18
124-38-9	Carbon dioxide	13.711	-188.33389	-187.83000	3
1304-56-9	Beryllium oxide	9.944	-89.74210	-89.37668	2
1309-48-4	Magnesium oxide	7.487	-274.82075	-274.54559	3
13283-31-3	Borane	13.276	-26.53831	-26.05041	1
1333-74-0	Hydrogen	16.403	-1.17234	-0.56954	0
13768-60-0	Boron fluoride	11.086	-124.50565	-124.09823	2
14452-59-6	Lithium dimer	5.266	-14.97173	-14.77820	0
14868-53-2	Pentasilane	9.273	-1452.46227	-1452.12151	25
1590-87-0	Disilane	10.645	-581.69013	-581.29894	10
1603-84-5	Carbonyl selenide	10.785	-510.90583	-510.50949	7
17108-85-9	Gallium monochloride	9.771	-2383.25081	-2382.89173	14
17739-47-8	Phosphorus mononitride	11.735	-395.54205	-395.11080	6
19287-45-7	Diborane	12.263	-53.14413	-52.69348	2
23878-46-8	Arsenic dimer	9.781	-4468.93504	-4468.57560	18
25681-79-2	Disodium	4.952	-324.07268	-323.89072	2
25681-80-5	Dipotassium	4.061	-1198.66996	-1198.52072	10
25681-81-6	Dirubidium	3.925	-47.83576	-47.69153	0
302-01-2	Hydrazine	9.720	-111.69757	-111.34037	2
392-56-3	Hexafluorobenzene	9.930	-826.57654	-826.21162	12
39297-86-4	Sodium tetramer	4.225	-648.16043	-648.00516	4
39297-88-6	Sodium hexamer	4.351	-972.26391	-972.10400	6
463-58-1	Carbonyl sulfide	11.173	-510.91854	-510.50795	7
50-00-0	Formaldehyde	10.840	-114.33754	-113.93918	2
507-25-5	Tetraiodomethane	9.266	-1226.56328	-1226.22278	17
542-92-7	1,3-Cyclopentadiene	8.675	-193.73778	-193.41896	5
544-92-3	Copper cyanide	10.854	-1732.08572	-1731.68684	11
558-13-4	Carbon tetrabromide	10.463	-10328.40258	-10328.01807	57
56-23-5	Carbon tetrachloride	11.558	-1876.91391	-1876.48915	21
57-13-6	Urea	10.053	-224.94394	-224.57448	4
593-60-2	Vinyl bromide	9.269	-2650.39277	-2650.05215	16
593-66-8	Iodoethene	9.327	-374.98027	-374.63750	6
60-29-7	Ethyl ether	9.816	-233.27152	-232.91080	5
62-53-3	Aniline	7.993	-287.08460	-286.79087	7
629-20-9	1,3,5,7-Cyclooctatetraene	8.348	-309.00373	-308.69694	8
630-08-0	Carbon monoxide	14.209	-113.12514	-112.60296	2
64-17-5	Ethanol	10.685	-154.79842	-154.40577	3
64-18-6	Formic acid	11.421	-189.50876	-189.08905	3
65-71-4	Thymine	9.081	-453.43230	-453.09859	9
66-22-8	Uracil	10.125	-414.18628	-413.81420	8
67-56-1	Methyl alcohol	11.042	-115.55511	-115.14933	2
71-30-7	Cytosine	9.512	-394.30944	-393.95987	8
71-43-2	Benzene	9.292	-231.80652	-231.46506	6
73-24-5	Adenine	8.330	-466.55772	-466.25159	10
73-40-5	Guanine	8.034	-541.70369	-541.40846	11
7439-90-9	Krypton	13.940	-2752.19658	-2751.68430	14

(continued)

Table 5. (Continued).

CAS Nr.	Compound	VIE	Neutral	Cation	Core
7440-01-9	Neon	21.321	-128.80982	-128.02628	1
7440-37-1	Argon	15.544	-527.03513	-526.46390	5
7440-59-7	Helium	24.512	-2.89895	-1.99814	0
7446-09-5	Sulfur dioxide	13.486	-547.98422	-547.48862	7
74-82-8	Methane	14.373	-40.43858	-39.91037	1
74-84-0	Ethane	13.040	-79.67544	-79.19621	2
74-85-1	Ethylene	10.666	-78.44008	-78.04809	2
74-86-2	Acetylene	11.424	-77.18900	-76.76920	2
74-90-8	Hydrogen cyanide	13.869	-93.27764	-92.76794	2
74-98-6	Propane	12.048	-118.91548	-118.47272	3
75-01-4	Chloroethene	10.093	-537.56943	-537.19851	7
75-02-5	Fluoroethene	10.554	-177.57694	-177.18908	3
75-07-0	Acetaldehyde	10.207	-153.58887	-153.21376	3
75-15-0	Carbon disulfide	9.981	-833.50059	-833.13380	11
75-19-4	Cyclopropane	10.865	-117.67189	-117.27259	3
7553-56-2	Iodine	9.509	-594.29002	-593.94057	8
75-73-0	Tetrafluoromethane	16.301	-437.01919	-436.42014	5
7580-67-8	Lithium hydride	7.961	-8.05642	-7.76385	0
7647-01-0	Hydrogen chloride	12.593	-460.33126	-459.86847	5
7647-14-5	Sodium chloride	9.027	-621.83437	-621.50262	6
7664-39-3	Hydrogen fluoride	16.026	-100.34453	-99.75561	1
7664-41-7	Ammonia	10.807	-56.47596	-56.07881	1
7693-26-7	Potassium hydride	6.128	-599.88776	-599.66257	5
7722-84-1	Hydrogen peroxide	11.586	-151.36359	-150.93779	2
7726-95-6	Bromine	10.536	-5145.18622	-5144.79903	28
7727-37-9	Nitrogen	15.569	-109.37735	-108.80519	2
7732-18-5	Water	12.565	-76.33702	-75.87525	1
7758-02-3	Potassium bromide	8.127	-3172.02123	-3171.72257	19
7782-41-4	Fluorine	15.708	-199.30396	-198.72668	2
7782-50-5	Chlorine	11.412	-919.41359	-918.99420	10
7782-65-2	Germanium tetrahydride	12.497	-2077.98648	-2077.52724	9
7782-79-8	Hydrogen azide	10.676	-164.54382	-164.15149	3
7783-06-4	Hydrogen sulfide	10.310	-398.93112	-398.55222	5
7783-40-6	Magnesium fluoride	13.710	-399.39822	-398.89440	4
7783-60-0	Sulfur tetrafluoride	12.588	-796.64012	-796.17751	9
7783-63-3	Titanium tetrafluoride	15.476	-1248.10343	-1247.53471	9
7784-18-1	Aluminum fluoride	15.457	-541.46294	-540.89491	8
7784-23-8	Aluminum iodide	9.815	-1133.60602	-1133.24532	17
7784-42-1	Arsine	10.398	-2236.24568	-2235.86357	9
7786-30-3	Magnesium chloride	11.665	-1119.38891	-1118.96022	12
7789-24-4	Lithium fluoride	11.321	-107.30084	-106.88480	1
7803-51-2	Phosphine	10.523	-342.68938	-342.30265	5
7803-62-5	Silane	12.796	-291.43566	-290.96540	5

variations with the functional than the G_0W_0 QP energies. The latter are not much dependent on the underlying exchange–correlation functional. The x_α - G_0W_0 , tda- G_0W_0 and rpa- G_0W_0 QP energies are all very similar, not only for the HOMO energy but also for the other QP-energy levels.

Table 4 displays the CCSD(T) total energies of the neutral and cationic molecules of the GW27 test set, which was used in Ref. [7] in 2013. The geometries of these molecules are given in the supplemental data to Ref. [7], and the molecules are identified by their Chemical-Abstracts-Service Registry Number (CAS Nr.). The compounds’ names are those used in the NIST Chemistry WebBook [34]. The VIEs were computed as CCSD(T) energy differences; that is, as differences between the coupled-cluster

energies of the cationic and neutral systems,

$$\Delta\text{CCSD(T)} = \text{CCSD(T)}_{\text{cationic}} - \text{CCSD(T)}_{\text{neutral}}. \quad (16)$$

Note that some molecules (e.g., benzene) occur not only in the GW27 but also in the GW100 test set. Due to small differences in the geometries, their VIE reference values differ. Instabilities occurred for one-third of the neutral, closed-shell systems of Table 4 when computed at the restricted Hartree–Fock level; for example, for the aromatic molecules benzene, anthracene, naphthalene, and naphthacene (tetracene). Accordingly, the unrestricted CCSD(T)/def2-TZVPP computation on the neutral

Table 6. Mean signed difference (MSD), mean absolute error (MAE), root-mean-square error (RMSE) and maximum error (and corresponding system) of the GW27 test set with respect to the Δ CCSD(T)/def2-TZVPP vertical ionisation energies (all data in eV).

Method	α	MSD	MAE	RMSE	Maximum error	
OPTX		-4.75	4.75	4.96	7.58	7782-41-4
OPTX x_α -G ₀ W ₀	0.907	-0.17	0.50	0.59	1.36	7782-41-4
OPTX rpa-G ₀ W ₀		-0.58	0.58	0.64	1.47	7580-67-8
PBE		-3.84	3.84	4.08	6.49	7782-41-4
PBE x_α -G ₀ W ₀	0.726	-0.07	0.35	0.46	1.22	1333-74-0
PBE rpa-G ₀ W ₀		-0.46	0.46	0.52	0.92	7580-67-8
PBE0		-2.58	2.58	2.73	4.36	1333-74-0
PBE0 x_α -G ₀ W ₀	0.643	-0.08	0.38	0.46	1.20	1333-74-0
PBE0 rpa-G ₀ W ₀		-0.22	0.22	0.25	0.55	74-84-0

Table 7. Mean signed difference (MSD), mean absolute error (MAE), root-mean-square error (RMSE) and maximum error (and corresponding system) of the GW100 test set with respect to the Δ CCSD(T)/def2-TZVPP vertical ionisation energies (all data in eV).

Method	α	MSD	MAE	RMSE	Maximum error	
OPTX		-4.95	4.95	5.12	9.72	7440-59-7
OPTX x_α -G ₀ W ₀	0.885	-0.18	0.63	0.73	1.61	7783-63-3
OPTX rpa-G ₀ W ₀		-0.71	0.71	0.80	1.94	7446-09-5
PBE		-4.01	4.01	4.20	8.88	7440-59-7
PBE x_α -G ₀ W ₀	0.703	-0.09	0.45	0.59	1.72	1309-48-4
PBE rpa-G ₀ W ₀		-0.58	0.59	0.66	1.81	7446-09-5
PBE0		-2.67	2.67	2.80	6.38	7440-59-7
PBE0 x_α -G ₀ W ₀	0.622	-0.08	0.39	0.51	1.57	7440-59-7
PBE0 rpa-G ₀ W ₀		-0.30	0.30	0.37	1.45	7446-09-5

naphthacene molecule represented, technically, the most challenging computation of the present work.

Table 5 displays the total CCSD(T) energies of the neutral and cationic molecules of the GW100 test set. The geometries of these molecules are given in the present article's supplemental content. About 25% of the neutral, closed-shell systems in this test set exhibit instabilities when computed at the restricted Hartree–Fock level. Because the cationic systems are treated at the unrestricted Hartree–Fock level anyway, we feel that it is important to also compute the unstable neutral systems at the same level of theory to obtain balanced results.

Tables 6 and 7 show statistical data obtained from the assessment of various G₀W₀ methods. We report the mean signed differences (MSDs), mean absolute errors (MAEs) and root-mean-square errors (RMSEs) with respect to comparisons with the GW27 (Table 6) and GW100 (Table 7) test sets. The computed G₀W₀ VIEs are displayed graphically on Figures 1–3 for the exchange–correlation functionals OPTX, PBE and PBE0, respectively. Clearly, the VIEs from G₀W₀ QP energies represent significant improvements over the plain Kohn–Sham HOMO eigenvalues. The latter show RMSEs of about 3–5 eV, whereas the G₀W₀ results are accurate to within 0.25–0.80 eV (RMSEs). The results become more and more accurate when going from OPTX, PBE, to PBE0. For the GW100 test set, the RMSEs are 0.80, 0.66

and 0.37 eV, respectively, for the full rpa-G₀W₀ approach. This observation is reflected in Figures 1–3. With respect to the x_α -G₀W₀ approach, we observe that the optimised (by linear least-squares fitting) parameter α is rather different for the three exchange–correlation functionals studied. It

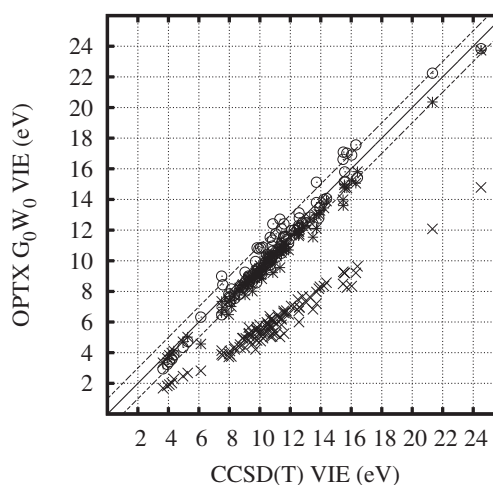


Figure 1. Vertical ionisation energies (VIEs) of the GW100 test set computed using the OPTX functional. Results are plotted for the OPTX (x), OPTX x_α -G₀W₀ (o, $\alpha = 0.885$) and OPTX rpa-G₀W₀ (*) methods against the CCSD(T) reference values.

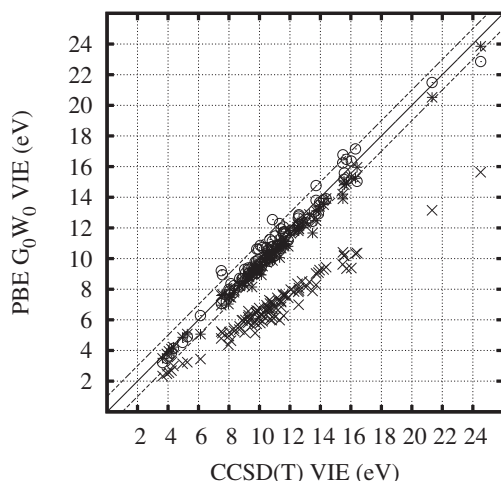


Figure 2. Vertical ionisation energies (VIEs) of the GW100 test set computed using the PBE functional. Results are plotted for the PBE (\times), PBE x_α - G_0W_0 (\circ , $\alpha = 0.703$) and OPTX rpa- G_0W_0 ($*$) methods against the CCSD(T) reference values.

amounts to about 0.9, 0.7 and 0.6 for the functionals OPTX, PBE and PBE0, respectively. It seems that this parameter is smaller for functionals whose Kohn–Sham HOMO eigenvalues are already close to the VIE reference values than for functionals with larger Kohn–Sham errors. After optimising the parameter α , the statistical data for the x_α - G_0W_0 method are not significantly different from the full rpa- G_0W_0 approach. Computationally, the x_α - G_0W_0 method is of course much less demanding, since neither excitation energies ω_{ai} nor transition densities ρ_{ai} are required to be computed in this method.

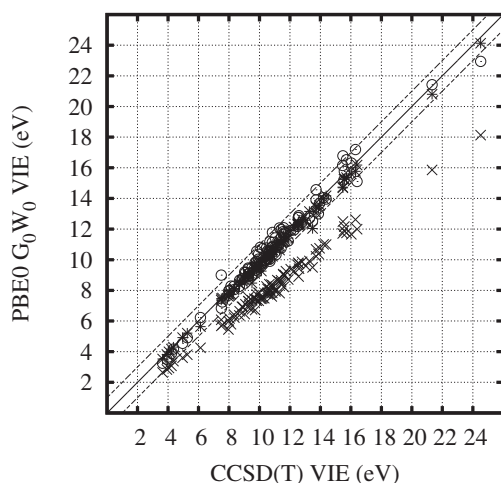


Figure 3. Vertical ionisation energies (VIEs) of the GW100 test set computed using the PBE0 functional. Results are plotted for the PBE0 (\times), PBE0 x_α - G_0W_0 (\circ , $\alpha = 0.622$) and PBE0 rpa- G_0W_0 ($*$) methods against the CCSD(T) reference values.

5. Concluding remarks

In the present article, we have reported CCSD(T) reference values for the VIEs of two test sets with 27 and 100 molecules, respectively. These reference values allow for the assessment of advanced GW methods that aim at the computation of accurate QP energies of molecular systems. It is recommended that such assessments are carried out using exactly the same geometries, basis sets and pseudopotentials as in the present work. The reference values, for example, allow for testing various approximations to the full, RPA-based G_0W_0 approach, for example, by taking into account only the exchange contributions (x_α - G_0W_0). We conclude this article by expressing the hope that our CCSD(T) reference values will be useful for many researchers in the field.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed at <http://dx.doi.org/10.1080/00268976.2015.1025113>

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References

- [1] D.J. Tozer and N.C. Handy, *Mol. Phys.* **101**, 2669 (2003).
- [2] D.J. Tozer and N.C. Handy, *J. Chem. Phys.* **109**, 10180 (1998).
- [3] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, *Phys. Rev. Lett.* **49**, 1691 (1982).
- [4] X. Blase, C. Attaccalite, and V. Olevano, *Phys. Rev. B* **83**, 115103 (2011).
- [5] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, and M. Scheffler, *New J. Phys.* **14**, 053020 (2012).
- [6] F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, *Phys. Rev. B* **88**, 075105 (2013).
- [7] M.J. van Setten, F. Weigend, and F. Evers, *J. Chem. Theory Comput.* **9**, 232 (2013).
- [8] C. Faber, P. Boulanger, C. Attaccalite, I. Duchemin, and X. Blase, *Phil. Trans. R. Soc. A* **372**, 20130271 (2014).

- [9] S. Körbel, P. Boulanger, I. Duchemin, X. Blase, M.A.L. Marques, and S. Botti, *J. Chem. Theory Comput.* **10**, 3934 (2014).
- [10] P. Koval, D. Foerster, and D. Sánchez-Portal, *Phys. Rev. B* **89**, 155417 (2014).
- [11] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, and F. Weigend, *WIREs Comput. Mol. Sci.* **4**, 941 (2014).
- [12] Turbomole V6.6 (including GW version 101014), a development of Universität Karlsruhe (TH) and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007. <http://www.turbomole.com>.
- [13] M.J. van Setten (private communication).
- [14] K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- [15] N.C. Handy and A.J. Cohen, *Mol. Phys.* **99**, 403 (2001).
- [16] W.-M. Hoes, A.J. Cohen, and N.C. Handy, *Chem. Phys. Lett.* **341**, 319 (2001).
- [17] N.C. Handy, *Mol. Phys.* **107**, 721 (2009).
- [18] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [19] J.P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).
- [20] M. Ernzerhof and G.E. Scuseria, *J. Chem. Phys.* **110**, 5029 (1999).
- [21] C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999).
- [22] W. Klopper, A.M. Teale, S. Coriani, T.B. Pedersen, and T. Helgaker, *Chem. Phys. Lett.* **510**, 147 (2011).
- [23] CFOUR, Coupled-cluster techniques for Computational Chemistry, a quantum-chemical program package by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay, with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, L.A. Mück, D.P. O'Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A.V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
- [24] M.E. Harding, T. Metzroth, J. Gauss, and A.A. Auer, *J. Chem. Theory Comput.* **4**, 64 (2008).
- [25] C. Hättig, A. Hellweg, and A. Köhn, *Phys. Chem. Chem. Phys.* **8**, 1159 (2006).
- [26] C. van Wüllen, *J. Comput. Chem.* **32**, 1195 (2011).
- [27] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [28] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, and H. Preuß, *Theor. Chim. Acta* **77**, 123 (1990).
- [29] K.A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, *J. Chem. Phys.* **119**, 11113 (2003).
- [30] T. Leininger, A. Nicklass, W. Küchle, H. Stoll, M. Dolg, and A. Bergner, *Chem. Phys. Lett.* **225**, 274 (1996).
- [31] U. Ekström, L. Visscher, R. Bast, A.J. Thorvaldsen, and K. Ruud, *J. Chem. Theory Comput.* **6**, 1971 (2010).
- [32] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, *Chem. Phys. Lett.* **294**, 143 (1998).
- [33] A. Hellweg, C. Hättig, S. Höfener, and W. Klopper, *Theor. Chem. Acc.* **117**, 587 (2007).
- [34] P.J. Linstrom and W.G. Mallard, editors, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (National Institute of Standards and Technology, Gaithersburg, MD, 20899), see: <http://webbook.nist.gov>.