Evaluating the $G_W$ approximation with CCSD(T) for charged excitations across the oligoacenes

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Abstract

Charged excitations of the oligoacene family of molecules, relevant for astrophysics and technological applications, are widely studied and therefore provide an excellent system for benchmarking theoretical methods. In this work, we evaluate the performance of many-body perturbation theory (MPBT) within the $GW$ approximation, relative to new high-quality CCSD(T) reference data, for charged excitations of the acenes. We compare $GW$ calculations with a number of hybrid density functional theory starting points and with eigenvalue self-consistency. Special focus is given to elucidating the trend of $GW$-predicted excitations with molecule length, from benzene to hexacene. We find that $GW$ calculations with starting points based on an optimally-tuned range separated hybrid (OTRSH) density functional and eigenvalue self-consistency can yield quantitative ionization potentials for the acenes. However, for the larger acenes, the predicted electron affinities can deviate considerably from reference values. Our work paves the way for predictive and cost-effective $GW$ calculations of charged-excitations of molecules and identifies certain limitations of current $GW$ methods used in practice for larger molecules.

1 Introduction

The oligoacene molecules belong to a class of aromatic hydrocarbons consisting of linearly fused benzene rings (Fig. 1). This family of molecules has been studied in the context of a variety of opto-electronic applications, and in particular, the larger acenes and their derivatives are used for field-effect transistors and in solar-cell devices. In addition, acenes and other polycyclic aromatic hydrocarbons are abundant in the universe and their properties are of importance to astrophysics.

![Figure 1: The acenes general formula.](image)

Charged excitations, namely excited states associated with electron addition and removal, have been well-studied for acene molecules with a variety of computational approaches, including density functional theory (DFT), many-body perturbation theory (MBPT), and wavefunction-based quantum chemistry methods, and hence constitute an excellent benchmark case for the development and refinement of methods. Additionally, aspects of charged excitations for acenes are still not entirely understood. For example, anion states of benzene and naphthalene are unbound, and hence challenging to measure; further, whether measured excitations are strictly vertical or adiabatic can be ambiguous.

Numerous theoretical approaches can be used to compute charged excitations, including wavefunction-based methods, such as coupled cluster techniques and quantum Monte Carlo (QMC), as well as DFT and MBPT. While wavefunction-based methods are regarded as highly accurate and the gold standard, they exhibit poor scaling and are currently intractable for many complex systems. On the other hand, MBPT within the $GW$ approximation, a Green’s function-based approach built upon Kohn-Sham DFT wavefunctions and eigenvalues, scales more modestly with the number of basis functions and is broadly applicable to a range of molecules, solids, surfaces, and nanostructures. It is therefore useful to quantify the performance of $GW$ approaches relative to high-accuracy wavefunction-based methods for molecular systems, such as the acenes.

Previous studies have benchmarked $GW$
calculations against experiment and couple-cluster techniques for small- to medium-sized molecules, including some acenes. In particular, these works have examined the performance of different DFT starting points and self-consistent GW (see Section 2.2 for details), and have found that some GW approaches are more predictive for charged excitations in organic molecules than others. However, as valuable as these studies are, they, by design, were not all-inclusive; further, there has yet to be a report of trends for charged excitations across a series of acenes of increasing size.

In this work, we calculate ionization potentials (IPs) and electron affinities (EAs) of acenes, from benzene to hexacene, using MBPT within the GW approximation. We compare our GW results to highly-accurate coupled-cluster calculations, with single, double, and perturbative triple excitations [CCSD(T)]. Since prior CCSD(T) reference calculations relied on extensive extrapolations, especially for the larger acenes, we perform new CCSD(T) calculations and include a comparison to these new results. For completeness, we also benchmark recently-developed exchange-correlation DFT functionals that make use of a system-dependent non-empirically determined amount of exact exchange via the optimally-tuned range-separated hybrid (OTRSH) class of functionals. Special attention is given to the accuracy of approximations within GW: we test convergence issues; the performance of DFT starting points for GW, including global hybrids and OTRSHs; and the performance of eigenvalue self-consistent GW approaches (see Section 2.2 for details).

2 Theoretical methods

For small gas-phase molecules, such as the acenes considered here, in principle, IPs and EAs can be determined from DFT via total energy differences between charged and neutral species. However, this ∆SCF approach is limited to frontier orbital energies, ill-defined for states above the vacuum energy (i.e., with negative EA), and can be inaccurate especially for large molecules due to the nature of approximate DFT exchange-correlation functionals. In this work, we produce a quantitative benchmark of ab initio MBPT within the GW approximation, an alternative and more general approach for electron addition and removal energies of acene molecules. Our GW calculations are based on DFT and, as we will show below, they are quantitatively dependent on the solutions to the underlying generalized Kohn-Sham equations (and therefore sensitive to the functional used). Moreover, recent developments in generalized Kohn-Sham DFT suggest that appropriately-constructed exchange-correlation functionals can lead to accurate charged-excitation spectra. In the following sub-sections, we describe our GW approach after first summarizing a class of range-separated hybrid (RSH) functionals that we use both as a starting point for our GW calculations and as an independent reference for comparison with GW.

2.1 Optimally-tuned range separated hybrid functionals

We first consider two representative tuned range-separated hybrid DFT schemes: the Baer-Neuhauser-Lifshitz (BNL) functional (see details in Ref. 34) and a recent OTRSH functional, described below. OTRSH partitions the Coulomb operator to balance exact exchange with generalized gradient approximation (GGA) exchange and correlation as:

\[
\frac{1}{r_{12}} = \frac{\alpha}{r_{12}} + \frac{\beta}{r_{12}} \left(1 - \left(\alpha + \beta \text{erf}(\gamma r_{12})\right)\right),
\]

where, in this case, the first term is treated with Hartree Fock (HF) and the second is treated with the GGA Perdew-Burke-Ernzerhof (PBE) functional. This partition leads to the following form of the OTRSH exchange correlation energy:

\[
E_{xc}^{\text{OTRSH}} = \alpha E_x^{\text{HF}} + (1 - \alpha - \beta) E_x^{\text{PBE}} + \beta E_x^{\text{HF,LR}}(\gamma) + \beta E_x^{\text{PBE,SR}}(\gamma) + E_c^{\text{PBE}},
\]
where $E_{c}^{\text{PBE}}$ is the PBE correlation energy and the mixing parameters $\alpha$, $\beta$, and $\gamma$ are tuned so as to fulfill exact conditions and theorems of DFT.\(^\text{22}\)

Although $\alpha$ can be determined from first principles in some cases,\(^\text{29–31,38–39}\) we follow Refs.\(^\text{29}\)\(^\text{30}\) and \(^\text{40}\) and set $\alpha$ to 0.2, corresponding to a fraction of short-range exchange similar to that of a conventional hybrid functional. Additionally, we set $\alpha + \beta = 1$ to enforce long-range asymptotic exact exchange. Then, $\gamma$, the range-separation parameter, is varied to achieve a minimization of the target function

$$ J^2(\gamma) = [\text{IP}^\gamma(N) + E_{\text{HOMO}}^\gamma(N)]^2 \quad + \quad [\text{IP}^\gamma(N+1) + E_{\text{HOMO}}^\gamma(N+1)]^2, $$

where $\text{IP}^\gamma(N)$ is determined via a $\Delta SCF$ approach from total energy differences as $\text{IP}^\gamma(N) = \epsilon_{\text{tot}}^\gamma(N) - \epsilon_{\text{tot}}^\gamma(N-1)$, where $\epsilon_{\text{tot}}^\gamma(N)$ and $\epsilon_{\text{tot}}^\gamma(N-1)$ are total energies of the neutral and cation species respectively. This procedure is often referred to as “gap-tuning”.\(^\text{22}\) and in the limit of vanishing $J^2(\gamma)$, this enforces the ionization potential theorem of DFT, namely that minus the energy of the Kohn-Sham highest occupied molecular orbital (HOMO) equals the first ionization potential energy.\(^\text{11–13}\) For both benzene and naphthalene, the $N + 1$ anionic state is unbound, so only the first of these two terms is minimized. Within this framework, the optimal $\gamma$ parameters for benzene through hexacene are found to be 0.25, 0.21, 0.19, 0.17, 0.15, and 0.14 bohr\(^{-1}\) respectively.

In this work, all OTRSH and BNL calculations are performed with the Q-Chem 4.2 software package\(^\text{18–20,54–57}\) and all geometries are relaxed with Q-chem with DFT using the B3LYP\(^\text{17–18}\) functional and a cc-pVTZ basis set.

### 2.2 Many body perturbation theory within the GW approximation

In MBPT, the $GW$ approximation consists of a closed set of equations for the Green’s function $G$, the screened-exchange $W$, and the electronic self-energy

$$ \Sigma(r,r',\omega) = i \int d\omega' e^{i\omega'} G(r,r',\omega + \omega') \times W(r',r,\omega'), $$

which is non-local, non-Hermitian, and frequency dependent.\(^\text{11–12,24}\) A fully self-consistent solution of the $GW$ equations using large basis sets is currently unfeasible for most systems of interest and further approximations are required. Most frequently, the $GW$ self-energy is applied perturbatively as a first-order correction to generalized Kohn-Sham states obtained from a DFT calculation. This is the so called “one-shot” $GW$ or $G_0W_0$, in which for a given $i$th state, the Kohn-Sham (KS) wavefunction $|i\rangle$ is kept constant and the corresponding eigenvalue $E_i$ is corrected, as follows:\(^\text{53}\)

$$ E_i^{\text{QP}} = E_i^{\text{KS}} + \langle i | \Sigma(\omega = E_i^{\text{QP}}) - \nu_{xc} | i \rangle. $$

It follows directly from the previous expression that the one-shot $GW$ result may depend much on the quality of the underlying exchange-correlation (XC) functional.

A well-known workaround is to use an XC functional whose generalized Kohn-Sham mean-field spectrum is closer to the actual charged excitation energies, a so-called improved starting point, e.g. hybrid functionals.\(^\text{15–18,23–24}\) In this work, we will consider some promising hybrid functionals that have been identified in previous studies,\(^\text{54–55}\) including PBE0\(^\text{56}\) and BHLYP\(^\text{17}\) with 25% and 50% exact exchange, respectively. We will also consider the OTRSH functional\(^\text{18}\) described above. In the following, we indicate the mean-field starting point with an “@” sign, i.e., $G_0W_0@PBE0$, $G_0W_0@BHLYP$ and $G_0W_0@OTRSH$, to refer to one-shot $GW$ on top of PBE0, BHLYP and OTRSH, respectively.

Another approach to mitigate starting-point dependence would be to perform a self-consistent calculation.\(^\text{57–59}\) An approximate self-consistent scheme that only updates the eigenvalues entering $\Sigma$, while keeping the KS wavefunctions frozen, has been highlighted.
for molecules recently with promising results. This scheme is known as eigenvalue self-consistent GW, or “evGW”, and involves the iterative updating of the eigenvalues in both the Green’s function G and the screened Coulomb interaction W. A partial eigenvalue self-consistent scheme that only updates eigenvalues in G and not in W has been proposed and used extensively for solids.64 This approach, “evGW0”, has been previously reported to be less effective for molecules,63 but we test it here for completeness. In this work, we perform three to four iterations to converge the partial self-consistent GW results within 0.01 eV; when using a “good” GW starting point (with energies close to the evGW solution, such as BHLYP) only two iterations are needed to reach the same convergence threshold for the molecules considered here.

2.3 GW calculations in a Gaussian basis

Our GW calculations, and the computations generating our DFT starting points, are performed with molgw65 code, using Gaussian basis sets. A comprehensive description of this code can be found in Refs. 58, 54 and 66; but briefly, after a self-consistent DFT calculation, molgw evaluates the GW self-energy via a spectral representation of the dynamical polarizability χ, allowing analytical calculation of the self-energy without any loss of information; i.e., χ is calculated exactly in a given basis set. molgw makes use of external libraries for the evaluation of electron repulsion integrals, LibINT,67 and for exchange-correlation potentials, LibXC.68

The present study uses relatively large basis sets; e.g., hexacene C_{26}H_{16} in aug-cc-pVTZ requires as many as 1564 basis functions. To deal with these large systems, four-center integrals are evaluated approximately via an approach referred to as the resolution-of-the-identity in the Coulomb metric.69,70 This approximation has been used successfully in past GW calculations10,11,12,23 and it leads to a drastic reduction in the computational burden: the scaling of the atomic to molecular orbital transforms is reduced to N^4 from N^5. More specifically, this method involves approximating the 4-center electron repulsion integrals according to

\[ \langle \alpha\beta | \frac{1}{r} | \gamma\delta \rangle \approx \sum_{PQ} \langle \alpha\beta | \frac{1}{r} | P \rangle \langle P | \frac{1}{r} | Q \rangle^{-1} \langle Q | \frac{1}{r} | \gamma\delta \rangle, \] (6)

where Mülliken notation is used. The Greek letters represent the basis functions for the wavefunction, whereas the capitals P and Q run over an auxiliary basis set. In practice, we use an approach71 in which the square root of the matrix \( P | \frac{1}{r} | Q \) is calculated and thus the evaluation of Eq. (6) is further accelerated.

The accuracy of the approximation in Eq. (6) relies critically on the ability of the auxiliary basis set to represent the Coulomb interaction properly. In this work, we use the well-established auxiliary basis sets of Weigend,70 an atom-centered basis consistent with the Dunning basis.74 We have explicitly determined that approximate use of the resolution-of-the-identity affects the GW energies by at most 1 meV in the case of benzene.

molgw analytically treats the frequency dependence of Σ by calculating the polarizability χ within the random-phase approximation. Then χ is written as a matrix containing all the single excitations available in the basis set, except for the carbon 1s states which are kept frozen. Therefore, the only convergence criteria is the basis set size, which will be carefully checked below.

2.4 Basis set convergence

As mentioned above, in this work we use the augmented basis sets of Dunning,74 which are designed to converge smoothly towards the complete basis set limit (CBS). For simplicity, we refer to these basis sets as aDZ, aTZ, and so on, instead of their full-length names aug-cc-pVDZ, aug-cc-VTZ, etc.

In Figure 2 we show the convergence of our calculated values for the ionization potential (IP), the electron affinity (EA), and the IP–EA gap with respect to basis set size for benzene to hexacene. All results are obtained with
$G_0W_0@PBE0$. The basis set is increased in size in the aug–pVnZ series from n=D to 5. To better compare the rate of convergence across the acene series, we have set their aDZ values equal to zero in each case. For anthracene ($n = 3$) and larger acenes, we forgo some calculations with the largest basis sets, aug–pV5Z and aug–pVQZ, due to the significant computational burden.

We find that the calculated IPs and EAs converge monotonically and are well-fit with a simple function, as indicated in Figure 2. Remarkably, the IPs and EAs of all acene molecules converge in the same manner, independent of the length of the molecule. In fact, the energy difference between IPs/EAs calculated with the aTZ basis set and the CBS limit is $\sim 0.26$ eV. Thus, one may evaluate IPs and EAs at the CBS limit for these molecules by first performing $GW$ calculations with the aTZ basis set, and then adding 0.26 eV.

## 3 Ionization potentials and electron affinities

### 3.1 Obtaining reference values

Here, we revisit CCSD(T) IP energies in the CBS limit for acene molecules, following the focal point analysis (FPA) approach laid out in Ref. [10]. In the FPA, CCSD(T) best estimates are obtained from single-point calculations at the restricted-HF level and adding incremental improvements to the correlation energy at the second-, third- and partial fourth-order Møller-Plesset levels (MP2, MP3 and MP4SDQ). In turn, these are followed by improvements from coupled-cluster calculations including singles and doubles (CCSD) and a perturbative estimate of the triples (CCSD(T)), and by extrapolating to the CBS limit using Dunning basis sets of increasing size. Interestingly, the data in Ref. [10] exhibit a significant break of $\sim 0.1$ eV in the trend along the oligoacene series at hexacene. Exploring this further, we find that the MP3 contribution to CCSD(T) is not entirely converged for hexacene, and as indicated in Table S1 of the SI, the MP3 basis set size dependence increases with increasing system size. By repeating the FPA and extrapolating the MP3 corrections from trends observed in smaller acenes and basis sets, we find a difference of $-0.1$ eV in the resulting IP of hexacene with respect to Ref. [10]. Our resulting CCSD(T) best theoretical estimates (BTEs) for the vertical IPs are shown in Table 1. Our CCSD(T) calculations are performed with the Gaussian 09 E.01 code with standard settings, including core electrons in the correlation computation and neglecting relativistic effects as usual. Details of our calculations and analysis of the FPA in Ref. [10] are provided in the SI. In addition, we adopt the EA CCSD(T) reference values of Ref. [76].

| Ref. [10] | This work |
|-----------|-----------|
| Benzene   | 9.45      | 9.44 ± 0.01 |
| Naphthalene | 8.24     | 8.25 ± 0.01 |
| Anthracene | 7.47      | 7.48 ± 0.03 |
| Tetracene  | 6.95      | 6.96 ± 0.03 |
| Pentacene  | 6.57      | 6.58 ± 0.03 |
| Hexacene   | 6.43      | 6.32 ± 0.03 |

### 3.2 Charged excitations with GW and DFT-OTRSH

In this section, we present and discuss IPs and EAs calculated using DFT-OTRSH and $GW$, comparing to our CCSD(T) BTEs as defined in the previous section. Experimental values for IPs and EAs of the acenes are given in Refs. [77–79] and are described as vertical; however, recent work [9,10] with CCSD(T) has suggested that these values are actually adiabatic since their best adiabatic estimates match the experimental values within 0.02 eV. Note that the naphthalene EA of 0.190 eV measured by electron transmission spectroscopy [12] first as-
described as vertical, is now considered adiabatic due to the presence of vibrational features in the spectrum.\textsuperscript{80} For these reasons, we choose not to compare explicitly with experiments in this work and instead benchmark against high-level CCSD(T) calculations: we use our own CCSD(T) IPs, as shown in Section 3.1 and take CCSD(T) EAs from Ref. \textsuperscript{9}. We note that vertical IP/EAs of anthracene calculated with QMC are in excellent agreement with our CCSD(T) references.\textsuperscript{11}

In Figure 3, calculated charged-excitations are compared to the CCSD(T) reference data (in black dotted lines and squares). For clarity, only a few representatives of each GW and DFT scheme are shown; \( G_0W_0 @ \text{BHLYP} \) (blue dashed lines and crosses), \( G_0W_0 @ \text{OTRSH} \) (pink dotted lines and filled circles), \( \text{evGW@BHLYP} \) (green lines and crosses) and OTRSH (yellow dashed lines and circles). Note that quantum Monte Carlo data\textsuperscript{11} (dark-grey triangles) agree well with the CCSD(T) BTE values for anthracene. For completeness, the mean signed deviation (MSD = \( 1/N \sum_i^{N_i} E_i - E_{\text{ref}} \)) and mean absolute deviation (MAD = \( 1/N_i \sum_i |E_i - E_{\text{ref}}| \)) with respect to the CCSD(T) BTEs for all of the approximations considered in this work are shown in Figure 4.

In Figure 3, we plot the IP/EA/gap calculated with OTRSH in yellow circles and dashed lines; the calculations shown here agree well (within 0.05 eV) with previous works.\textsuperscript{28,30} For benzene, the OTRSH IP and EA are in perfect agreement with the CCSD(T) reference. However, the agreement deteriorates for larger acenes, in agreement with Ref. \textsuperscript{28}, possibly due to the fact that as OTRSH is tuned to fulfill the DFT ionization potential theorem, its performance is dependent on the reliability of ΔSCF; larger molecules can show larger frontier-orbital delocalization and ΔSCF is known to perform poorly when orbitals are delocalized, e.g. in the asymptotic limit of infinite molecules and in extended systems due to approximate exchange-correlation potentials.\textsuperscript{23,51,54} Note that BNL gives the best overall agreement to the reference values, with an MAD of only \( \sim 0.1 \) eV for the IPs, EAs and gaps, as already found in Ref. \textsuperscript{85} OTRSH exhibits a larger MAD, e.g. \( \sim 0.3 \) eV for the IP–EA gap.

We now turn to our results with \( G_0W_0 \). First, \( G_0W_0 @ \text{PBE} \), severely underestimates the QP gaps, with a MAD of \( -1.0 \) eV, in agreement with previous findings.\textsuperscript{16,18,54,86} The shortcomings of \( G_0W_0 @ \text{PBE} \) are well-known and discussed in Refs. \textsuperscript{16,18,54}. Note that standard \( G_0W_0 \) calculations of charged excitations of the acenes have been reported using plane-wave approaches,\textsuperscript{21,30,85,86} and the level of convergence and the nature of the frequency-integration schemes can lead to qualitative differences from the work presented here that are well documented.\textsuperscript{28,64}

One known strategy to improve over \( G_0W_0 @ \text{PBE} \) is to use an XC functional with a fraction of exact exchange as starting point.\textsuperscript{17,54} We find that the global hybrid providing the best results (lower MAD) is \( G_0W_0 @ \text{BHLYP} \), which has an MAD of 0.3 eV in the calculated IP–EA acene gaps (See Figure 4), good accuracy at a reasonable computational cost. Notably, the OTRSH starting point leads to highly accurate QP energies, with a MAD for the IP–EA gap of only 0.2 eV, and in close agreement with more expensive ev\textit{GW} schemes (see Figure 3).

The excellent performance of \( G_0W_0 @ \text{OTRSH} \), as hypothesized in Ref. \textsuperscript{29} is consistent with the conclusions of Gallandi and Körzdörfer\textsuperscript{19} who explored several \textit{GW} approaches and found that a tuned long-range separated hybrid (namely the IP-tuned LC-\( \omega \text{PBE} \)\textsuperscript{28} equivalent to OTRSH with \( \alpha = 0 \) and \( \beta = 1 \)) \( G_0W_0 \) starting point yields charged excitation energies within 0.1 eV of experiment and ev\textit{GW} in a set of molecules that includes some (but not all) of the acenes. Their work was extended in Refs. \textsuperscript{20} and \textsuperscript{26} where a CCSD(T) reference was used, and where it was reported that the LC-\( \omega \text{PBE} \) starting point leads to the smallest MAD (0.2 eV for EAs and 0.1 for IPs) in a set of short- to medium- sized molecules. In agreement with the findings of Ref. \textsuperscript{26}, the RSH starting point for \( G_0W_0 \) with fixed \( \alpha \) and \( \gamma \) parameters can lead to the same level of accuracy than \( G_0W_0 @ \text{OTRSH} \) in the IP and EA energy levels of the acene molecules (with a MAD of \( \leq \)
0.3), see Sect. 2 of the SI for details. Prior calculations, including some acene molecules, report that the PBE0 starting point provides the best overall QP energies relative to photoemission experiments along a broad energy range; here, we compare to CCSD(T) and focus only on the frontier molecular levels.

A second approach known to provide accurate QP energies is eigenvalue self-consistency. Here, we test two different levels of eigenvalue self-consistency: partial self-consistency, updating eigenvalues only in \( G \) (\( \text{ev} GW_0 \)); and full self-consistency, updating eigenvalues in both \( G \) and \( W \) (\( \text{ev} GW \)). We find that \( \text{ev} GW_0 \) leads to unsatisfactory results for these molecules, unless \( W_0 \) from BHLYP is used, e.g., \( \text{ev} GW_0 \text{@PBE} \), \( \text{ev} GW_0 \text{@PBE} \) and \( \text{ev} GW_0 \text{@BHLYP} \) result in a MAD of 0.7, 0.4 and 0.3 eV, respectively, for the IP–EA gap. Moreover, no clear improvement is found with \( \text{ev} GW \) over \( G_0 W_0 \text{@BHLYP} \); the two approaches result in nearly equivalent QP energies (within 0.05 eV). On the other hand, \( \text{ev} GW \) results in overall good agreement to the reference values, with an MAD of \( \sim 0.2 \) eV for the QP gap (see Figure 4). We also highlight that there is not much spread in the \( \text{ev} GW \) QP energies with respect to the DFT starting point; in fact, the \( \text{ev} GW \) gap of benzene is predicted to be 10.9 eV independent of the DFT starting points considered here. For larger molecules, \( \text{ev} GW \) with different starting points can, in some cases, lead to more appreciable differences: for example, a difference of 0.2 eV in QP is observed with PBE or BHLYP starting points for tetracene. In Ref. 17 by considering the extreme starting-points, PBE and HF (with 0% and 100% exact exchange, respectively), a larger difference (\( \sim 0.4 \) eV) was found in the resulting \( \text{ev} GW \) gaps of organic molecules. Nevertheless, the starting-point dependence of \( \text{ev} GW \) is less than in the case of \( G_0 W_0 \), which is typically \( \sim 1.4 \) eV for aromatic molecules. Hence, the \( \text{ev} GW \) method is an attractive approach due to its relatively-minimal starting-point dependence and good accuracy, in spite of its higher cost with respect to one-shot \( G_0 W_0 \).

The \( \text{ev} GW \) and \( G_0 W_0 \) approaches and their corresponding self-energy corrections are linearly correlated. In Figure 5, we show corrections to the IP–EA gap \( \text{[gap}(GW) − \text{gap}(\text{DFT})] \) obtained from both \( G_0 W_0 \) and \( \text{ev} GW \). As expected, \( \text{ev} GW \) leads to larger gaps than \( G_0 W_0 \text{@PBE} \). Interestingly, independent of starting point, we find that our \( G_0 W_0 \) corrections are consistently 87% of the corresponding \( \text{ev} GW \) corrections (see dashed blue line in Fig. 5 with a slope of 0.87 and a standard deviation of \( < 0.01 \) eV). Note that six points between 4 and 7 eV lie slightly below this linear trend (dashed blue line); these points use a PBE starting point and are best fit with a slightly smaller slope of 0.85 (not shown). This simple relation, consistent with the tendency of \( G_0 W_0 \) to underestimate gaps due to over screening and the fact that the screening is similar enough across the acene series, would allow for an accurate estimation of the \( \text{ev} GW \) gap from \( G_0 W_0 \) corrections for acenes, or even of the \( G_0 W_0 \) gap from other DFT starting points.

![Figure 5](image-url)

**Figure 5:** Correlation and linear fit between \( \text{ev} GW \) gaps and their corresponding \( G_0 W_0 \) gaps for the oligoacenes. Results of \( GW \) calculations with PBE, PBE0 and BHLYP starting points are used in constructing this plot. All energies are in units of eV.

In agreement with recent work, we find that RSH or \( GW \) can provide highly accurate frontier orbital energies for small acenes; for benzene, OTRSH and \( GW\text{@OTRSH} \) gives...
IPs and EAs within 0.1 eV of the CCSD(T) reference. For medium-sized molecules the accuracy of both RSH and GW decreases; for hexacene OTRSH presents deviations of \(\sim 0.3\) eV in both the IP and the EA, adding to an MAD of \(\sim 0.6\) eV in the gap; the more accurate GW approaches tested in this work (\(GW@OTRSH\), \(GW@BHLYP\) and \(evGW\)) predict IPs within 0.1 eV but can overestimate EAs by up to \(0.4 - 0.5\) eV (see Fig. 3). Nevertheless, since the deviation grows linearly with the number of rings \((N_{\text{ring}})\), the EAs can be linearly extrapolated from the GW results as:

\[
EA = EA_{GW@OTRSH} - (0.087\ eV)N_{\text{ring}} + 0.06\ eV,
\]

where we have subtracted a linear function of the number of rings from the \(GW@OTRSH\) EA energies, and obtained the EA energies within 0.02 eV of the CCSD(T) reference. This simple relation, though effective here, may not be transferable to other aromatic hydrocarbon families, and in general will not be applicable for any other non-ringed system; \(GW\) calculations beyond the approaches used in this work may yield further insight into this trend. It is worth noticing that wavefunctions of larger acenes have some multi-reference character, which might explain the observed limited performance of GW in the large molecule regime.

In this work we fix the fraction of short-range exact exchange in all DFT-RSH calculations; thus one straightforward extension is to tune the \(\alpha\) parameter with theorems of DFT, along the lines of Refs. 38, 29 and 39. Tuning the short-range HF parameter may lead to a better description of systems with localized electrons; nevertheless, for the acenes, with only \(s\) and \(p\) electrons, it is not evident a priori that such tuning would improve the accuracy of both OTRSH and GW based on an OTRSH starting point. In fact, for benzene and pentacene, setting \(\alpha\) to either 0.0 or 0.2 leads to negligible changes (by \(< 0.1\) eV) in the IPs or EAs, as shown in Refs. 29 and 31. Further, when it comes to the \(\pi\) and \(\pi^*\) orbital energies of representative organic molecules, it has been shown in Ref. 26 that the tuning of the \(\alpha\) parameter does not significantly affect the performance of OTRSH or \(G_0W_0@OTRSH\). Beyond eigenvalue self-consistent GW, total energy differences from \(GW\) might also result in more accurate frontier orbital energies. We leave these considerations to be explored in future work.

In summary, our results indicate that going beyond standard \(G_0W_0\) is crucial to achieve CCSD(T) accuracy; including self-consistency, such as in the \(evGW\) method, or adding a fraction of exact exchange are both successful strategies for describing charged-excitations. Notably, using OTRSH as a starting point for \(G_0W_0\) provides highly accurate energetics relative to CCSD(T), in agreement with the more expensive \(evGW\) results.

### 4 Conclusions

In this work, we have calculated IPs and EAs of acene molecules with DFT, GW, and wavefunction-based approaches. We have built upon and extended the CCSD(T) reference data of Ref. 10 for IPs of the larger acenes. Using this new CCSD(T) reference, we have benchmarked GW under several approximations and DFT with range-separated hybrid methods and found that both \(G_0W_0@OTRSH\) and \(evGW\) consistently perform well, yielding quantitative IP energies within 0.1 eV of CCSD(T) across the acene series. Nevertheless, all GW approaches studied here lead to qualitative deviations for the larger acenes, suggesting the need to go beyond eigenvalue-self-consistent GW methods to do better. Moreover, we have found that DFT with OTRSH or BNL functionals can perform as well as the most effective GW approaches for benzene, but their resulting IPs and EAs deteriorate as the molecules get larger in the series, a behavior attributable to the known deficiencies of \(\Delta\text{SCF}\) in the asymptotic limit of large molecules towards extended systems.

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Supporting Information Available: We tabulate all charged excitation energies calculated in this work, we provide the relaxed geometries used in this work, and we give a detailed explanation on the way we obtain the revised CCSD(T) data. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Figure 2: Convergence of charged excitations with respect to the basis set size for the oligoacene molecules within \( GW \) based on a PBE0 starting point. Calculated IP–EA gap energies \( (E_g) \) converge fast with respect to the basis set size, whereas IPs and EAs are extrapolated to the basis set (CBS) limit using a function of the form \( f(x) = a + b/(x - x_0) \) (dotted-blue lines). Note that as the molecule size increase, calculations with large basis sets become unfeasible, and hence some points are omitted in the figures. For convenience, we show the energy difference with respect to the results obtained with the aDZ basis, \( \Delta E_{aDZ} = E - E_{aDZ} \); In fact, points for different molecules overlap making evident that all quantities converge at similar rates for the different molecules considered here.

Figure 3: Charged excitations of oligoacenes calculated within \( GW \) and DFT are compared to CCSD(T); our IPs in Table 1 and EAs from Refs. 9. Calculated IP–EA gaps, vertical ionization potentials (IP), electron affinities (EA) and their corresponding difference with respect to the theoretical reference, \( \Delta \), are shown in panels a - f. Several \( GW \) approaches are considered (see text). For comparison, quantum Monte Carlo (QMC) data from Ref. 11 for anthracene are also shown.
Figure 4: Top: Mean absolute deviation (MAD) with respect to the theoretical reference [CCSD(T)] in the calculated IPs (green bars), EAs (orange bars) and IP–EA gaps (blue bars) of the acene family of molecules. Bottom: Mean signed deviation (MSD). Several DFT and GW approximations are considered (see text).
