

Assessing GW Approaches for Predicting Core Level Binding Energies

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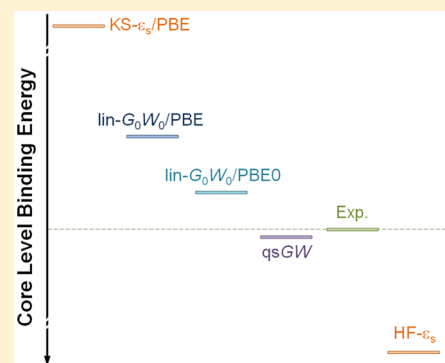
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S Supporting Information

ABSTRACT: Here we present a systematic study on the performance of different GW approaches: G_0W_0 , G_0W_0 with linearized quasiparticle equation (lin- G_0W_0), and quasiparticle self-consistent GW (qsGW), in predicting core level binding energies (CLBEs) on a series of representative molecules comparing to Kohn–Sham (KS) orbital energy-based results. KS orbital energies obtained using the PBE functional are 20–30 eV lower in energy than experimental values obtained from X-ray photoemission spectroscopy (XPS), showing that any Koopmans-like interpretation of KS core level orbitals fails dramatically. Results from qsGW lead to CLBEs that are closer to experimental values from XPS, yet too large. For the qsGW method, the mean absolute error is about 2 eV, an order of magnitude better than plain KS PBE orbital energies and quite close to predictions from Δ SCF calculations with the same functional, which are accurate within ~ 1 eV. Smaller errors of ~ 0.6 eV are found for qsGW CLBE shifts, again similar to those obtained using Δ SCF PBE. The computationally more affordable G_0W_0 approximation leads to results less accurate than qsGW, with an error of ~ 9 eV for CLBEs and ~ 0.9 eV for their shifts. Interestingly, starting G_0W_0 from PBE0 reduces this error to ~ 4 eV with a slight improvement on the shifts as well (~ 0.4 eV). The validity of the G_0W_0 results is however questionable since only linearized quasiparticle equation results can be obtained. The present results pave the way to estimate CLBEs in periodic systems where Δ SCF calculations are not straightforward although further improvement is clearly needed.



INTRODUCTION

Core level binding energies (CLBEs), experimentally accessible through X-ray photoelectron spectroscopy (XPS),¹ provide direct insight into the elemental chemistry of molecules, nanostructures, and solid materials. They contain information about the chemical environment, oxidation state, hybridization, and coordination of a given type of atom in a given sample.^{2,3} XPS applied to solid samples is, in addition, surface sensitive, and hence, XPS is broadly used in surface science and catalysis. However, the assignment of XPS features is not always straightforward, and assistance from theoretical calculations becomes necessary as recognized in several reviews.^{2,4} For instance, XPS of atomic O on Al(111) exhibit two well-defined peaks that one would naively assign to O above and below the surface. However, theoretical analysis reveals that this hypothesis is not consistent with results from ab initio cluster model calculations, and these offer indeed an alternative explanation.^{5,6}

The landmark paper of Bagus⁷ on the application of the Hartree–Fock (HF) method applied to core level energy determination the variational determination of CLBE as a difference of the total energy between the molecule’s ground

state and the cation with a core hole. The resulting procedure is generally known as Δ SCF since it implies the difference of two self-consistently determined energies. Because the involved energies are obtained from a variational calculation, it turns out that, for a given method used to obtain the total energy of atoms, molecules or solids, Δ SCF constitutes the best possible estimate of CLBEs. The use of Hartree–Fock to predict CLBEs has an additional advantage since the orbital energies (HF orbital energies or HF- ϵ_s) fulfill the Koopmans theorem,⁸ and hence, the core orbital energies provide an estimate of the so-called initial state effects, those already present in the neutral molecule. The difference between the CLBEs estimated from the HF orbital energy and the Δ SCF calculation is usually referred to as orbital relaxation energy and essentially contains the response of the electron density to the presence of the core hole, usually denoted as a final state effect.^{2,3} Note, however, that the distinction between initial and final state is usually applied to XPS main peaks only, i.e., excluding satellites and multiplets. Nevertheless, one has to point out that Hartree–

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Fock lacks electron correlation effects, which although modestly contributing to the CLBES would need to be considered. Electron correlation effects can be explicitly included through post-Hartree–Fock methods such as configuration interaction or coupled cluster, or implicitly through the exchange–correlation potential in density functional theory (DFT) based methods. The latter have the additional advantage of being *easily* implemented for periodic systems, which is very appealing when dealing with solid materials.

In practice, DFT-based methods rely on the Kohn–Sham implementation, a formalism closely resembling Hartree–Fock to the point that upon solving the so-called Kohn–Sham equations one obtains a set of single particle orbitals (KS orbitals) and energies (KS orbital energies or $\text{KS-}\epsilon_s$). However, there are important differences between HF- ϵ_s and KS- ϵ_s since the latter do not fulfill the Koopmans’ theorem, and in the case of core states, the numerical values are smaller than the experimental CLBES. Although not rigorously supported from theory, it has been claimed that conceptually HF and KS orbitals are similar.^{9,10} From this perspective, taking the KS- ϵ_s as a measure of initial state CLBES will lead to an unphysical positive orbital relaxation energy.^{11,12} The alternative view to interpret KS orbitals as an approximation to Dyson orbitals,^{13,14} which as such would contain orbital relaxation, hence seems more physical. This point of view is developed in detail in the review papers by Ortiz¹⁵ and by Ortiz and Öhrn.¹⁶

Yet, KS- ϵ_s become very useful when aiming at analyzing CLBE shifts (ΔCLBE), that is, the difference between CLBES for a given element in the system of interest and a reference value.⁸ For the 1s core level of carbon atoms, for instance, the energy ranges from 290 to about 300 eV. To distinguish between carbon atoms in similar surroundings, however, an accuracy of the order of 0.1 eV is often needed. Accurate predictions of CLBES by means of DFT methods are well possible within a ΔSCF formalism, and recent work shows that depending on the functional used the calculated values are of a quality similar or superior to those predicted by Hartree–Fock.^{17,18} However, apart from the inconvenient dependence on the choice of the functional, it is necessary to point out that ΔSCF in periodic systems is problematic since it involves the use of charged unit cells yet different, more or less accurate, ways to counteract this have been proposed. These range from the use of a uniform negative background that may distort the electron density, to various pseudopotential-based approaches,¹⁹ among which a common choice is to make use of a pseudopotential extracted from a core ionized atom²⁰ with concomitant limitations due to constraints in the extent of core electron density relaxation. Recent work shows that these procedures are useful on determining ΔCLBE s but, unfortunately, fail to predict accurate absolute values of CLBES.²¹

A possible way to overcome the difficulties arising from the use of DFT methods to approach CLBES in periodic systems is to make use of the *GW* formulation, earlier introduced by Hedin.²² The *GW* method includes many body effects beyond the mean-field description of the electron–electron interaction in DFT via the so-called self-energy, which is nonlocal and energy dependent and, in a sense, replaces the exchange correlation potential in DFT.^{23,24} Reviewing the *GW* formalism here is beyond the scope of this article, and the interested reader is addressed to the excellent review of Aryasetiawan and Gunnarsson for detailed information.²⁵ All available practical implementations of *GW* have a common feature, the need for large computational resources. This has led to different levels of

approximations resulting in various flavors denoted as G_0W_0 , GW_0 , eigenvalue self-consistent *GW*, or quasiparticle self-consistent *GW*.²⁶ All these approximations convert the KS particles into quasi-particles (qp) with a well-defined physical meaning. In the case of occupied states, the qp energies effectively represent ionization potentials, whereas in the case of unoccupied states they represent electron affinities. In the case of periodic insulators and semiconductors, qp from *GW* calculations provide an accurate estimate of the fundamental band gap of these materials^{27,28} and also of states associated with point defects such as F-centers in simple oxides.^{29,30} Apart from the high computational cost of the *GW* calculations, one must also point out the dependence of the results with respect to the starting density,³¹ when the results are not obtained from a fully self-consistent approach as is the case in G_0W_0 , lowest level of this theoretical framework. In particular, it has been suggested that hybrid functionals should provide a better starting point.³²

The *GW* method has also been applied to molecular systems and small clusters.^{33–42} In particular, the G_0W_0 level has been applied to 100 molecules (the *GW100* database)⁴³ with excellent performance for the vertical ionization potential; the same database has more recently been used to benchmark different implementations and levels of self-consistency of the theory.^{44,45} The rather good success of *GW* in predicting the ionization potential of molecular systems strongly suggest that it may as well provide an estimate of the CLBES in molecules and solids where, as above commented, ΔSCF calculations are cumbersome. The calculation of CLBES obviously requires the presence of actual core levels in the calculation. Note, however, that many solid-state codes use pseudopotentials with a frozen core approximation. These make the direct calculation of CLBES impossible although different approximations have been proposed to predict ΔCLBE s.¹⁴ Moreover, one must point out that *GW* calculations for core levels may be very tricky since describing the self-energy at deep energies requires a full frequency method and solving the quasiparticle equation can be very complicated as discussed later on. The goal of the present work is precisely to investigate the performance of *GW* on predicting CLBES using a series of simple molecules, where experimental data and ΔSCF results for several exchange–correlation functionals are available, as a convenient benchmark.

■ COMPUTATIONAL DETAILS

The ground-state calculations are based on density functional theory within the Perdew–Burke–Ernzerhof (PBE)⁴⁶ generalized-gradient approximation (GGA) for the exchange–correlation functional. The molecular data set has been taken from previous work.¹⁷ The molecular structures have been fully relaxed using the PBE functional and a tight Tier 2 numerical atom-centered orbitals (NAO) basis set^{47–49} using the FHI-AIMS code.⁴⁷ The quasiparticle calculations are performed with the Turbomole package using the def2-TZVP and def2-QZVP Gaussian basis sets⁵⁰ and extrapolated to the complete basis-set limit.⁵¹ In addition to electron correlation, relativistic effects also play a role in determining the final value of calculated CLBES.^{2,12,17} Within the *GW* method, these can be introduced through various formalisms.^{52,53} Nevertheless, for sake of comparison, relativistic effects have been omitted. We note, however, that the relativistic contribution to the CLBES is essentially atomic in nature, and it increases with the atomic number. For the core levels studied in the present work,

Table 1. Core Level Energies as Obtained from KS, $\text{lin-}G_0W_0@PBE$, $\text{lin-}G_0W_0@PBE0$, and Quasiparticle Self-Consistent (qsGW) Methods Starting from PBE^a

Core level	Molecule	KS	$\text{lin-}G_0W_0@PBE$	$\text{lin-}G_0W_0@PBE0$	qsGW	Experiment
C(1s)	CH ₄	-268.83	-284.10	-287.82	-293.54	290.90
	CF ₄	-277.89	-292.18	-299.39	-302.84	301.80
	CO ₂	-273.69	-287.48	-294.40	-298.78	297.91
	HCN	-270.41	-286.13	-290.45	-294.67	293.50
	H ₃ COCH ₃	-269.96	-284.99	-289.14	-294.13	292.30
	H ₃ COH	-269.96	-286.15	-291.14	-294.69	292.30
	Pyrrrole	-268.87	-282.88	-286.78	-293.02	290.80
O(1s)	H ₂ O	-510.09	-529.45	-534.90	-542.13	539.70
	CO ₂	-512.42	-530.41	-536.28	-542.46	541.30
	H ₃ COH	-510.13	-528.72	-534.28	-541.12	538.90
	H ₃ COCH ₃	-510.35	-528.15	-533.24	-540.77	539.03
N(1s)	NH ₃	-379.82	-397.04	-401.75	-407.84	405.60
	HCN	-381.18	-397.38	-402.21	-408.78	406.80
	Pyridine	-380.51	-395.24	-400.66	-407.4 ^b	404.90
	Pyrrrole	-381.74	-397.10	-402.31	-408.11	406.10
F(1s)	CF ₄	-661.79	-683.19	-689.26	-696.15	692.40

^aAll values correspond to a linear extrapolation of the def2-TZVP and def2-QZVP results to the complete basis set limit. Experimental values (positive as they correspond to ionization processes) are provided for comparison. ^bdef2-TZVP value; see text.

contribution of relativistic effects to the CLBE vary from 0.13 eV for C to 0.75 eV for F,¹⁷ increasing along the C–F series.

Different levels of GW calculations have been carried out including the so-called one shot G_0W_0 approach, where both the Green's function G and the screened Coulomb potential W are obtained only once from an initial electron density arising from a given density functional approach and the quasiparticle self-consistent GW (qsGW), where both G and W are iterated until self-consistency is achieved. We investigated the residual starting point dependence of qsGW for NH₃, NCH and CO₂ and observe that the final qsGW results depend almost two orders of magnitude less on the starting exchange-correlation functional than the G_0W_0 results. This reduction of starting point dependence is similar to that observed for valence levels. However, due to the smaller absolute values of the valence levels and the already smaller difference between the G_0W_0 results, the remaining starting point dependence becomes smaller than the numerical precision. It is also noted that the remaining starting point dependence in qsGW is smaller than the basis set extrapolation. Consequently, qsGW results are taken here as benchmark.^{54,55} Note also that two different implementations of the simpler G_0W_0 level are used. Nevertheless, both the G_0W_0 and qsGW approaches use the full analytic expression of the self-energy from the reducible response function. Both sets of the results are hence obtained from a full frequency method. The difference in the two G_0W_0 approaches used lies only in how the quasiparticle equation is solved. In one case, the quasiparticle equation is iteratively solved; in the other, denoted as $\text{lin-}G_0W_0$, the quasiparticle equation is linearized. For the HOMO level, the linearized and solved version often give very similar results. For core levels, this is not the case. Due to the much larger corrections for core levels, in all molecules studied here, the $G_0W_0@PBE$ self-energy has poles in the region where the quasiparticle equation (QPE) needs to be solved to resolve the core-levels. A unique solution hence becomes impossible. The final G_0W_0 results reported in this work are all obtained from the linearized version, which

circumvents this problem. Besides the PBE functional, we also report $\text{lin-}G_0W_0$ starting from PBE0. For the PBE0 starting point, the solving the QPE is also not uniquely possible. Only for a HF starting point does this becomes feasible (Supporting Information). For a complete description of the GW implementations including the two G_0W_0 approaches mentioned above, the reader is referred to the original work on the implementation of GW in Turbomole⁵⁶ reporting also the result for valence ionization potentials of a broad set of molecules for G_0W_0 , and in Kaplan et al. for qsGW.⁵⁷

RESULTS AND DISCUSSION

The set of molecules used to assess the reliability of the different methods considered here consists of CH₄, CF₄, CO₂, HCN, H₃COCH₃, H₃COH, H₂O, NH₃, pyridine, and pyrrole. The calculations are carried out for the C, N, O, and F 1s core levels for which experimental data is available. For reproducibility, all molecular geometries are reported in Table S1 of the Supporting Information. In addition, Table S2 reports the PBE total energy at the optimized geometry corresponding to the tight Tier 2 NAO basis set. To provide insight into the quality of this basis set, Table S2 also reports the PBE total energy, at the same geometry, obtained with Gaussian type orbital (GTO) basis sets of aug-cc-pCVTZ and aug-cc-pCVSZ level of quality,^{58,59} computed using Gaussian 09.⁶⁰ Inspection of Table S2 clearly shows that the tight Tier 2 NAO basis set quality is even higher than that of aug-cc-pCVTZ and only slightly below aug-cc-pCVSZ.

Table 1 collects the CLBEs for the whole set of molecules as obtained from the different levels of theory together with experimental values taken from the literature.^{61,62} Nevertheless, one must admit that with the current implementation, fully analytic frequency treatment, and only a shared memory parallelism in the response routines of TURBOMOLE the calculation for pyridine using the def2-QZVP basis set is not feasible, and the corresponding extrapolated result could not be obtained. Here, the def2-TZVP value is listed instead. A quick

inspection of Table 1 shows that, on average, going from KS to lin-G_0W_0 to qsGW, the calculated results are progressively approaching the experiment with best results attained for the qsGW method. A deeper insight into the relative errors is provided in Table 2 showing that the error for each core level is

Table 2. Mean Absolute Error (MAE) for Core Level Binding Energies Reported in Table 1 and Obtained from KS, lin-G_0W_0 @PBE, lin-G_0W_0 @PBE0, and Quasiparticle Self-Consistent (qsGW) Methods

Core level	MAE			
	KS	lin-G_0W_0 @PBE	lin-G_0W_0 @PBE0	qsGW
C(1s)	22.84	7.94	2.91	1.74
O(1s)	28.99	10.55	5.06	1.89
N(1s)	25.04	9.16	4.12	2.08
TOTAL	25.41	8.98	3.76	1.98

different with a mean absolute error (MAE) larger than 25 eV for the KS- ϵ_s estimates, about 3–9 eV for G_0W_0 , and slightly less than 2 eV at the highest qsGW level. These results illustrate that qsGW significantly improves the agreement with the experiment as compared to the KS eigenvalues, a result which is in line with previous findings concerning the first ionization potential (HOMO) in molecules.^{43,63} Nevertheless, the accuracy reached by qsGW may not be sufficient to properly interpret XPS experiments. The present results illustrate the difficulties of the GW methods on describing CLBEs. We stress that describing the self-energy at deep energies requires a full frequency method, which makes the calculations quite costly. Also, for CLBEs, G_0W_0 starting from the PBE functional faces fundamental problems since the self-energy has poles in the region where the quasiparticle equation is solved giving rise to a multitude of possible solutions. Besides the obvious numerical issues, this grossly complicates the physical interpretation. Using the linearized quasiparticle equation solves at least the numerical part of the problem: solutions become numerically stable and unique but accuracy remains poor. In practice, it is more suitable to predict the quasiparticle energies of valence

states.³⁰ Using a hybrid functional as starting point may remediate this deficiency as shown in valence states comparing to experiment³¹ and also to scGW calculations.⁶⁴ This is because the core levels are already deeper causing the poles of the self-energy to be deeper in energy as well. Alternatively, one can start from the HF density, but here, the lin-G_0W_0 leads to values which not surprisingly are overestimating. The advantage is that in this case the QPE can be solved because the original poles are further away and come up in energy during the self-consistency process. The average overestimation is however roughly 6 eV (Table S4), a significant improvement over HF- ϵ_s , again with the correct physical ingredients where final state effects are introduced by the many body terms of the GW approach but a deterioration with respect to G_0W_0 @PBE0. In the case of the qsGW, the poles move deeper as well, and in addition, the contribution of the off-diagonal terms of the self-energy matrix elements make it less sharply peaked.

For CLBEs calculated using the PBE functional and employing a Δ SCF approach, the MAE is of ~ 1 eV; this is larger than the 0.3–0.4 eV corresponding values for calculations at the Hartree–Fock level or using the meta-GGA TPSS functional.¹⁷ In this sense, the MAE of ~ 2 eV for the qsGW results is really remarkable and puts this method as a good choice to estimate CLBEs, especially in periodic solids. Here, one must point out that the qsGW result does not depend on the starting point; yet the fact that the accuracy reached is lower than Δ SCF with PBE0 or TPSS functionals¹⁷ indicates that higher order terms are likely to be needed in the expansion of the screened potential W and the self-energy.

Finally, it is also important to note that, in most practical cases, one is not interested in the absolute CLBEs but in their shifts with respect to a given reference (Δ CLBE). Taking CH_4 , H_2O , and NH_3 as references for the C(1s), O(1s), and N(1s), the values for the Δ CLBEs arising from KS- ϵ_s , lin-G_0W_0 @PBE, lin-G_0W_0 @PBE0, and qsGW are reported in Table 3 and the statistic analysis of errors in Table 4. The later shows that MAE values of 0.7, 0.9, 0.4, and 0.6 eV are found for KS- ϵ_s , lin-G_0W_0 @PBE, lin-G_0W_0 @PBE0, and qsGW, respectively. Note, however, that the experimental Δ CLBE values seldom exceed

Table 3. Δ CLBEs as Obtained from KS, lin-G_0W_0 @PBE, lin-G_0W_0 @PBE0, and Quasiparticle Self-Consistent (qsGW) Methods Starting from PBE, Using CH_4 , H_2O , and NH_3 as Reference for C(1s), O(1s), and N(1s) Core Levels^a

Core level	Molecule	KS	lin-G_0W_0 @PBE	lin-G_0W_0 @PBE0	qsGW	Experiment
C(1s)	CH_4	0.00	0.00	0.00	0.00	0.00
	CF_4	−9.06	−8.08	−11.57	−9.30	−10.90
	CO_2	−4.86	−3.38	−6.58	−5.24	−7.01
	HCN	−1.58	−2.03	−2.63	−1.13	−2.60
	H_3COCH_3	−1.13	−0.89	−1.32	−0.59	−1.40
	H_3COH	−1.13	−2.05	−3.32	−1.15	−1.40
	Pyrrrole	−0.04	1.22	1.04	0.52	0.10
O(1s)	H_2O	0.00	0.00	0.00	0.00	0.00
	CO_2	−2.33	−0.96	−1.38	−0.33	−1.60
	H_3COH	−0.04	0.73	0.62	1.01	0.80
	H_3COCH_3	−0.26	1.30	1.66	1.36	0.67
N(1s)	NH_3	0.00	0.00	0.00	0.00	0.00
	HCN	−1.36	−0.34	−0.46	−0.94	−1.20
	Pyridine	−0.69	1.80	1.09	—	0.70
	Pyrrrole	−1.92	−0.06	−0.56	−0.27	−0.50

^aAll values are given in eV.

Table 4. Mean Absolute Error (MAE), in eV, for Δ CLBEs Reported in Table 3 and Obtained from KS, $\text{lin-}G_0W_0$ @PBE, $\text{lin-}G_0W_0$ @PBE0, and Quasiparticle Self-Consistent (qsGW) Methods

Core level	MAE			
	KS	$\text{lin-}G_0W_0$ @PBE	$\text{lin-}G_0W_0$ @PBE0	qsGW
C(1s)	0.81	1.33	0.58	0.90
O(1s)	0.63	0.34	0.35	0.54
N(1s)	0.74	0.60	0.30	0.16
TOTAL	0.74	0.87	0.44	0.64

10 eV, which makes the relative errors still rather large. Another important feature emerges when comparing calculated and experimental Δ CLBE values. The histogram of mean absolute errors in Figure 1 shows that while the trends are well reproduced there is a significant dispersion with the best values corresponding to $\text{lin-}G_0W_0$ @PBE0 and qsGW respectively.

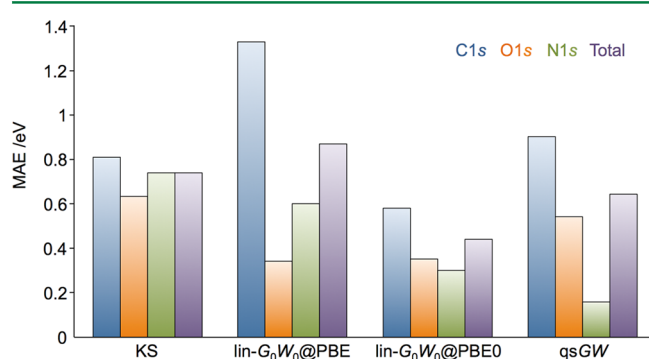


Figure 1. Histogram of the mean absolute error (MAE) for calculated KS, $\text{lin-}G_0W_0$ @PBE, $\text{lin-}G_0W_0$ @PBE0, and quasiparticle self-consistent (qsGW) relative to experimental core level binding energy shifts (Δ CLBE).

CONCLUSIONS

A study has been carried out to assess the performance of different GW approaches in predicting core level binding energies (CLBEs). Results presented for a series of representative molecules allows us to establish some first conclusions.

First, the present calculations agree with previous studies^{9,10} showing that the Kohn–Sham orbital energies cannot be taken as a measure of the CLBEs, and they do not represent an estimate of initial state effects. The Kohn–Sham orbital energies are always smaller than experimental CLBEs with differences with respect to experiment in the 20–30 eV range. Interpreting them as approximate initial states would hence imply unphysical positive relaxation energies. In the framework of DFT, initial state effects can be recovered by computing the molecular system with a core hole with the fixed electron density of neutral molecule as discussed in previous works¹⁰ and will not be further commented here. The interpretation of the KS-orbitals as approximate Dyson orbitals hence seems more physical especially for core levels.

The most accurate results, as compared to the experiment, are obtained at the quasiparticle self-consistent GW level (qsGW). Nevertheless, to achieve good agreement with the experiment, extrapolation to the complete basis set limit is needed, especially for the absolute CLBE although it may be

less problematic for the shifts. In any case, the rather good agreement with experiment evidences that GW is able to largely correct the failure of the KS and HF orbital energies covering a large part of relaxation energy, thus going in the direction of the right answer for the right reason.

We find that the qsGW calculated CLBEs are always larger than the experimental values, which is in agreement with an expected underscreening. The mean absolute error with respect to experiment is reduced to about 2 eV, 1 order of magnitude smaller than for KS values and close to predictions from variational Δ SCF calculations which, for the PBE functional, are in the 1 eV range. Here, it is important to point out that an absolute error of 2 eV on a quantity in the 300–500 eV range implies a percent error of 0.6% only, which is quite remarkable and, actually, even smaller than the percent error of 2% achieved when considering the qsGW prediction of the first ionization potential.⁴⁴ A somehow larger error (6.5%) is obtained in the case of $\text{lin-}G_0W_0$ @HF. Note also that adding contribution from relativistic effects will further decrease the Δ SCF error to less than 1 eV. Yet, the error bar of XPS, especially when synchrotron radiation is used, can be as small as 0.1 eV, meaning that further developments are needed. Smaller errors of roughly 0.6 eV are found for the qsGW calculated core level binding energy shifts (Δ CLBE) although these are surprisingly larger than those arising from Kohn–Sham orbital energies. This is an indication that qsGW effects on same core level in different molecules are not equally taken into account.

The simpler G_0W_0 and computationally more affordable level of the theory also leads to a significant overall improvement with respect to KS orbital energies. However, starting from the PBE density, the calculated CLBEs are still smaller than the experiment evidencing limitations inherent to this level of approximation as commented in the previous section. The absolute mean errors (8.98 and 3.76 eV for the PBE and PBE0 starting points, respectively) are significantly larger than the corresponding value for qsGW but smaller than the one arising from the direct use of KS orbital energies. A paired *t* test indeed proves that the differences are significant.

To summarize, CLBEs derived from GW approaches represent a considerable improvement with respect to KS energies although the accuracy reached with the present implementations, even for the qsGW, is still lower than the one obtained from Δ SCF calculations. The simpler G_0W_0 method applied on top of the PBE density also lead to results improved with respect to KS predictions but with too large errors. These errors are considerably reduced when starting the G_0W_0 calculations from a density obtained from a hybrid functional. Similar considerations apply to the core level binding energy shifts with rather satisfactory results for the $\text{lin-}G_0W_0$ @PBE0 and qsGW methods. For practical applications in computational materials science, G_0W_0 on top of single point PBE0 density at the PBE optimized structure may provide a practical approach since this will be computationally less demanding than going to the qsGW level and lead to similar accuracy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.7b01192.

Table S1: Cartesian coordinates of the molecules studied in the present work as optimized FHI-AIMS tight Tier 2 PBE. Table S2: Total PBE energy (eV) of the molecules

studied in the present work with geometries as in Table S1 and corresponding to numerical atomic orbital (NAO) tight Tier 2 basis set using the aims code and using the FHI-AIMS code and to the aug-cc-pCVTZ and aug-cc-pCV5Z Gaussian type orbitals (GTO) basis sets as obtained with the Gaussian09 code. Table S3: Total PBE energy (eV) of the molecules studied in the present work with geometries as in Table S1 as obtained with the def2-VPTZ GTO basis and different codes. Table S4: CLBEs as obtained from $\text{lin-}G_0W_0\text{@HF}$. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Barr, T. L. *The Principles and Practice of X-Ray Photoelectron Spectroscopy*; Taylor and Francis, London, 1994.
- (2) Bagus, P. S.; Ilton, E. S.; Nelin, C. J. The interpretation of XPS spectra: Insights into materials properties. *Surf. Sci. Rep.* **2013**, *68*, 273–304.
- (3) Bagus, P. S.; Illas, F.; Pacchioni, G.; Parmigiani, F. Mechanisms responsible for chemical shifts of core-level binding energies and their relationship to chemical bonding. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *100*, 215–236.
- (4) Egelhoff, W. F. Core-level binding-energy shifts at surfaces and in solids. *Surf. Sci. Rep.* **1987**, *6*, 253–415.
- (5) Bagus, P. S.; Parmigiani, F.; Polzonetti, G.; Illas, F.; Brundle, C. R. X-ray photoelectron spectroscopy of oxygen adsorbates on Al(111) Theory and experiment. *J. Vac. Sci. Technol., A* **1991**, *9*, 1747–1748.
- (6) Bagus, P. S.; Brundle, C. R.; Illas, F.; Parmigiani, F.; Polzonetti, G. Evidence for oxygen island formation on Al(111) Cluster model theory and X-ray photoelectron spectroscopy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *44*, 9025–9034.

(7) Bagus, P. S. Self-Consistent-Field Wave Functions for Hole States of Some Ne-Like and Ar-Like Ions. *Phys. Rev.* **1965**, *139*, 619–634.

(8) Koopmans, T. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen eines Atoms. *Physica* **1934**, *1*, 104–113.

(9) Baerends, E. J.; Gritsenko, O. V. A Quantum Chemical View of Density Functional Theory. *J. Phys. Chem. A* **1997**, *101*, 5383–5403.

(10) Stowasser, R.; Hoffmann, R. What Do the Kohn–Sham Orbitals and Eigenvalues Mean? *J. Am. Chem. Soc.* **1999**, *121*, 3414–3420.

(11) Pueyo Bellafont, N.; Illas, F.; Bagus, P. S. Validation of Koopmans' theorem for density functional theory binding energies. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4015–4019.

(12) Pueyo Bellafont, N.; Bagus, P. S.; Illas, F. Prediction of core level binding energies in density functional theory: Rigorous definition of initial and final state contributions and implications on the physical meaning of Kohn–Sham energies. *J. Chem. Phys.* **2015**, *142*, 214102.

(13) Duffy, P.; Chong, D. P.; Casida, M. E.; Salahub, D. R. Assessment of Kohn–Sham density-functional orbitals as approximate Dyson orbitals for the calculation of electron-momentum-spectroscopy scattering cross sections. *Phys. Rev. A: At., Mol., Opt. Phys.* **1994**, *50*, 4707–4728.

(14) Gritsenko, O. V.; Baerends, E. J. The analog of Koopmans' theorem in spin-density functional theory. *J. Chem. Phys.* **2002**, *117*, 9154–9159.

(15) Ortiz, J. V. Brueckner Orbitals, Dyson Orbitals, and Correlation Potentials. *Int. J. Quantum Chem.* **2004**, *100*, 1131–1135.

(16) Öhrn, Y.; Ortiz, J. V. The electron propagator. *Mol. Phys.* **2010**, *108*, 2871–2875 and references therein.

(17) Pueyo Bellafont, N.; Viñes, F.; Illas, F. Performance of the TPSS Functional on Predicting Core Level Binding Energies of Main Group Elements Containing Molecules: A Good Choice for Molecules Adsorbed on Metal Surfaces. *J. Chem. Theory Comput.* **2016**, *12*, 324–331.

(18) Pueyo Bellafont, N.; Álvarez Saiz, G.; Viñes, F.; Illas, F. Performance of Minnesota functionals on predicting core-level binding energies of molecules containing main-group elements. *Theor. Chem. Acc.* **2016**, *135*, 35–43.

(19) Pehlke, E.; Scheffler, M. Evidence for Site-Sensitive Screening of Core Holes at the Si and Ge (001). *Phys. Rev. Lett.* **1993**, *71*, 2338–2341.

(20) Köhler, L.; Kresse, G. Density functional study of CO on Rh(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 165405.

(21) Pueyo Bellafont, N.; Viñes, F.; Hieringer, W.; Illas, F. Accurate Prediction of Core Level Binding Energies Shifts: Suitability of Projector Augmented Wave Approach as implemented in VASP. *J. Comput. Chem.* **2017**, *38*, 518–522.

(22) Hedin, L. New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem. *Phys. Rev.* **1965**, *139*, A796–A822.

(23) Strinati, G.; Mattausch, H. J.; Hanke, W. Dynamical Correlation Effects on the Quasiparticle Bloch States of a Covalent Crystal. *Phys. Rev. Lett.* **1980**, *45*, 290–294.

(24) Hybertsen, M. S.; Louie, S. G. Electron Correlation in Semiconductors and Insulators: Band Gaps and Quasiparticle Energies. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 5390–5413.

(25) Aryasetiawan, F.; Gunnarsson, O. The GW method. *Rep. Prog. Phys.* **1998**, *61*, 237–312.

(26) Faleev, S.; van Schilfgarde, M.; Kotani, T. All-electron self-consistent GW approximation: Application to Si, MnO, and NiO. *Phys. Rev. Lett.* **2004**, *93*, 126406.

(27) Kang, W.; Hybertsen, M. S. Quasiparticle and Optical Properties of Rutile and Anatase TiO₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 085203.

(28) Zhu, T.; Gao, S. P. The Stability, Electronic Structure, and Optical Property of TiO₂ Polymorphs. *J. Phys. Chem. C* **2014**, *118*, 11385–11396.

(29) Rinke, P.; Schleife, A.; Kioupakis, E.; Janotti, A.; Rödl, C.; Bechstedt, F.; Scheffler, M.; Van de Walle, C. G. First-principles

optical spectra for F centers in MgO. *Phys. Rev. Lett.* **2012**, *108*, 126404.

(30) Tosoni, S.; Fernandez Hevia, D.; Perez Peña, J.; Illas, F. Accurate description of optical absorption of F centers from quasiparticle band structure calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 115114.

(31) Liao, P.; Carter, E. A. Testing variations of the GW approximation on strongly correlated transition metal oxides: hematite (α -Fe₂O₃) as a benchmark. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15189–15199.

(32) Ren, X.; Rinke, P.; Scheffler, M. Exploring the Random Phase Approximation: Application to CO adsorbed on Cu(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 045402.

(33) Ishii, S.; Ohno, K.; Kawazoe, Y.; Louie, S. G. Ab Initio GW Quasiparticle Energies of Small Sodium Clusters by an All-electron Mixed-basis Approach. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *63*, 155104.

(34) Tiago, M. L.; Chelikowsky, J. R. Optical Excitations in Organic Molecules, Clusters, and Defects Studied by First-Principles Green's Function Methods. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 205334.

(35) Bruneval, F. GW Approximation of the Many-Body Problem and Changes in the Particle Number. *Phys. Rev. Lett.* **2009**, *103*, 176403.

(36) Rostgaard, C.; Jacobsen, K. W.; Thygesen, K. S. Fully Self-consistent GW Calculations for Molecules. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 085103.

(37) Baumeier, B.; Andrienko, D.; Ma, Y.; Rohlfing, M. Excited States of Dicyanovinyl-Substituted Oligothiophenes from Many-Body Green's Functions Theory. *J. Chem. Theory Comput.* **2012**, *8*, 997–1002.

(38) Caruso, F.; Rinke, P.; Ren, X.; Scheffler, M.; Rubio, A. Unified Description of Ground and Excited States of Finite Systems: The Self-consistent GW Approach. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 081102.

(39) Faber, C.; Boulanger, P.; Duchemin, I.; Attacalite, C.; Blase, X. Many-body Green's Function GW and Bethe-Salpeter Study of the Optical Excitations in a Paradigmatic Model Dipeptide. *J. Chem. Phys.* **2013**, *139*, 194308.

(40) Govoni, M.; Galli, G. Large Scale GW Calculations. *J. Chem. Theory Comput.* **2015**, *11*, 2680–2696.

(41) Laflamme Janssen, J.; Rousseau, B.; Cote, M. Efficient Dielectric Matrix Calculations Using the Lanczos Algorithm for Fast Many-body G₀W₀ Implementations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 125120.

(42) Maggio, E.; Kresse, G. GW Vertex Corrected Calculations for Molecular Systems. *J. Chem. Theory Comput.* **2017**, *13*, 4765–4778.

(43) van Setten, M. J.; Caruso, F.; Sharifzadeh, S.; Ren, X.; Scheffler, M.; Liu, F.; Lischner, J.; Lin, L.; Deslippe, J. R.; Louie, S. G.; Yang, C.; Weigend, F.; Neaton, J. B.; Evers, F.; Rinke, P. GW100: Benchmarking G₀W₀ for Molecular Systems. *J. Chem. Theory Comput.* **2015**, *11*, 5665–5687.

(44) Caruso, F.; Dauth, M.; van Setten, M. J.; Rinke, P. Benchmark of GW Approaches for the GW100 Test Set. *J. Chem. Theory Comput.* **2016**, *12*, 5076–5087.

(45) Maggio, E.; Liu, P.; van Setten, M. J.; Kresse, G. GW100: A Plane Wave Perspective for Small Molecules. *J. Chem. Theory Comput.* **2017**, *13*, 635–648.

(46) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(47) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab Initio Molecular Simulations with Numeric Atom-centered Orbitals. *Comput. Phys. Commun.* **2009**, *180*, 2175–2196.

(48) Havu, V.; Blum, V.; Havu, P.; Scheffler, M. Efficient O(N) Integration for All-electron Electronic Structure using Numerically Tabulated Basis Functions. *J. Comput. Phys.* **2009**, *228*, 8367–8379.

(49) Ren, X.; Rinke, P.; Blum, V.; Wieferink, J.; Tkatchenko, A.; Sanfilippo, A.; Reuter, K.; Scheffler, M. Resolution-of-identity

Approach to Hartree-Fock, Hybrid Density Functionals, RPA, MP2, and GW with Numeric Atom-centered Orbital Basis Functions. *New J. Phys.* **2012**, *14*, 053020.

(50) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(51) TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007. <http://www.turbomole.com> (accessed January 2018).

(52) Kühn, M.; Weigend, F. One-Electron Energies from the Two-Component GW Method. *J. Chem. Theory Comput.* **2015**, *11*, 969–979.

(53) Scherpelz, P.; Govoni, M.; Hamada, I.; Galli, G. Implementation and Validation of Fully Relativistic GW Calculations: Spin-Orbit Coupling in Molecules, Nanocrystals, and Solids. *J. Chem. Theory Comput.* **2016**, *12*, 3523–3544.

(54) van Schilfhaarde, M.; Kotani, T.; Faleev, S. Quasiparticle Self-Consistent GW Theory. *Phys. Rev. Lett.* **2006**, *96*, 226402.

(55) Kotani, T.; Van Schilfhaarde, M.; Faleev, S. V. Quasiparticle self-consistent GW method: A basis for the independent-particle approximation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 165106.

(56) van Setten, M. J.; Weigend, F.; Evers, F. The GW-Method for Quantum Chemistry Applications: Theory and Implementation. *J. Chem. Theory Comput.* **2013**, *9*, 232–246.

(57) Kaplan, F.; Seiler, C.; Weigend, F.; Evers, F.; van Setten, M. J.; Harding, M. E. Quasiparticle-selfconsistent GW for molecules. *J. Chem. Theory Comput.* **2016**, *12*, 2528–2541.

(58) Feller, D. The Role of Databases in Support of Computational, Chemistry Calculations. *J. Comput. Chem.* **1996**, *17*, 1571–1586.

(59) Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorhi, V.; Chase, J.; Li, J.; Windus, T. L. Basis set exchange: a community database for computational sciences. *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.

(60) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, P. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(61) Bakke, A. A.; Chen, H. W.; Jolly, W. L. A table of absolute core-electron binding-energies for gaseous atoms and molecules. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333–366.

(62) Myrseth, V.; Borve, K. J.; Thomas, T. D. The Substituent Effect of the Methyl Group. Carbon 1s Ionization Energies, Proton Affinities, and Reactivities of the Methylbenzene. *J. Org. Chem.* **2007**, *72*, 5715–5723.

(63) Rostgaard, C.; Jacobsen, K. W.; Thygesen, K. S. Fully Self-consistent GW Calculations for Molecules. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 085103.

(64) Gao, S. P. Cubic, Wurtzite, and 4H-BN Band Structures Calculated using GW Methods and Maximally Localized Wannier Functions Interpolation. *Comput. Mater. Sci.* **2012**, *61*, 266–269.