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Piecewise linearity in the GW approximation for accurate quasiparticle energy predictions

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We identify the *deviation from the straight-line error* (DSLE)—i.e., the spurious nonlinearity of the total energy as a function of fractional particle number—as the main source for the discrepancy between experimental vertical ionization energies and theoretical quasiparticle energies, as obtained from the GW and GW +SOSEX approximations to many-body perturbation theory (MBPT). To check whether a DSLE is present in GW , we propose an indicator that only invokes observables at integer particle numbers. For self-consistent calculations, we show that GW suffers from a small DSLE. Conversely, for perturbative G_0W_0 and G_0W_0 +SOSEX calculations the DSLE depends on the starting point. We exploit this starting point dependence to reduce (or completely eliminate) the DSLE. We find that the agreement with experiment increases as the DSLE reduces. DSLE-minimized schemes thus emerge as promising avenues for future developments in MBPT.

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Electronic structure theory has developed into an essential tool in materials science because it offers a parameter-free, quantum mechanical description of solids, molecules, and nanostructures. This success is due to the continuous development of electronic structure methods such as density-functional theory (DFT) [1] and many-body perturbation theory (MBPT) in the GW approximation [2]. This development is guided in part by comparisons with experimental reference data and in part by exact constraints, imposed by the theoretical framework itself. We will demonstrate in this Rapid Communication that invaluable insight into the GW approach can be gained from such an exact constraint. The GW method has long been heralded as the method of choice for band gaps and band structures of solids and quasiparticle spectra of molecules and nanostructures [3–5]. Yet, its accuracy is not always satisfying and the starting point dependence in the perturbative G_0W_0 variant can be very pronounced [5–7]. Here, we will show that the accuracy of GW is closely related to the exact constraint that the ionization energy of the neutral system must equal the electron affinity of the cation, which is a direct consequence of the piecewise linearity of the total energy [8]. Its violation gives rise to the *deviation from the straight-line error* (DSLE), which has been extensively studied in DFT [9–14]. The starting point dependence in G_0W_0 can then be exploited to minimize the DSLE, which uniquely defines the optimal starting point.

In 1982 Perdew *et al.* showed that the total energy of a quantum mechanical system has to change linearly with respect to the fractional removal (or addition) of an electron [8],

$$E(f) = (1 - f)E(N_0 - 1) + fE(N_0). \quad (1)$$

Here, N_0 is the number of electrons in the neutral system and $E(N_0)$ the associated total energy. $E(N_0 - 1)$ is the total energy of the singly ionized system and f varies in the interval $[0, 1]$. This piecewise linearity condition was initially derived in the context of DFT, but applies to any total energy method.

In the following, we introduce a formal definition of the deviation from linearity at fractional occupation numbers that

employs only quantities directly accessible by quasiparticle energy calculations, that is, the ionization potential (IP) and the electron affinity (EA). The linearity condition in Eq. (1) implies that the first derivative of the total energy with respect to the fractional occupation number f (i.e., $\partial E/\partial f$) should be constant and that it exhibits discontinuities at integer occupations ($f = 0$ and $f = 1$). Additionally, $\partial E/\partial f$ equals the electron removal energy $E(N_0) - E(N_0 - 1)$ or, equivalently, the energy for adding an electron to the positively charged system. Therefore, the vertical IP of the neutral system with N_0 electrons can be expressed as

$$\left. \frac{\partial E(f)}{\partial f} \right|_1 = E(N_0) - E(N_0 - 1) = -\text{IP}(N_0). \quad (2)$$

A similar relation holds for the electron affinity of the cation (EA_c):

$$\left. \frac{\partial E(f)}{\partial f} \right|_0 = E(N_0) - E(N_0 - 1) = -\text{EA}_c(N_0 - 1). \quad (3)$$

Equations (2) and (3) illustrate that $\text{IP} = \text{EA}_c$ in an exact theory. We thus define the difference between IP and EA_c as the DSLE,

$$\Delta_{\text{DSLE}} = \text{EA}_c(N_0 - 1) - \text{IP}(N_0). \quad (4)$$

$\Delta_{\text{DSLE}} = 0$ is a necessary condition for piecewise linearity. However, in an approximate treatment of electronic exchange and correlation, as, e.g., in GW , IP and EA_c may differ. A nonvanishing Δ_{DSLE} indicates a curvature in the total energy versus fractional electron number curve, as illustrated in Fig. 1, causing an erroneous deviation from the straight line [15,16].

The DSLE is most easily seen in the deviation from the straight line

$$\Delta E(f) = E(f) - E_{\text{lin}}(f), \quad (5)$$

where, following Eq. (1), $E_{\text{lin}}(f)$ is the straight line between $E(N_0)$ and $E(N_0 - 1)$. We will first examine the DSLE and Eq. (5) for different DFT functionals before proceeding to our GW analysis [17]. In DFT, common (semi)local functionals typically exhibit a convex curvature and suffer from a large

FIG. 1. Schematic representation of the DSLE for total energies E (left) and their derivatives $\partial E/\partial f$ (right) as a function of the occupation number f .

DSLE, whereas Hartree-Fock (HF) is concave with a moderate DSLE [9–14]. We show this tendency in terms of $\Delta E(f)$ for the examples of the O_2 and the benzene molecule in Fig. 2.

To quantify the DSLE by means of Eq. (4) we use the eigenvalue of the highest molecular orbital (HOMO) of the neutral system ($\epsilon_{N_0}^H$) for $IP(N_0)$ and the eigenvalue of the lowest unoccupied molecular orbital (LUMO) of the cation ($\epsilon_{N_0-1}^L$) for $EA_c(N_0 - 1)$ [8,18–20]. For O_2 , the Perdew-Burke-Ernzerhof (PBE) functional gives $\Delta_{DSLE} = \epsilon_{N_0}^H - \epsilon_{N_0-1}^L = 11.6$ eV, which agrees with the pronounced convexity observed in Fig. 2. For benzene, the DSLE in PBE reduces to half the size ($\Delta_{DSLE} = 5.9$ eV), which is also apparent from the maximal extent of $\Delta E(f)$ in Fig. 2. Conversely, HF exhibits a concave DSLE manifested in $\Delta_{DSLE} = -3.5$ eV for O_2 and $\Delta_{DSLE} = -2.5$ eV for benzene. All in all, the magnitude of Δ_{DSLE} can be taken as a measure for the severity of the DSLE, whereas the sign indicates the curvature. A positive value of Δ_{DSLE} corresponds to a concave and a negative sign to a convex curvature. Convexity gives rise to a delocalization of the electron density and concavity to an overlocalization [9].

We now move on to discuss the DSLE in the GW approximation. In GW , the total energy is only available at integer occupation numbers because a rigorous ensemble

FIG. 2. Deviation from the straight line $\Delta E(f)$ for O_2 (left) and benzene (right). The slopes of ΔE are indicated by arrows obtained by evaluating Eq. (6) with an scGW quasiparticle and total energies or RPA@PBEh($\alpha = 0.6$) total and G_0W_0 @PBEh($\alpha = 0.6$) quasiparticle energies. α defines the fraction of HF exchange in the PBEh(α) hybrid. The blurred curves qualitatively show how $\Delta E(f)$ could behave (see main text for a discussion).

generalization of G to fractional particle numbers has not yet been achieved and might give rise to additional self-energy diagrams at fractional particle numbers [21]. For the exact Green's function our analysis is warranted, because it satisfies Eqs. (2) and (3) and $\Delta_{DSLE} = 0$. Even if diagrams beyond GW would change $\partial E/\partial f$ so that it does not equal the quasiparticle energies at the integer end points of an approximate theory such as GW , $E(f)$ can still not be a straight line if Δ_{DSLE} , as defined by the quasiparticle energy difference in Eq. (4), is not equal to zero. It therefore makes sense to anticipate the severity of the deviation from the straight line by Δ_{DSLE} , which we will discuss for GW in the following.

Another reason for inspecting Δ_{DSLE} is related to the self-screening problem in GW . In the calculation for the $N - 1$ particle system, the screening in W will be that of $N - 1$ electrons and thus typically less than that in the N particle system. This is most evidently seen for one-electron systems such as the hydrogen (H) atom where the calculation for the proton gives the correct screening, i.e., zero, whereas the calculation for the neutral H atom already includes screening [22]. Thus, deviations between $EA_c(N - 1)$ and $IP(N)$ also measure the severity of the self-screening.

Among the different GW flavors only fully self-consistent GW (scGW), in which the Dyson equation is solved iteratively, gives results that are independent of the starting point [23,24]. Therefore, scGW provides an unbiased assessment of the DSLE. Most importantly, in scGW also the ground state is treated at the GW level and the scGW density does not inherit the (de)localization error of the starting point, as is the case in G_0W_0 calculations. First, we evaluate Eq. (4) with the scGW quasiparticle HOMO and LUMO energies and obtain $\Delta_{DSLE} = 0.9$ eV for O_2 . This clearly indicates that self-screening and a DSLE is present in scGW calculations. Making the analogy to the DSLE in DFT, $\Delta_{DSLE} = 0.9$ eV would indicate convexity in the GW total energy curve, however, much less pronounced than in PBE.

Extending the DFT DSLE analogy, we would like to estimate how the GW total energy would behave if it could be calculated for fractional particle numbers. For this we assume that an ensemble generalization of GW exists and that potential additional diagrams yield only a negligible contribution near integer particle numbers. The slopes of ΔE then are

$$\partial \Delta E / \partial f = \partial E / \partial f - \partial E_{lin} / \partial f. \quad (6)$$

For the reference straight line we use $\partial E_{lin} / \partial f = E(N_0 - 1) - E(N_0)$. Identifying the GW quasiparticle energies with the electron affinity, respectively, the ionization potential, allows us to connect $\partial E / \partial f$ with the GW quasiparticle energies according to Eqs. (2) and (3). Equation (6) then becomes

$$\frac{\partial \Delta E}{\partial f} = \begin{cases} \epsilon_{N_0}^H + E(N_0 - 1) - E(N_0) & \text{for } N_0, \\ \epsilon_{N_0-1}^L + E(N_0 - 1) - E(N_0) & \text{for } N_0 - 1, \end{cases} \quad (7a)$$

$$(7b)$$

where we calculate the total energies $E(N_0 - 1)$ and $E(N_0)$ with scGW [23,24]. The resulting slopes are displayed as arrows in Fig. 2. For the example of O_2 , the slopes at the two end points of the scGW curve confirm the convex behavior predicted by Δ_{DSLE} , because they are pointing in different

FIG. 3. Left panel: Average Δ_{DSLE} for the $G2_{\text{ip}}$ set. Right panel: Mean average error (MAE) of the ionization potential.

directions, i.e., they have different signs. The behavior between the end points can be schematically illustrated in the spirit of DFT total energies. Since we cannot calculate intermediate points at fractional particle numbers, we indicate a possible behavior schematically by the blurred curves. For our second example, benzene, the behavior is markedly different. The signs of $\partial\Delta E/\partial f$ are equal at both ends of the occupation interval. To connect both end points—again schematically sketched by the blurred curve in Fig. 2— ΔE inevitably has to cross zero at some point. Hence, we expect the ΔE curve to be divided into two regimes. Beginning from the cation, the positive slope at $N_0 - 1$ gives rise to a concave DSLE. When we approach the N_0 electron limit, the positive slope at N_0 requires a convex curvature. For benzene, the absolute value of the slope at $N_0 - 1$ is higher than at the other end of the interval. As a result, we expect the concave deviation on the $N_0 - 1$ side to be more pronounced than the convex part. This is also reflected by a negative Δ_{DSLE} of -0.7eV , which we associate with a concave DSLE.

To provide a comprehensive assessment of the DSLE in the GW approximation, we have further performed calculations for a benchmark set consisting of 48 atoms and molecules selected from the quantum chemical G2 ion test set [25,26] based on the availability of experimental vertical IPs—referred to as $G2_{\text{ip}}$ in the following [27]. For scGW we find a mean DSLE of $\bar{\Delta}_{\text{DSLE}} = -0.5\text{eV}$. The average over the absolute $\bar{\Delta}_{\text{DSLE}}$ amounts to 0.9eV . The scGW DSLE is thus much smaller than that of PBE and HF (Figs. 2 and 3). Our results suggest that scGW predominantly exhibits a concave DSLE and thus has the tendency to overlocalize electron density, which is consistent with previous work [16] on the quasiparticle self-consistent GW approach [28].

Most commonly, GW is not carried out fully self-consistently, but applied in first-order perturbation theory (G_0W_0). This introduces a dependence on the reference ground state encoded in G_0 . Logically, also the DSLE should depend on the chosen starting point.

For O_2 , G_0W_0 calculations based on orbitals and eigenvalues from PBE ($G_0W_0@PBE$) yield an IP of -11.6eV , which differs from the EA_c of the cation (-13.0eV). Thus, $G_0W_0@PBE$ also violates the straight-line condition, as quantified through Eq. (4), which yields $\Delta_{\text{DSLE}} = 1.4\text{eV}$. The positive value of Δ_{DSLE} indicates a convex total energy at fractional particle numbers as in PBE, albeit an order of magnitude smaller than in PBE. Conversely, we find $\Delta_{\text{DSLE}} = -0.6\text{eV}$ with opposite sign if we use G_0W_0 based on the PBE hybrid functional $\text{PBEh}(\alpha)$ with $\alpha = 1$. $\text{PBEh}(\alpha)$ mixes

FIG. 4. Δ_{DSLE} (red), $\partial\Delta E/\partial f$ for O_2 , and benzene at $N_0 - 1$ (blue) and N_0 (black) particles for $G_0W_0@PBEh(\alpha)$ and $\text{RPA}@PBEh(\alpha)$ total energies.

PBE exchanges with HF exchange according to $E_{\text{xc}}^{\text{PBEh}(\alpha)} = E_{\text{c}}^{\text{PBE}} + (1 - \alpha)E_{\text{x}}^{\text{PBE}} + \alpha E_{\text{x}}^{\text{HF}}$ [29,30].

Now one could ask if our DSLE definition may prove useful for the design of novel DSLE-free approaches for quasiparticle energy calculations. Since in our two examples Δ_{DSLE} changes sign for $\alpha = 0$ and $\alpha = 1$, it is conceivable to postulate that an intermediate, optimal α exists for which the DSLE in G_0W_0 is eliminated or at least considerably reduced. To test this postulate, we evaluate the DSLE for several α values in the range $[0, 1]$. As illustrated in the lower panel of Fig. 4, an increasing α gradually decreases Δ_{DSLE} for O_2 and benzene. At an optimal α of ≈ 0.4 for benzene and ≈ 0.6 for O_2 , the DSLE vanishes. Beyond this point, Δ_{DSLE} becomes increasingly negative with a further increase in α , indicating an increasingly concave total energy curve.

We can support the G_0W_0 Δ_{DSLE} results by examining the slopes of ΔE as defined in Eq. (6). Within an approximate ensemble generalization of the noninteraction Green's function G_0 [31,32], G_0W_0 quasiparticle energies become equivalent to the derivative of the total energy in the random phase approximation (RPA) with respect to the particle number [31]. We show $\partial\Delta E/\partial f$ for $N_0 - 1$ and N_0 as a function of α for O_2 and benzene in Fig. 4. Both molecules show the trend expected from the Δ_{DSLE} calculations. Beginning at small α , the slopes support convexity because ΔE falls away from $N_0 - 1$ and rises again approaching N_0 . Conversely, for large α , the signs of the slopes are reversed, implying concavity. Both slopes approach zero around $\alpha = 0.6$ for O_2 and $\alpha = 0.4$ for benzene, which is consistent with the α values for which Δ_{DSLE} vanishes. Figure 2 shows the expected behavior of the total energy for $\alpha = 0.6$.

Next, we return to our benchmark set of 48 molecules. As illustrated in the upper panel of Fig. 5, G_0W_0 exhibits the largest DSLE, when starting from PBE. The DSLE decreases for increasing α and approaches a negative DSLE in the limit of 100% HF exchange that is almost as large in absolute value as for $G_0W_0@PBE$. The optimal α that eliminates the DSLE again amounts to ≈ 0.4 . We also determined the optimal α values for each molecule, individually. Here, too, the optimal α amounts to $\alpha \approx 0.4$ on average.

We now establish a correlation between the DSLE and the agreement with experimental reference data for ionization potentials. For all M molecules of the $G2_{\text{ip}}$ test set, we evaluated the $G_0W_0@PBEh(\alpha)$ HOMO energies for different α and calculated the mean absolute error ($\text{MAE} \equiv \sum_{i=1}^M |\epsilon_i^{\text{H}} - \text{IP}_i^{\text{exp}}|/M$) with respect to the experimental

FIG. 5. Upper panel: Average Δ_{DSLE} for the $G_{2\text{ip}}$ set computed with scGW , G_0W_0 , and $G_0W_0 + \text{SOSEX}$, as a function of the HF exchange parameter α employed in the $\text{PBEh}(\alpha)$ starting point. Lower panel: MAE of the predicted ionization potential depending on the starting point.

vertical IPs [33]. As shown in the lower panel of Fig. 5, the MAE exhibits a minimum at $\alpha \approx 0.4$ when $G_0W_0@PBEh(\alpha)$ becomes DSLE minimized. At this point, the MAE amounts to 0.20 eV [34], which can be seen as the intrinsic accuracy of G_0W_0 based on global hybrid functionals. With increasing DSLE we observe a concomitant increase of the MAE.

As the minimum in the G_0W_0 MAE curve is rather shallow, hybrid functional starting points with 30%–50% HF exchange produce reasonable MAEs. This is consistent with the empirical findings of Bruneval [35], Marom *et al.* [7], and the work of Körzdörfer *et al.* [36].

Consistent with the analysis above, the MAE of scGW (0.36 eV) is slightly higher than for DSLE-minimized G_0W_0 . However, the MAE of the IPs from the total energy difference, in scGW amounts to only 0.22 eV, and is thus comparable to DSLE-minimized G_0W_0 . Our results strongly suggest that the DSLE is largely responsible for the discrepancies between GW quasiparticle energies and experimental ionization energies.

Finally, we illustrate that the concept of DSLE-minimized quasiparticle calculations is generally applicable and can be transferred to other self-energy approximations. Motivated by the good results of renormalized second-order perturbation theory (rPT2) for electron correlation energies [37], Ren and co-workers recently proposed a beyond- GW scheme [38] that combines GW with a second-order screened exchange self-energy ($G_0W_0 + \text{SOSEX}$). In the following, we apply our DSLE analysis to $(G_0W_0 + \text{SOSEX})@PBEh(\alpha)$ calculations for the $G_{2\text{ip}}$ test set. In the upper panel of Fig. 5 we display the corresponding DSLE and in the lower panel the MAE as a function of α . Compared to G_0W_0 , the starting point dependence is weaker and the DSLE is always negative. Also, the DSLE and the MAE are minimized at smaller α values. This confirms our previous, heuristic findings, that rPT2 and $G_0W_0 + \text{SOSEX}$ perform best for starting points that are close to PBE. The smallest MAE amounts to 0.21 eV, which is comparable to G_0W_0 .

In conclusion, we have shown that the DSLE is a prominent source of discrepancy between experimental and theoretical vertical IPs. Through a formal definition of the DSLE for quasiparticle calculations, we show that the GW approach has an intrinsic DSLE of -0.5 eV and a tendency towards concavity, i.e., localization of electrons. We then establish a correlation between the DSLE and the deviation from experimental ionization energies. This allowed us to propose a recipe for obtaining DSLE-minimized approximations to many-body perturbation theory. The DSLE-minimized G_0W_0 and $G_0W_0 + \text{SOSEX}$ schemes give the best agreement with experimental data, as illustrated for the 48 molecules of the $G_{2\text{ip}}$ test set.

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