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Off-Diagonal Self-Energy Terms and Partially Self-Consistency in *GW* Calculations for Single Molecules: Efficient Implementation and Quantitative Effects on Ionization Potentials

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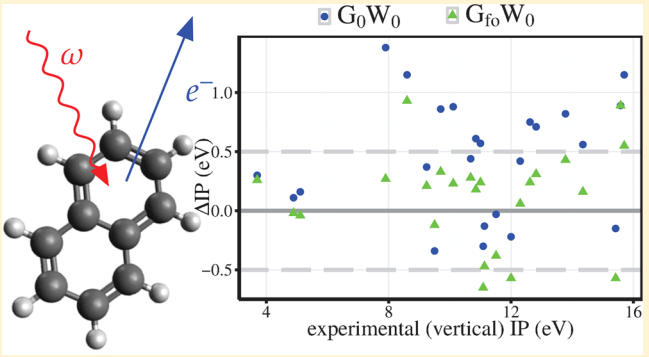
ABSTRACT: The *GW* method in its most widespread variant takes, as an input, Kohn−Sham (KS) single particle energies and single particle states and yields results for the single-particle excitation energies that are significantly improved over the bare KS estimates. Fundamental shortcomings of density functional theory (DFT) when applied to excitation energies as well as artifacts introduced by approximate exchange-correlation (XC) functionals are thus reduced. At its heart lies the quasi-particle (qp) equation, whose solution yields the corrected excitation energies and qp-wave functions. We propose an efficient approximation scheme to treat this equation based on second-order perturbation theory and self-consistent iteration schemes. We thus avoid solving (large) eigenvalue problems at the expense of a residual error that is comparable to the intrinsic uncertainty of the *GW* truncation scheme and is, in this sense, insignificant.



1. INTRODUCTION

A convenient theoretical tool to study interacting electron systems in condensed matter theory is the (causal) Green's function (G).[1,2] There are two reasons for its popularity. First, several important observables, such as the ground state particle density, the local density of states, and the electronic addition spectrum, can be derived from G straightforwardly.[1] Second, a systematic perturbative treatment of G in the (screened) Coulomb interaction is relatively straightforward to organize.[3] Accordingly, in the last decades, many approaches applying methods based on Green's function have been developed for the study of the electronic structure of solids.[4−13] Recently, also applications have been advanced in the context of quantum chemistry.[14−45]

Our work indicates that, for molecular systems, G_0W_0 energies employing (nonselfconsistent) single-shot approximations to the quasi-particle equation (and starting from a semilocal functional) acquire significant corrections, on the order of 1 eV, when including self-consistency on the pole positions; by contrast, corrections on the orbitals (probed by off-diagonal terms), in most cases, appear less relevant. For many applications, such uncertainties are not acceptable. Therefore, developments in the direction of self-consistency should be welcome. Indeed, these developments are becoming more common practice, especially in the applications to solids.[12,46−63]

For the purpose of this paper, we consider $G(z)$ to be a family of matrices $G(x,x';z)$ with indices x denoting the combined spin and position coordinates ($x = (\mathbf{r}\sigma)$) and a family parameter z representing the (complex valued) energy. Let G_H denote the Hartree approximation of G. Then, we can define the self-energy Σ via the Dyson equation $G(z) = G_H(z) - G_H(z)\Sigma(z)G(z)$, where the conventional matrix notation was used. Σ can be obtained as a solution of Hedin's equations.[64] However, the exact solution of the full set of equations is computationally too demanding. Therefore, in practice, Σ is approximated. A common scheme is the G_0W_0 approximation.[3] However, we would like point out that the self-energy could also be another approximation to the self-energy, such as the Moeller−Plesset second-order (MP2) self-energy. The approach proposed in this paper is generally applicable. For the MP2 self-energy, the quantities needed to calculate the perturbative corrections proposed here are already available in standard quantum chemistry codes, since they are also needed for the computation of quantities like geometry gradients.[65]

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In this paper, we consider a many-body system, such as a molecule, assuming that the corresponding Kohn−Sham (KS) states (ψ_n) and energies (ϵ_n^{KS}) of the associated density-functional problem are already known ($n = 1, ..., N$). Furthermore, we also take the self-energy as a given functional of the KS−Green's function, $\Sigma[G_{KS}](z)$, for instance constructed on a G_0W_0 level. The question that we here address is how (for given functional $\Sigma[G_{KS}](z)$) to calculate the perturbative corrections to ϵ_n^{KS} efficiently, in order to estimate the quasi-particle energies $\epsilon_n^{QP}(z)$ (i.e., the poles of $G(z)$) that belong to this molecule. Technically speaking, we would like to solve the *quasi-particle equation*,

$$\sum_{\underline{n}=1}^{N} \mathcal{A}_{n',\underline{n}} \langle n|\Sigma(\epsilon_{n'}^{QP}) - V_{xc}|\underline{n}\rangle = (\epsilon_{n'}^{QP} - \epsilon_n^{KS})\mathcal{A}_{n',n} \tag{1}$$

where the poles ϵ_n^{QP} and the matrices $\mathcal{A}_{n,n'} \equiv \mathcal{A}_{n,n'}(\epsilon_n^{QP})$ are to be found. The matrix elements $\langle n|\Sigma(z) - V_{xc}|\underline{n}\rangle$ are assumed to be given functions of z.[66]

Equation 1 has a formal structure reminiscent of an eigenvalue problem. However, it is more challenging to solve, because the self-energy matrix entering the left-hand side (LHS) is dependent on the pole positions, ϵ_n^{QP}. Two difficulties arise from this. First, each pole comes with its own set of matrix elements $\Sigma(\epsilon_n^{QP})$. Therefore, if one were to determine all poles, one would must solve N eigenvalue problems, each of the size $N \times N$. Second, since the pole positions are not known *a priori*, the LHS of eq 1 is not exactly known either. Hence, the solution relies upon a self-consistency procedure. Because of the energy dependency of Σ, the solution of the qp equation defined by eq 1 is at least $O(N^4)$ and, thus, very expensive. Therefore, in view of current efforts striving at approximate schemes for Σ of $O(N^3)$ (and less expensive),[31] the efficient solution of eq 1 becomes a relevant topic.

1.1. Commonly Adopted Approximation Schemes. The standard schemes to solve eq 1 have in common that (i) they focus on $n = n'$ and, hence, select one out of possibly several solutions and (ii) they ignore corrections to the quasi-particle states, Ψ_n, i.e., the real space structure of the Green's function is adopted from the KS reference states and $\mathcal{A}_{n,\underline{n}} \to \delta_{n,\underline{n}}$:

$$\epsilon_n^{KS} + \langle n|\Sigma(\epsilon_n^{QP}) - V_{xc}|n\rangle = \epsilon_n^{QP} \tag{2}$$

Thus, we are left with N self-consistent iterations.

Considering the decomposition

$$\langle n|\Sigma(z) - V_{xc}|\underline{n}\rangle = \underbrace{\mathcal{D}_n(z)}_{\text{diagonal}}\delta_{n\underline{n}} + \lambda \cdot \underbrace{M_{n\underline{n}}(z)}_{\text{off-diagonal}} \tag{3}$$

Equation 2 would be exact if $\lambda = 0$, i.e., in the absence of off-diagonal terms in Σ. Here, λ is a formal parameter used later to organize a perturbation theory in off-diagonal matrix elements.

In order to avoid self-consistency loops, often one more approximative step is taken. To the extent that corrections to the KS energies are small enough, one can try to expand the self-energy in eq 2 near the KS energies. This approximation is typically valid if the initial guess for the quasi-particle energy, i.e., the KS energy, is sufficiently remote from a pole of the self-energy. The linearized qp spectrum reads

$$\epsilon_n^{QP^{lin}} = \epsilon_n^{KS} + Z_n\langle n|\Sigma(\epsilon_n^{KS}) - V_{xc}|n\rangle$$

introducing the qp weight,

$$Z_n = \left[1 - \left\langle n\left|\frac{\partial\Sigma(E)}{\partial E}\right|_{E=\epsilon_n^{KS}}\right|n\right\rangle\right]^{-1}$$

1.2. Motivation and Idea Behind This Work. In this work, we calculate the leading corrections to the qp spectrum described by eq 2 that originate from (i) self-consistency in the poles of G (implying a shift of the self-energy poles of $\epsilon_n^{QP} - \epsilon_n^{KS}$) and (ii) from off-diagonal elements of Σ. The latter account for the deviations of the qp-wave functions Ψ_n, from their KS parents ψ_n.

(i) The particular type of self-consistency effects that we would like to address here relate to the fact that the Green's function, G_{KS}, that is fed into the functional $\Sigma[G_{KS}]$ could be taken having the poles belonging to the KS system, but it could also be another Green's function, G_{fo} that derives from G_{KS} by shifting the bare KS energies to the (updated) qp positions, but keeping the KS wave functions fixed; in other words,

$$\langle n|G_{fo}(E)|n'\rangle = \frac{\delta_{nn'}}{E - \epsilon_n^{QP} + i\eta}$$

Thus, we have the trivial property $\langle n|G_{fo}(E)|n'\rangle = \langle n|G_{KS}(E + \epsilon_n^{KS} - \epsilon_n^{QP})|n'\rangle$ (where fo denotes fixed orbital). It ensures that the numerical cost for determining a self-consistent solution of eq 2 is the same, irrespective of whether the poles of Σ are updated in each iteration (i.e., working with G_{fo}) or not (i.e., working with G_{KS}). Further details can be found in the appendix.

(ii) Physically, one expects that wave function corrections should be small for those cases where the spatial structure of the qp states is plane-wave like: wave functions are extended, and the charge density is almost homogeneous. For solids, this condition generally holds and, only in special cases, corrections from off-diagonal elements of Σ contribute significantly, namely, when the underlying DFT calculation wrongly predicts a metal or the localization of d-electrons.[12,55,67,68] In contrast, in situations with more structured charge distributions, as they occur with small molecules, off-diagonal terms could be significant. [Note: Even if the node-structure of wave functions is dictated largely by molecular or crystal symmetries, the ground-state charge distribution may not be given sufficiently accurately by common DFT functionals in order to reproduce hybridization and charging effects properly. This situation typically arises with open-shell molecules or in the presence of degeneracies. In particular, a strong impact of off-diagonal terms in Σ might be expected in charge-transfer compounds, where the amount of charge transfer is controlled by level alignment and hybridization.[69] In this case, the ground-state charge density may differ significantly from KS-LDA or KS-GGA estimates, so that wave function updates should be very important to understand the ground-state structure. This situation typically arises with open-shell molecules or in the presence of degeneracies.] In order to illustrate quantitative aspects, we consider two examples: benzene and acrolein. The corresponding self-energies Σ (G_0W_0 level) are displayed in Figures 1 and 2. These examples suggest that typically off-diagonal matrix elements are smaller than diagonal entries by an order of magnitude. However, they cannot be neglected, because

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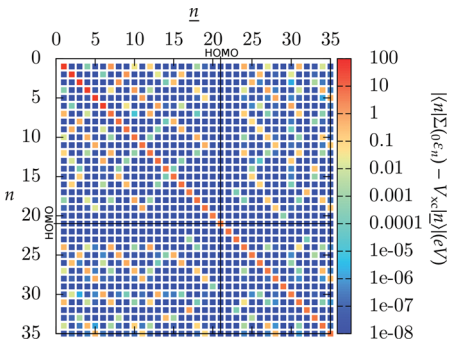

Figure 1. Visualization of the matrix that governs the G_0W_0 correction on KS eigenvalues expressed in KS reference states. The matrix elements $\langle n|\Sigma({}_0\epsilon_n^{QP}) - V_{xc}|\underline{n}\rangle$ are calculated at fully converged G_0W_0 qp energies ${}_0\epsilon_n^{QP}$ from the diagonalized qp equation. The data show that off-diagonal elements are significantly smaller than the diagonal ones. Thus, a perturbative treatment of off-diagonal elements is justified. The high number of nonzero elements suggests that they introduce significant corrections on the qp energies. The matrix shown is representative for the molecule benzene.

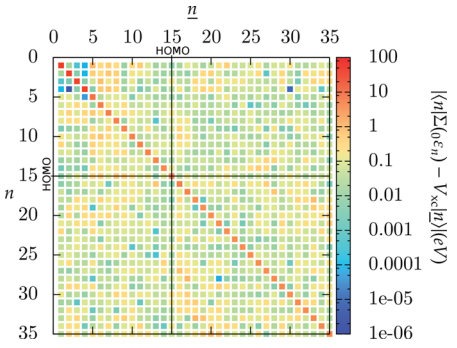

Figure 2. Visualization of the matrix that governs the G_0W_0 corrections on KS eigenvalues expressed in KS reference states, similar to Figure 1. The matrix in this figure is representative for the molecule acrolein. Again, we find diagonal matrix elements, which are orders of magnitude larger than off-diagonal elements.

there are many of them ($O(N^2)$). This suggests a perturbative treatment of off-diagonal terms in the matrix depicted by eq 1.

Paragraphs (i) and (ii) outline the route that we explore in this work. We will show that the solution of the diagonal equation, eq 2, acquires significant corrections upon updating the poles of the self-energy. To investigate the effect of off-diagonal terms of Σ on the spectrum, we implement a second-order perturbative analysis of eq 1 that operates in a quantitative and computationally very affordable way. As it turns out, off-diagonal corrections, in most cases, are quantitatively negligible within the test set of molecules that we have studied.

2. MODEL AND METHOD

We analyze eq 1 by employing conventional perturbation theory in λ. Up to second order, the (generalized) eigenvectors and eigenvalues read

$$\mathcal{A}_{n',n}(\epsilon_{n'}^{QP}) = {}_0\mathcal{A}_{n',n}(\epsilon_{n'}^{QP})\delta_{n\underline{n}} + \lambda\cdot{}_1\mathcal{A}_{n',n}(\epsilon_{n'}^{QP}) + \lambda^2\cdot{}_2\mathcal{A}_{n',n}(\epsilon_{n'}^{QP}) + O(\lambda^3) \quad (4)$$

$$\epsilon_{n'}^{QP} = {}_0\epsilon_{n'}^{QP} + \lambda\cdot{}_1\epsilon_{n'}^{QP} + \lambda^2\cdot{}_2\epsilon_{n'}^{QP} + O(\lambda^3) \quad (5)$$

Plugging this into the qp expression represented by eq 1, we find that the first-order energy correction vanishes,

$${}_1\epsilon_{n'}^{QP} = 0 \quad (6)$$

while the second-order calculation yields

$${}_2\epsilon_{n'}^{QP} = \sum_{\underline{n}\neq n} \frac{\mathcal{M}_{n'\underline{n}}(\epsilon_{n'}^{QP})\mathcal{M}_{\underline{n}n'}(\epsilon_{n'}^{QP})}{{}_0\epsilon_{n'}^{QP} - \epsilon_{\underline{n}}^{KS} - \mathcal{M}_{n'}(\epsilon_{n'}^{QP})} \quad (7)$$

Equation 7 gives the corrections to the spectrum originating from off-diagonal terms of $\langle n|\Sigma(\epsilon_{n'}^{QP}) - V_{xc}|\underline{n}\rangle$. Since the pole positions are not known *a priori*, one still must iterate the initial guess of poles and matrix elements to self-consistency. We call the self-consistent solution of the jth-order approximation $z_n^{(j)}$. Details of the calculation are given in the Appendix.

2.1. Validation. In order to validate the accuracy of the second-order treatment, we will compare to exact solutions of eq 1 obtained by full diagonalizion. These terms are ${}^{fo}z_n^{(\infty)}$ and $z_n^{(\infty)}$, representing the two situations with and without updating the self-energy poles. Such solutions are available for small system sizes and benchmark our second-order results.

In the exact diagonalization approach, the qp equation described by eq 1 is solved for every single pole $\epsilon_{n'}^{QP}(z)$ separately. This is necessary, because the solution involves a generalized eigenvalue problem with a matrix (operator) that is dependent on its eigenvalues. To tackle the problem, we choose an initial guess, then diagonalize the matrix operator for this guess and determine its eigenvalues. One of these eigenvalues is closer to the initial (previous) guess than all others. We choose this (closest) eigenvalue as an improved guess and reiterate until self-consistency is reached. We mention that, by construction, this procedure delivers a number of N solutions, but many additional solutions are being discarded. A discussion of their physical significance has been given in recent work.[70]

2.2. Calculational Details. The implementation of the perturbative expressions described by eq 7 has been done in the framework of the G_0W_0 module integrated in the TURBOMOLE package within a local version basing on V6.6.[42,71] For the screening, we employed KS-RPA with resolution of the identity approximation (RI). All calculations employ the TZVPP basis set.[72] For the DFT part the PBE functional was used.[73]

To accelerate convergence, we found it helpful to initialize the self-consistency cycles of higher-order approximations with the estimates obtained from lower-order ones: initial guesses to obtain the diagonal approximation, $z_n^{(0)}$, have been the bare KS energies ϵ_n^{KS}: the second-order cycle (result $z_n^{(2)}$) was initialized with $z_n^{(0)}$. Finally, the full diagonalization (exact) cycle was initialized with the self-consistent second-order result, $z_n^{(2)}$.

2.3. Observables. We have performed calculations of ionization energies/potentials (IPs) on a subset of 24 molecules of the test set GW27.[42] IPs are a standard observable for testing electronic structure methods, because (i) they are an important indicator to understand charge transfer processes and (ii) reliable experimental reference data are available. The first IP measures the (negative) energy of the highest occupied molecular orbital (HOMO).

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2.4. Computational Cost. Since the self-consistency cycle associated with solving the qp equation described by eq 1 requires recalculation of the matrix elements of Σ anyway, there is no extra computational cost for updating the self-energy poles, i.e., for the replacement of G_{KS} with ${}^{fo}G_{KS}$.

The computational effort solving the qp equation exactly exceeds the bare G_0W_0 time by almost 2 orders of magnitude (see Figure 3). Therefore, large-scale applications of this

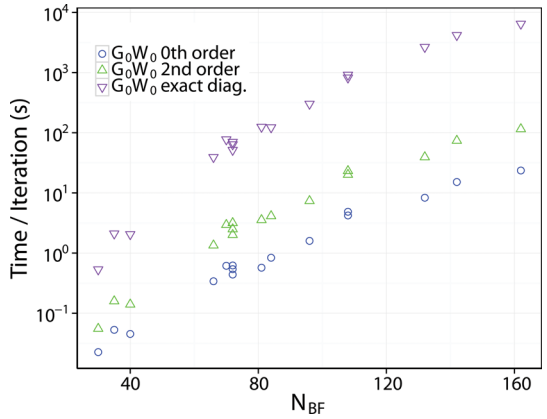

Figure 3. Growth of the computation time (per cycle) with the number of basis functions for solving the qp equation (eq 1). Different approximations scheme are compared: zeroth-order, second-order, exact treatment of off-diagonal matrix elements of the self-energy. The calculations were performed on the HC3 cluster of the Karlsruhe Institute of Technology using the standard nodes (two Quad-Core Intel Xeon E5540 processors with 2.53 GHz and 24 GB RAM).

solution strategy are strongly discouraged. However, as our results will show, typically the effect of off-diagonal matrix elements are small in a sense (but not necessarily negligible); hence, they are already captured in second-order perturbation theory. This allows one to reduce the computational cost significantly. In our present implementation, it is typically a factor of 2−5 above the common diagonal approximation (see Figure 3). [Note that no rigorous attempt to fully optimize has yet been made.]

In second-order calculations most of the computational time of the GW calculation is spent in the construction of Σ, like in the zeroth-order approach. For the latter, the solution of the diagonal qp equation requires a maximum of 15% of the time needed for the construction of Σ. Because of the calculation of the off-diagonal matrix elements of Σ, the enhancement at the second-order level is particularly large. Finding the exact solution of the qp equation is even more expensive; however, the iterative diagonalization of the qp equation also requires a significant amount of time (about as much as the construction of Σ). [Note that the full *GW* calculation consists of three steps: DFT, response function, and *GW* (constructing Σ and solving the qp equation). For small systems, the computational cost of the DFT part is already <5% of the total. The calculation of the response consumes most of the total time (∼85% of a zeroth-order G_0W_0 calculation). These computational costs are the same for both zeroth-order, second-order, and full-diagonalization calculations. Therefore, the increased computational effort of a second-order calculation, discussed above, is only ∼40%−50% when we consider the entire calculation.] Notice that the second-order approach does not deteriorate the scaling of the computational cost with system size. Once the polarization has been calculated, which is formally a fourth-order process, we can construct the diagonal elements in a formally third-order process and the off-diagonal elements in a formally fourth-order process. Hence, the overall scaling exponent is not changed by moving from zeroth order to second order.

3. RESULTS AND DISCUSSION

Table 1 summarizes the key results of this work. It displays the estimates for the ionization potential of 24 molecules based on the (negative of the) HOMO energy as obtained from the different approximation strategies to the qp equation.

3.1. Updating Self-Energy Poles. Figure 4 displays the IP (energy of the HOMO) as it is obtained from solving the diagonal equation described by eq 2, with and without updating the self-energy poles. Two observations are to be made:

(i) The differences between updated and nonupdated calculation, ${}^{fo}z_n^{(0)} - z_n^{(0)}$, are seen to be relatively small, compared to the bare G_0W_0 shift $z_n^{(0)} - \epsilon_n^{KS}$ from the KS result.

(ii) Updating the pole positions is still important in the sense that updating brings ${}^{fo}z_n^{(0)}$ much closer to the coupled-cluster reference solution than the bare result $z_n^{(0)}$. It is seen that updating self-energy poles helps to reduce the deviation between the coupled cluster and the solutions of the G_0W_0 qp equation by typically 1 order of magnitude.

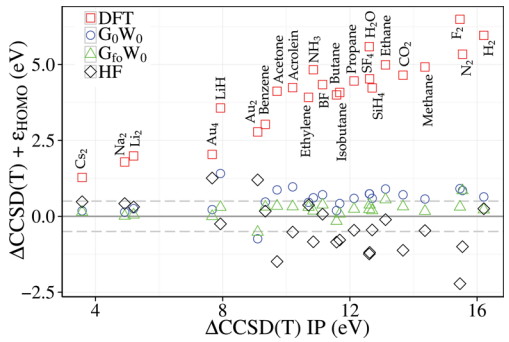

Figure 4. Deviations to leading IP estimates from ΔCCSD(T)[74] to HOMO energies obtained from the diagonal qp equation without (G_0W_0) and with updating the poles ($G_{fo}W_0$). Methods: Hartree−Fock (HF), DFT with PBE, G_0W_0, and $G_{fo}W_0$ (@PBE using RPA response for W_0). The dashed horizontal line gives the deviations (±0.5 eV). As seen from the data, self-consistency in the poles improves the agreement with the reference by up to 1 eV, in comparison to the G0W0 results.

3.2. Accuracy of Second-Order Approximation (Leading Ionization Potential). As one sees directly from Table 1, the second-order corrections from off-diagonal elements of the self-energy have a tendency to be smaller than the diagonal corrections, typically by an order of magnitude. Thus, the perturbative treatment is justified *a posteriori*. This observation holds true regardless of whether the poles of the self-energy are updated or not. In other words, the solutions of the diagonal equation, $z_{HOMO}^{(0)}$ and ${}^{fo}z_{HOMO}^{(0)}$, are already close to the exact ones ($z_{HOMO}^{(\infty)}$ and ${}^{fo}z_{HOMO}^{(\infty)}$). To illustrate this point, we plot only the deviations of the diagonal and the second-order HOMOs to the exact

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Table 1. Table of the Experimental (Vertical) Ionization Potentials (Exp), the (Vertical) IP in the ΔCCSD(T) Approximation (ΔCCSD(T)) and Minus the Calculated HOMO Energies for DFT(with functional PBE), Hartree-Fock (HF) as well as at the Zeroth-Order G_0W_0 ($G_0^{(0)}W_0$), Second-Order G_0W_0 ($G_0^{(2)}W_0$), Zeroth-Order $G_{fo}W_0$ ($G_{fo}^{(0)}W_0$), Second-Order $G_{fo}W_0$ ($G_{fo}^{(2)}W_0$), and Exact $G_{fo}W_0$ ($G_{fo}^{(\infty)}W_0$) Levels of Theory

	Ionization Potential (eV)								
molecule	DFT	HF	$G_0^{(0)}W_0$	$G_0^{(2)}W_0$	$G_{fo}^{(0)}W_0$	$G_{fo}^{(2)}W_0$	$G_{fo}^{(\infty)}W_0$	ΔCCSD(T)[74]	Exp
H_2	10.25	15.96	15.57	15.58	15.99	16.00	16.01	16.21	15.42
Li_2	3.21	4.89	4.95	4.98	5.15	5.16	5.19	5.20	5.11
Na_2	3.13	4.50	4.78	4.79	4.91	4.92	4.94	4.92	4.89
Cs_2	2.30	3.10	3.40	3.43	3.44	3.49	3.56	3.58	3.70
F_2	8.97	17.68	14.55	14.59	15.15	15.19	15.19	15.46	15.70
N_2	10.20	16.54	14.69	14.71	14.69	15.22	15.26	15.54	15.58
BF	6.80	11.07	10.43	10.45	10.76	10.78	10.77	11.14	11.00
LiH	4.36	8.18	6.52	6.57	7.63	7.65	7.66	7.93	7.90
CO_2	9.02	14.79	12.96	13.01	13.35	13.40	13.40	13.67	13.78
H_2O	7.02	13.85	11.87	11.91	12.38	12.41	12.41	12.61	12.62
NH_3	6.02	11.69	10.24	10.28	10.67	10.70	10.70	10.85	10.85
SiH_4	8.47	13.15	12.11	12.13	12.51	12.53	12.53	12.70	12.82
SF_4	8.09	13.81	11.88	11.91	12.24	12.24	12.23	12.62	12.30
Au_2	6.32	7.90	9.84	9.74	9.62	9.11	9.09	9.10	9.50
Au_4	5.63	6.41	7.45	7.45	7.67	7.65	7.61	7.67	8.60
methane	9.44	14.83	13.79	13.82	14.19	14.21	14.21	14.36	14.35
ethane	8.13	13.23	12.22	12.24	12.57	12.59	12.60	13.12	12.00
propane	7.67	12.59	11.54	11.56	11.89	11.91	12.00	12.13	11.51
butane	7.58	12.43	11.39	11.40	11.74	11.42	11.44	11.58	11.09
isobutane	7.60	12.46	11.26	11.27	11.60	11.53	11.54	11.68	11.13
ethylene	6.78	10.33	10.24	10.26	10.40	10.45	10.43	10.70	10.68
acetone	5.59	11.20	8.84	8.87	9.37	9.44	9.43	9.71	9.70
acrolein	5.96	10.72	9.23	9.26	9.88	9.89	9.88	10.20	10.11
benzene	6.31	9.17	8.87	8.90	9.03	9.07	9.08	9.34	9.24

diagonalization results in Figure 5. Still, in some cases, such as the Au-dimer and the N-dimer, off-diagonal terms can reach

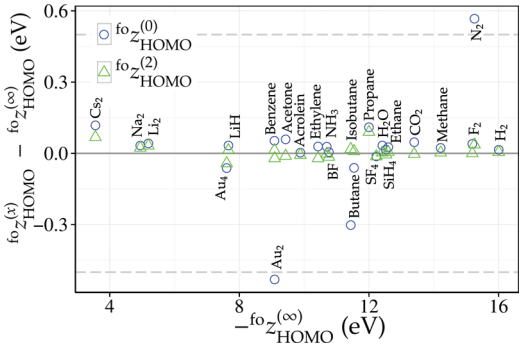

Figure 5. HOMO energy obtained from solving the qp equation with updating the self-energy poles, taking into account only the diagonal contributions ($^{fo}z^{(0)}_{HOMO}$) and second-order treatment of off-diagonal elements ($^{fo}z^{(2)}_{HOMO}$) as deviating from the exact diagonalization results ($^{fo}z^{(\infty)}_{HOMO}$). Dashed horizontal lines give the deviations (±0.5 eV).

values of 500 meV, bringing the $G_{fo}W_0$ result closer to the coupled-cluster reference. The second-order approach captures these corrections.

3.3. Higher Ionization Potentials. To further validate our methods, we investigate higher ionization energies. They correspond to the energies of quasi-particles that are bound more strongly than the valence electrons.

Figure 6 displays the 10 lowest IPs of benzene. The data confirm the earlier observations made for the first IP: updating the self-energy poles bring the approximate solutions of the qp equation significantly closer to the reference results. Importantly, in those cases where the bare qp equation (with Σ featuring poles at the bare KS energies) is not successful to significantly reduce the DFT error, updating the self-energy poles achieves this. Conversely, if the bare equation gives accurate results, the updating corrections are insignificant. This positive impression is further supported by two more test cases that we have considered. Figure 6 shows higher IPs also for the water and the nitrogen molecules. Again, updating self-energy poles has a tendency to improve the results obtained from the bare qp equation. In all cases, the contribution of off-diagonal self-energy matrix elements is typically small, with sizable corrections only for very high IPs.

4. CONCLUSION AND OUTLOOK

At the heart of any G_0W_0 calculation is the solution of the quasi-particle (qp) equation. It determines corrections to the single particle excitation energies of the reference calculation—typically Kohn−Sham (KS)-based density functional theory. In standard G_0W_0 implementations, the qp equation is solved within a diagonal approximation that (i) takes the poles of the self-energy at the (bare) KS-energies and (ii) neglects off-diagonal matrix elements of the self-energy. The latter step implies that the KS wave functions of the reference system are also adopted for the qp states.

In this paper, we investigated the effect that conditions (i) and (ii) can have on the ionization energies of small molecules. On a quantitative level, our findings suggest that shifting (updating) the self-energy poles (by the qp-correction) from their bare KS values to the (approximate)

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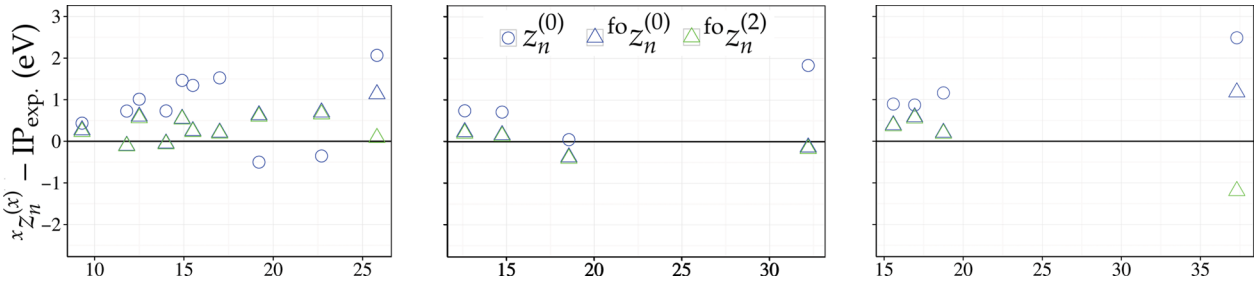

Figure 6. Deviation of the G_0W_0 HOMO energy from experimental ionization potentials using diagonal approximation without ($z_n^{(0)}$) and with self-consistency ($^{fo}z_n^{(0)}$) and second-order approximation of off-diagonal contributions ($^{fo}z_n^{(2)}$) for benzene (left), H_2O (center) and N_2 (right). As seen from the plot, the self-consistency reproduces higher IPs with roughly the same accuracy as for the first IP. The self-consistency solutions, as previously mentioned, brings bare results much closer to the experimental results.

qp positions contributes to the ionization energy (typically a few hundred millivolts) and are thus comparable in size to the corrections expected for fully self-consistent *GW* calculations. In this sense, updating energy poles is very significant. By contrast, our calculations suggest that the contributions of the off-diagonal matrix elements of the self-energy are, in most cases, smaller than the corrections due to updating, typically by an order of magnitude.

APPENDIX

A. Self-Consistency in Poles of *G*

Within the fixed-orbital approach, we aim only for self-consistency in the pole positions of *G*. To this end, we recall the real part of the matrix elements of the correlation part of the self-energy from the G_0W_0 implementation[42]

$$\begin{aligned}&\mathrm{Re}(\langle n|\Sigma_c^{G_0W_0}(E)|n'\rangle)\\ &= \sum_m \left[\sum_i^{\mathrm{occ}} (in|\rho_m)(\rho_m|n'i) \times \frac{E-\epsilon_i^{\mathrm{KS}}+\Omega_m}{(E-\epsilon_i^{\mathrm{KS}}+\Omega_m)^2+\bar{\eta}^2}\right.\\ &\quad \left. + \sum_a^{\mathrm{unocc}} (an|\rho_m)(\rho_m|n'a) \times \frac{E-\epsilon_a^{\mathrm{KS}}-\Omega_m}{(E-\epsilon_a^{\mathrm{KS}}-\Omega_m)^2+\bar{\eta}^2}\right]\end{aligned} \tag{A1}$$

with the KS energies (ϵ_i^{KS} and ϵ_a^{KS}), the excitation energies (Ω_m), and densities (ρ_m), and η, which is set to zero at the end of the calculation. In each iteration step, we replace all KS energies ϵ^{KS} with (current guesses for) the qp energies ϵ^{QP}. We thus construct, on the fly, the correlation contribution of $G_{\mathrm{fo}}W_0$:

$$\begin{aligned}&\mathrm{Re}(\langle n|\Sigma_c^{G_{\mathrm{fo}}W_0}(E)|n'\rangle)\\ &= \sum_m \left[\sum_i^{\mathrm{occ}} (in|\rho_m)(\rho_m|n'i) \times \frac{E-\epsilon_i^{\mathrm{QP}}+\Omega_m}{(E-\epsilon_i^{\mathrm{QP}}+\Omega_m)^2+\bar{\eta}^2}\right.\\ &\quad \left. + \sum_a^{\mathrm{unocc}} (an|\rho_m)(\rho_m|n'a) \times \frac{E-\epsilon_a^{\mathrm{QP}}-\Omega_m}{(E-\epsilon_a^{\mathrm{QP}}-\Omega_m)^2+\bar{\eta}^2}\right]\end{aligned} \tag{A2}$$

Here, the screening and, hence, Ω_m and ρ_m, are still calculated from the underlying KS reference system. Hence, the charge-neutral (particle-hole) excitations that enter the bare polarization function are not given by the differences of single-particle (charged excitation) energies. This feature of our approximation scheme is somewhat reminiscent of the effect of vertex corrections as they are imbedded in the Bethe–Salpeter equation.

B. Appendix B: Off-Diagonal Contributions

The formal structure of the qp equation reads as follows:

$$\sum_{\underline{n}} \mathcal{A}_{n'\underline{n}} \mathcal{M}_{n\underline{n}}(\epsilon_{n'}^{\mathrm{QP}}) = (\epsilon_{n'}^{\mathrm{QP}} - \epsilon_n^{\mathrm{KS}})\mathcal{A}_{n'n} \tag{B1}$$

The matrix family $\mathcal{M}(z)$ is assumed to be given, while $\epsilon_{n'}^{\mathrm{QP}}$ and the set of eigenvectors that forms the columns of $\mathcal{A}_{n'\underline{n}}$ are to be found. We face a typical self-consistency problem that features a (generalized) eigenvalue problem with a matrix operator that is dependent on the eigen-solutions. A peculiarity appears, compared to situations familiar from Hartree–Fock or Kohn–Sham theory, because $\mathcal{M}$ is dependent on the eigenvalues, but not on the eigenstates.

B.1. Formal Perturbation Theory. The matrix $\mathcal{M}$ has a grading in the sense that its diagonal elements are much larger than the off-diagonal ones. This suggests the following decomposition:

$$\mathcal{M}_{n\underline{n}}(\epsilon_n^{\mathrm{QP}}) = \mathcal{D}_n(\epsilon_n^{\mathrm{QP}})\delta_{n\underline{n}} + \lambda M_{n\underline{n}}(\epsilon_n^{\mathrm{QP}}) \tag{B2}$$

With eq B2, the solutions of B1 are dependent on λ: $\epsilon_{n'}^{\mathrm{QP}}(\lambda)$, $\mathcal{A}_{n'\underline{n}}(\lambda)$. The grading of $\mathcal{M}$ suggests a perturbative expansion,

$$\epsilon_n^{\mathrm{QP}}(\lambda) = \underbrace{{}_0\epsilon_n^{\mathrm{QP}}}_{\text{solution } \lambda=0} + \lambda\cdot{}_1\epsilon_n^{\mathrm{QP}} + \lambda^2\cdot{}_2\epsilon_n^{\mathrm{QP}} + O(\lambda^3) \tag{B3}$$

$$\mathcal{A}_{n\underline{n}} = {}_0\mathcal{A}_n\delta_{n\underline{n}} + \lambda\cdot{}_1\mathcal{A}_{n\underline{n}} + \lambda^2\cdot{}_2\mathcal{A}_{n\underline{n}} + O(\lambda^3) \tag{B4}$$

Note that we are aiming at self-consistency at every order of λ. In this way, the expansion coefficients will effectively pick up their own (weak) λ dependency.

B.1.1. Self-Consistency Cycle. The iteration cycle is initialized by defining the first guess for ϵ_n^{QP}, which we denote as $^{(0)}\epsilon_n^{\mathrm{QP}}$ (parent generation).

(1) For $j = 0, 1, \ldots$, calculate

$$\mathcal{M}_{n\underline{n}}(^{(j)}\epsilon_{n'}^{\mathrm{QP}}) \rightarrow^{(j)} \mathcal{M}_{n\underline{n};n'} \tag{B5}$$

(2) Decompose

$$^{(j)}\mathcal{M}_{n\underline{n};n'} = {}^{(j)}\mathcal{D}_{n;n'}\delta_{n\underline{n}} + \lambda^{(j)}M_{n\underline{n};n'} \tag{B6}$$

(3) Solve, in perturbation theory in λ, the substitute problem

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$$\sum_{\underline{n}}^{(j+1)} \mathcal{A}^{(j)}_{n'\underline{n}} \mathcal{M}_{n\underline{n};n'} = ({}^{(j+1)}\epsilon^{\mathrm{QP}}_{n'} - \epsilon^{\mathrm{KS}}_{n})\,{}^{(j+1)}\mathcal{A}_{n'\underline{n}} \tag{B7}$$

The perturbation theory has the structure given by eqs B3 and B4 for the quantities ${}^{(j+1)}\epsilon^{\mathrm{QP}}_{n}$ and ${}^{(j+1)}\mathcal{A}_{n\underline{n}}$.

(4) Return to step (1), replacing ${}^{(j)}\epsilon^{\mathrm{QP}}_{n}$ with its update ${}^{(j+1)}\epsilon^{\mathrm{QP}}_{n}$

As usual, the perturbation theory is organized via sorting powers of λ after inserting the formal expansions B3 and B4 into the expression

$$\sum_{\underline{n}} [{}_0\mathcal{A}_{n'}\delta_{n'\underline{n}} + \lambda\cdot{}_1\mathcal{A}_{n'\underline{n}} + O(\lambda^2)] \times [{}^{(j)}\mathcal{D}_{n;n'}\delta_{n\underline{n}} + \lambda\,{}^{(j)}M_{n\underline{n};n'}]$$
$$= ({}^{(j+1)}\epsilon^{\mathrm{QP}}_{n'} - \epsilon^{\mathrm{KS}}_{n})[{}_0\mathcal{A}_{n}\delta_{n'n} + \lambda\cdot{}_1\mathcal{A}_{n'n} + O(\lambda^2)] \tag{B8}$$

where, in our notation, we have dropped the prefixes of ${}^{(j+1)}{}_0\mathcal{A}_{n'}, {}^{(j+1)}{}_1\mathcal{A}_{n'n}$.

B.2. Lowest (Zeroth)-Order Perturbation Theory. In lowest-order perturbation theory, we obtain the diagonal approximation (eq 2).

$${}^{(j)}\mathcal{D}_{n;n} = {}^{(j+1)}{}_0\epsilon^{\mathrm{QP}}_{n} - \epsilon^{\mathrm{KS}}_{n} \tag{B9}$$

$${}^{(j)}\mathcal{A}_{n\underline{n}} = \delta_{n\underline{n}} \tag{B10}$$

There is no wavefunction update and eq 2 is iterated to self-consistency in ${}_0\epsilon^{\mathrm{QP}}_{n}$.

B.3. First-Order Perturbation Theory. As usual, we collect terms,

$${}^{(j+1)}{}_0\mathcal{A}_{n'}\cdot{}^{(j)}\mathcal{M}_{nn';n'} + {}^{(j+1)}{}_1\mathcal{A}_{n'n}\cdot{}^{(j)}\mathcal{D}_{n;n'}$$
$$= ({}^{(j+1)}{}_0\epsilon^{\mathrm{QP}}_{n'} - \epsilon^{\mathrm{KS}}_{n})\cdot{}_1\mathcal{A}_{n'n} + {}^{(j+1)}{}_1\epsilon^{\mathrm{QP}}_{n}\cdot{}_0\mathcal{A}_{n}\delta_{n'n} \tag{B11}$$

and then consider two cases. If $n = n'$, then (again, dropping the prefixes of ${}^{(j+1)}{}_0\mathcal{A}_{n'}, {}^{(j+1)}{}_1\mathcal{A}_{n'n}$)

$${}_0\mathcal{U}_{n}\cdot{}^{(j)}M_{\mathrm{nn};n} + {}_1\mathcal{A}_{nn}\cdot{}^{(j)}\mathcal{D}_{n;n}$$
$$= ({}^{(j+1)}{}_1\epsilon^{\mathrm{QP}}_{n} - \epsilon^{\mathrm{KS}}_{n})\,{}_1\mathcal{A}_{nn} + {}_0\mathcal{A}_{n}\,{}^{(j+1)}{}_1\epsilon^{\mathrm{QP}}_{n} \tag{B12}$$

By construction, the diagonal elements of $\mathcal{M}$, $\tilde{\mathcal{U}}$ are all zero and therefore the LHS of this equation vanishes; hence,

$${}^{(j+1)}{}_1\epsilon^{\mathrm{QP}}_{n} = 0 \tag{B13}$$

We conclude that corrections due to off-diagonal elements in $\mathcal{M}$ appear in the qp energies ϵ^{QP} only at second order in λ.

The linear corrections to the eigenvectors are extracted from the off-diagonal case, $n \neq n'$; we have

$${}_1\mathcal{A}_{n'n} = {}_0\mathcal{A}_{n'}\frac{{}^{(j)}M_{nn';n'}}{{}^{(j)}{}_0\epsilon^{\mathrm{QP}}_{n'} - \epsilon^{\mathrm{KS}}_{n} + {}^{(j)}\mathcal{D}_{n;n'}} \qquad n' \neq n \tag{B14}$$

while ${}_1\mathcal{A}_{\mathrm{nn}} = 0$. Equation B14 gives the leading order mixing of the KS states into the qp wave functions. (The set of coefficients ${}_0\mathcal{A}_{n}$ is found from the normalization condition.) Note that, as long as one is only interested in the leading order corrections to the eigenvectors, one can first find the self-consistent zero-order solution

$$\mathcal{D}_{n}(z^{(0)}_{n}) = z^{(0)}_{n} - \epsilon^{\mathrm{KS}}_{n} \tag{B15}$$

where $z^{(0)}_{n} = {}^{\infty}{}_0\epsilon^{\mathrm{QP}}_{n}$

$${}_1\mathcal{A}_{n'n} = {}_0\mathcal{A}_{n'}\frac{{}^{(j)}M_{nn'}(z^{(0)}_{n'})}{z^{(0)}_{n'} - \epsilon^{\mathrm{KS}}_{n} + \mathcal{D}_{n}(z^{(0)}_{n'})} \tag{B16}$$

B.4. Second-Order Perturbation Theory. We collect all terms of order λ^2:

$${}_2\mathcal{A}_{n'n}[{}^{(j)}\mathcal{D}_{n;n'} - ({}^{(j+1)}{}_0\epsilon^{\mathrm{QP}}_{n'} - \epsilon^{\mathrm{KS}}_{n})] + \sum_{\underline{n}} {}_1\mathcal{A}^{(j)}_{n'nun}M_{n\underline{n};n'}$$
$$= {}_0\mathcal{A}_{n'}\,{}^{(j+1)}{}_2\epsilon^{\mathrm{QP}}_{n'}\delta_{n'n} \tag{B17}$$

As in first-order calculation, we only need the diagonal case, $n' = n$, to obtain the energy corrections:

$$\sum_{\underline{n}} {}_1\mathcal{A}_{n\underline{n}}\,{}^{(j)}{}_1M_{n\underline{n};n} = {}_0\mathcal{A}_{n}\,{}^{(j+1)}{}_2\epsilon^{\mathrm{QP}}_{n} \tag{B18}$$

where ${}_2\mathcal{A}_{\mathrm{nn}} = 0$ has been employed. Using B14, we find

$${}^{(j+1)}{}_2\epsilon^{\mathrm{QP}}_{n} = \sum_{\underline{n}\neq n}\frac{{}^{(j)}M_{\underline{n}n;n}\,{}^{(j)}M_{n\underline{n};n}}{{}^{(j+1)}{}_0\epsilon^{\mathrm{QP}}_{n} - \epsilon^{\mathrm{KS}}_{\underline{n}} - {}^{(j)}\mathcal{D}_{\underline{n};n}} \tag{B19}$$

Also note that, in the second-order expression, only terms of type $m\mathcal{M}_{\underline{n}n;n\underline{n}n;n}$ survive, i.e., only two indices are different. From third-order calculations onward, terms with three different indices also appear in the energy correction.

We arrive at an updated qp energy, with

$${}^{(j+1)}\epsilon^{\mathrm{QP}}_{n} = {}^{(j+1)}{}_0\epsilon^{\mathrm{QP}}_{n} + \lambda^2\cdot{}^{(j+1)}{}_2\epsilon^{\mathrm{QP}}_{n} + O(\lambda^3) \tag{B20}$$

These improved estimates $({}^{(j+1)}\epsilon^{\mathrm{QP}}_{n})$ are plugged back into eq 1 to update the matrix elements when iterating the process toward the self-consistent point. The cycle is terminated after a fixed number of iterations. In our case, we choose 20. This way, we ensured that that the increment $|{}^{(j+1)}\epsilon^{\mathrm{QP}}_{n} - {}^{(j)}\epsilon^{\mathrm{QP}}_{n}|$ dropped below a threshold of $\delta = 0.1$ meV.

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Notes

The authors declare no competing financial interest.

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(66) Note that, in order to explain the physical meaning of the matrices $\mathcal{A}$, we recall a spectral decomposition of G into[42]

$$G(x, x'; z) = \sum_{n=1}^{N} \frac{\Psi_{r,n}(x, z)\Psi_{l,n}^{\dagger}(x', z)}{z - \epsilon_n^{QP}(z) + i\eta\mathrm{sgn}(\epsilon_n^{QP} - \mu)}$$

The right/left eigenvectors $\Psi_{r/l}$ can be expressed in terms of the KS states and the corresponding exchange correlation (XC) functional V_{XC} that are associated with the many-body-problem at hand:

$$\Psi_{r,n}(x, z) = \sum_{n'=1}^{N} \mathcal{A}_{n,n'}(z)\psi_{n'}(x)$$

$$\Psi_{l,n}(x, z) = \sum_{n'=1}^{N} \bar{\mathcal{A}}_{n,n'}(z)\psi_{n'}(x)$$

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