Improved density matrices for accurate molecular ionization potentials

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The ionization potential and the other quasiparticle energies of electrons in molecules or solids are often evaluated within the *GW* approximation. Though this approximation can be considered as a fantastic tradeoff between accuracy and simplicity, there exist ionization potentials of simple molecules that are unacceptably wrong. We derive here a working approximation to the density matrix that we name the *GW* density matrix. This relatively light approximation improves several physical properties and, in particular, it yields excellent electronic dipoles for the examined molecules. As a direct consequence, the ionization potentials are affected through the change in the electrostatic potential and in the exchange operator. Benchmarking on a set of 34 molecules, we demonstrate that most of the error in the *GW* ionization potentials is indeed eliminated thanks to this simple addition. This contribution is not a vertex correction, but nevertheless it is crucial when going beyond the standard *GW*.

Predicting the ionization potentials (IP) of electrons in a solid or a molecule is a common goal for both physicists and chemists. These calculated quasiparticle energies correspond to the peaks observed in solid-phase or gas-phase photoemission spectroscopy [1]. Calculating the IP is highly nontrivial since it requires in principle the solution of the many-electron Schrödinger equation for ground and excited states. Fortunately, these energies can be elegantly considered within the framework of the many-body perturbation theory (MBPT) [2]. However, the choice of the practical approximations within MBPT is a very delicate matter with no definitive answer as of today.

As a clear sign for this situation, quantum chemists and solid-state physicists have come up with different approximations, even though they all aim at solving the very same electronic Schrödinger equation, The former, targeting atoms and molecules, advocate for an order-by-order expansion with respect to the Coulomb interaction v [3,4]. This gives rise to second-order perturbation theory (PT2), third-order perturbation theory (PT3), etc. The latter, having the purpose of describing periodic and possibly metallic systems, have proposed the so-called *GW* approximation to the self-energy [5], which is an infinite summation over electron-hole pair terms which are summed up in the so-called screened Coulomb interaction W.

The physicists' *GW* approximation has been recognized for a few decades as a wonderful tool to calculate the electronic structure of materials, and in particular the band gaps of semiconductors [6–9]. Recently, the *GW* self-energy has been applied to molecules systematically with an unexpected quality [10–23].

Despite its recent successes for molecular systems, the *GW* approximation still shows surprisingly large errors for the IP of the simplest molecules. As an example, the IP of N_2 and CO deviates by about 0.4 eV with respect to experimental results. In general, we notice that the σ_p orbital quasiparticle energies are always rather poor using the state-of-the-art *GW*

implementations. The error in the *GW* approximation is most often ascribed to the higher order terms, the so-called vertex corrections [24–28].

In this Rapid Communication, we propose to complement the *GW* approximation to the self-energy with some selected terms which are not vertex corrections, but rather self-consistent Feynman diagrams. The additional terms contribute only to the static part of the self-energy. These terms are relatively light to calculate and are meant to simulate the effect of fully self-consistent *GW* calculations without actually performing it. We will show that these contributions improve (i) the electronic density, (ii) the electrostatic potentials and exchange operators, and (iii) the final ionization potentials. These last conclusions will be drawn from the calculation of an extensive set of 34 reference molecular ionization potentials.

In practice, besides a few exceptions for small molecular systems [29,30], the *GW* self-energy is most generally not obtained self-consistently. It is rather obtained from an input Green's function from a mean-field theory, such as Hartree-Fock (HF) or generalized Kohn-Sham. This is the one-shot procedure often coined G_0W_0. The best results for the ionization potentials (IP) are typically obtained when choosing an hybrid functional starting point for the Green's function [18,30–32]. An alternative procedure named eigenvalue-only self-consistency (ev*GW*), which only updates the poles of the Green's function, has been proven to be very successful [33]. Note that this last procedure conserves the electronic density and density matrix from the original underlying mean field.

When performing a strict order-by-order expansion based on HF as chemists do, corrections to the density matrix naturally appear starting with PT3. Indeed, when analyzing the third-order self-energy diagrams in the expansion of Cederbaum and coworkers [3,4], some static contributions are present (the A terms in their notations). They correspond to the Feynman diagrams in the upper part of Fig. 1. These diagrams account for the one-ring and the second-order exchange
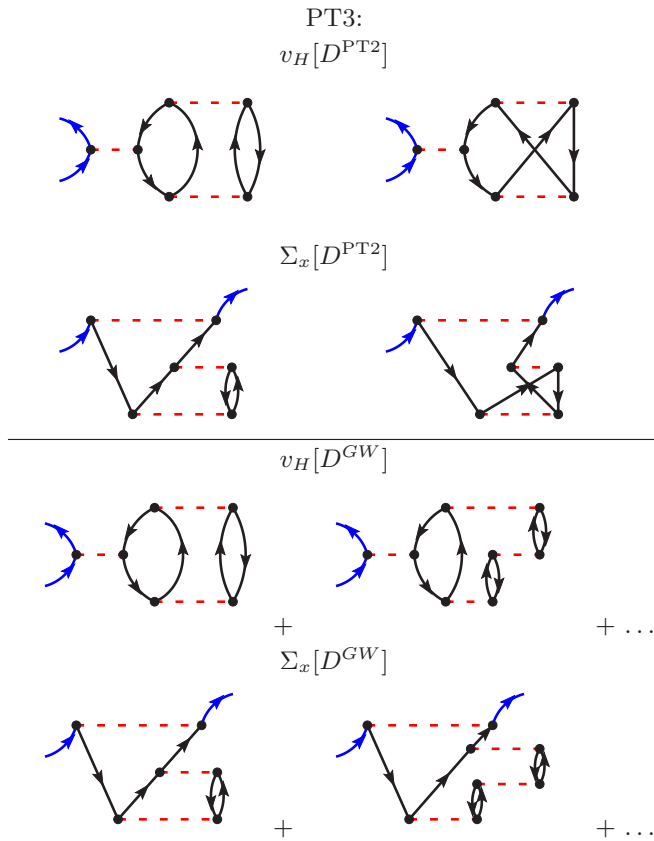
PT3:

$v_H[D^{\mathrm{PT2}}]$

$\Sigma_x[D^{\mathrm{PT2}}]$

$v_H[D^{GW}]$

$+$ $\qquad\qquad$ $+ \ldots$

$\Sigma_x[D^{GW}]$

$+$ $\qquad\qquad$ $+ \ldots$

FIG. 1. Feynman diagrams for the static self-energy in PT3 (upper panel) and for the *GW* density matrix inclusions in the Hartree potential and the exchange operator (lower panel). Green's functions are represented with a black arrow and Coulomb interactions with a red dashed horizontal line. Entry and exit points in the self-energies are symbolized with the blue arrows.

effect on the Hartree potential (first line) or on the exchange operator (second line). In other words, these are second-order corrections to the density matrix that appear in the third-order self-energy.

Following the same spirit, one can obtain a *GW* approximation to the density matrix, which will enter the Hartree and exchange terms as displayed in the lower part of Fig. 1. Let us write down the corresponding formulas here. We start with the Lehman representation of the dynamical part of the screened Coulomb interaction in the state product basis,

$$(v\chi^{\mathrm{RPA}}v)_{pq}^{rt}(\omega)$$
$$= \sum_s w_{pq}^s w_{rt}^s \left[\frac{1}{\omega - \Omega_s + i\eta} - \frac{1}{\omega + \Omega_s - i\eta} \right], \quad (1)$$

where v is the Coulomb interaction, χ^{RPA} is the random-phase approximation polarizability, Ω_s is the neutral excitation energy for excitation s, w_{pq}^s is the corresponding amplitude in the state product basis, and p, q, r, and t are state indexes. Real-valued wave functions have been assumed here for simplicity. Such a representation can be obtained in practice by diagonalization of the RPA matrix equation in the transition state basis [14,34,35], which is similar to Casida's equations [36].

TABLE I. Dipole moment in Debye of diatomic molecules for different density matrix approximations at the sc*GW* bond length (obtained from the earlier sc*GW* calculations of Caruso *et al.* [29]). Our work employs a cc-pVQZ basis set whereas Ref. [29] uses another accurate basis set.

	LiH	HF	LiF	CO
sc*GW* bond length [29]	1.579	0.919	1.586	1.118
sc*GW* [29]	5.90	1.85	6.48	0.07
D^{GW}	5.91	1.84	6.42	0.10
D^{PT2}	5.90	1.80	6.33	0.41
HF	5.96	1.93	6.52	−0.22
CCSD	5.92	1.85	6.37	0.10

With this expression for the dynamical part of the screened Coulomb interaction, one can adapt the PT2 density matrix formula to obtain the *GW* density matrix in the state basis D_{pq}^{GW} (see the Supplemental Material [37] for more details). The final expression in the spin-restricted case reads

$$D_{ij}^{GW} = 2\delta_{ij} - 2\sum_{sa} \frac{w_{ia}^s}{\epsilon_i - \epsilon_a - \Omega_s} \frac{w_{ja}^s}{\epsilon_j - \epsilon_a - \Omega_s}, \quad (2\mathrm{a})$$

$$D_{ab}^{GW} = 2\sum_{si} \frac{w_{ia}^s}{\epsilon_i - \epsilon_a - \Omega_s} \frac{w_{ib}^s}{\epsilon_i - \epsilon_b - \Omega_s}, \quad (2\mathrm{b})$$

$$D_{ib}^{GW} = -\frac{2}{\epsilon_i - \epsilon_b} \sum_{sj} \frac{w_{bj}^s w_{ij}^s}{\epsilon_j - \epsilon_b - \Omega_s}$$
$$+ \frac{2}{\epsilon_i - \epsilon_b} \sum_{sa} \frac{w_{ia}^s w_{ba}^s}{\epsilon_i - \epsilon_a - \Omega_s}, \quad (2\mathrm{c})$$

where i, j are occupied states and a, b are virtual states. These states and their energies ϵ_i are obtained from HF. Equations (2a)–(2c) are the different blocks in the state representation of D^{GW}: occupied-occupied, virtual-virtual, and occupied-virtual blocks respectively. This expression is only valid for the HF mean-field starting point, else the Brillouin theorem would not hold and some additional ill-behaved contributions would appear [38].

These equations have been introduced in the Gaussian basis code named MOLGW [39,40]. This code implements MBPT for gas-phase molecular systems using or not the resolution-of-the-identity approximation. The calculations presented in this paper all use the large Dunning correlation consistent basis set cc-pVQZ [41] with the corresponding auxiliary basis [42]. Reference coupled-cluster calculations have been performed with GAUSSIAN16 [43].

First of all, let us verify that this perturbative *GW* density matrix is indeed capable of simulating the self-consistent *GW* density matrix in practice. In Table I, we compare the dipole moment of a few diatomic molecules at the fixed bond length obtained within fully self-consistent *GW* (sc*GW*) by Caruso and coworkers [29] and as obtained with the *GW* density matrix expressed in Eqs. (2a)–(2c). The agreement is strikingly good for all molecules but LiF. Furthermore, comparing the D^{GW} dipole moment to the high-level coupled-cluster calculation (CCSD) with the same accurate basis set (cc-pVQZ) demonstrates that the D^{GW} electronic density yields
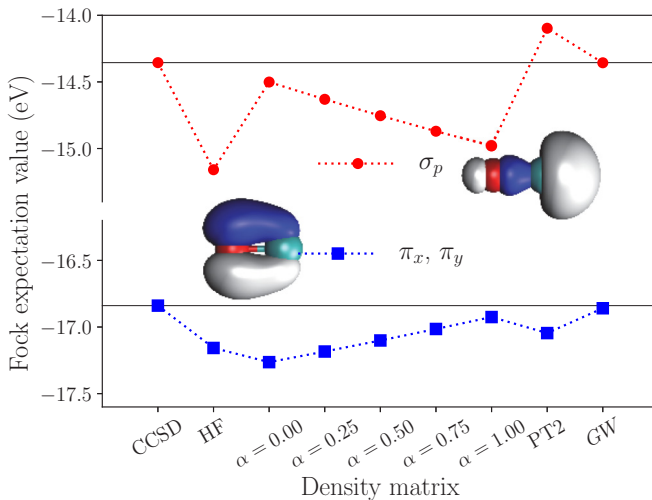
FIG. 2. Fock operator expectation values in eV for different density matrices for the two highest occupied orbitals of CO evaluated in between the highest occupied molecular orbital (HOMO) HF orbitals (σ_p) and the two previous degenerate HF orbitals (π_x and π_y). The α values in the x-axis labels stand for the fraction of exact exchange included in a tuned PBE0 density matrix.

very precise dipoles, much better than the density matrix at second order, D^{PT2}, and much better than HF.

Then a corollary question arises: How significant are the changes of density matrix on the electrostatic potential v_H and the exchange operator Σ_x used for the quasiparticle energies? To elucidate this, we propose to inspect the dependence of diagonal expectation values of the Fock operator as a function of the input density matrix D:

$$F_{pp} = \langle p| - \tfrac{1}{2}\nabla^2 + v_{ext} + v_H[D] + \Sigma_x[D]|p\rangle. \quad (3)$$

Figure 2 shows this expectation value as a function of D for the three highest occupied orbitals of carbon monoxide. The expectation value is evaluated with fixed wave functions within HF in the bra and ket so to isolate the sole effect of D. The reference is given by a CCSD calculation. Figure 2 confirms that the dependence of the Fock operator expectation values with respect to D is strong. For the σ_p orbital of CO, there is a 0.6 eV variation when tuning the content of exact exchange in PBE0. Furthermore, no mean-field approximation is able to capture the reference value for the Fock expectation value, not HF nor any tuned version of PBE0, ranging from 0% to 100% of exact exchange. The PT2 density matrix is already a good step toward the CCSD reference. Finally, the GW density matrix yields almost perfect Fock operator expectation values. Identical conclusions can be drawn from the analysis of the π_x and π_y orbitals. Note that the evolution of the π_x and π_y orbitals as a function of α in tuned PBE0 is opposite as the one for the σ_p orbital. Only the MBPT density matrices (PT2 and GW) are able to describe properly all these orbitals at the same time.

As the influence of the density matrix is large on the Fock operator expectation value, it is to affect the quasiparticle energies. Figure 3 presents the mean absolute error (the mean signed error is given in the Supplemental Material [37]) for the IP of 34 small molecules [12] as compared to CCSD(T)
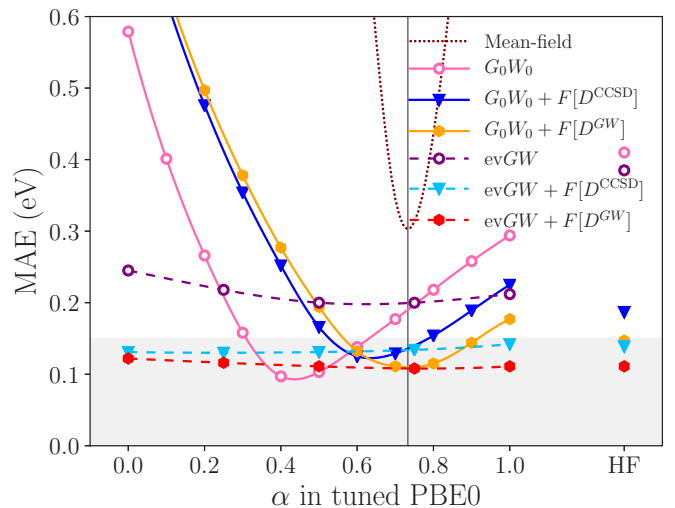

FIG. 3. Mean absolute error in eV for the benchmark of Refs. [12,18] based on the IP of 34 small molecules as function of the mean-field starting point (tuned PBE0 and HF). The dotted line stands for the mean-field error, the solid lines for the one-shot GW errors, and the dashed lines for the partially self-consistent evGW errors. The vertical line emphasizes the best mean-field Green's function. The shaded area shows a reasonable target accuracy, set to 0.15 eV. Note that the error of the mean-field techniques is larger than the maximum of the y axis for most of the values of α. A selection of the data summarized in this plot is given in the Supplemental Material [37].

references [18]. In practice, the CCSD(T) IP are obtained by performing two separate total energy calculations, one for the neutral molecule and another one for the positively charged molecule. The 34 molecules consists of 11 different light elements and their atomic coordinates are given in the Supplemental Material [37]. This benchmark against theoretical values avoids the difficulties due to experimental resolution, zero-point motion, theoretical geometries, and basis sets. The reported IP are the so-called vertical IP: They account for the sudden removal of an electron from the molecule without any structural relaxation. The difference between the vertical and the adiabatic IP (including structural relaxation) can be sizable in practice and the experimental vertical IP are not always available in the literature. The CCSD(T) reference value for P_2 has been updated with respect to our previous work [18]. Care has been taken about the highest occupied orbital that can change along with the choice of mean-field starting point as noticed by Maggio and Kresse [23].

In regular one-shot GW calculations, it is well known that the outcome strongly depends on the starting point. This is blatant from the G_0W_0 results (pink solid line) of Fig. 3. The G_0W_0 self-energy minimizes the error for functionals with about 40–50% of exact exchange, which corresponds to input mean-field Green's functions that have a large error in the IP (dotted brown line). Iterating the GW calculations with an update of the quasiparticle energies only (evGW) is often prescribed [33]. Indeed, after the evGW approximate self-consistency, the GW IP error is almost insensitive to the starting point (purple dashed line). However, the corresponding absolute error remains rather large, around 0.22 eV. This error

precisely corresponds to the error for G_0W_0 based on the tuned PBE0 functional that would minimize the IP error ($\sim$70% of exact exchange). Indeed, both approaches use a Green's function whose poles are the closest to the final quasiparticle energy. This particular exact exchange content is symbolized by a vertical line in Fig. 3.

Let us now complement the *GW* self-energy with better density matrices that improve the Fock operator expectation values. First, we start with the "almost exact" CCSD density matrix and evaluate the corresponding "almost exact" Fock operator. The subsequent one-shot *GW* results (solid blue line), labeled $G_0W_0 + F[D^{\text{CCSD}}]$ in Fig. 3, present a minimal error for input mean-field Green's functions with about 60% of exact exchange. This is close to the Green's function with the minimal error. As a direct consequence, applying the approximate eigenvalue self-consistency preserves this low error (ev$GW + F[D^{\text{CCSD}}]$ with dashed light blue line). Turning again to our example of the σ_p orbital of CO and N_2, the errors are then reduced to respectively 0.05 and 0.15 eV.

Of course, the almost exact CCSD density matrix is very cumbersome to obtain and would be out of reach for larger molecules. Let us consider now the effect of the cheaper *GW* density matrix D^{GW}. From Fig. 3, we observe that the $G_0W_0 + F[D^{GW}]$ results (dashed orange line) are very similar to those obtained with the CCSD density matrix. The minimal error is again obtained for the mean-field Green's functions with the lowest error ($\alpha \sim 0.75$). As a consequence, applying the evGW procedure produces robust and very accurate results (red dashed line). Whatever the starting Green's function, the mean average error is reduced down to 0.11 eV, which can be considered as an outstanding value. The corresponding mean signed error is as low as 0.05 eV [37].

In summary, in this Rapid Communication, we have identified that the error in the density matrix that permeates all the way to the final IP can be unacceptably large (as large as 0.6 eV). There are several routes to improve the density matrix. Full self-consistency on the Green's function is one of these. However, this would imply very heavy calculations and as the *GW* spectral functions have very strong satellite peaks [44], it might not be practical to iterate them. Here we have applied regular MBPT but within the *GW* approximation and have derived an expression for the *GW* density matrix. The obtained density matrices have a good accuracy together with a reasonable computational cost. They are shown to reproduce fully self-consistent *GW* dipole moments for four molecules available in the literature and to approach higher level of theory (CCSD dipole moments). With these density matrices and the corresponding Hartree and exchange expectation values, the IP of a series of 34 molecules is noticeably improved.

It would be instructive in the future to investigate the performance of vertex corrections in combination with the improved density matrices. The *GW* density matrix could be also extended to periodic solids as well, with consequences not only on band gaps but also on the electronic density itself.

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