Hybrid density functional theory meets quasiparticle calculations: a consistent electronic structure approach

Viktor Atalla,1 Mina Yoon,2 Fabio Caruso,1 Patrick Rinke,1 and Matthias Scheffler1
1Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
2Materials Science and Technology Division and Center for Nanophase Materials Sciences Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Dated: May 8, 2012)

We propose a scheme to obtain a system dependent fraction of exact exchange (\(\alpha\)) within the framework of hybrid density-functional theory. Employing the \(G_0W_0\) approach we identify the optimum \(\alpha\)-value for which the self-energy correction to the generalized Kohn-Sham highest occupied molecular orbital (HOMO) is minimized. We tested this scheme for the G2 dataset of atoms and small molecules and find \(\alpha\) values \(\geq 0.7\). The scheme results in a significantly improved energy-level spectrum with a mean absolute percentage error of \(\approx 3\%\) for the generalized Kohn-Sham compared to the experimental vertical ionization potentials.

In density-functional theory (DFT), hybrid functionals that contain a fraction \(\alpha\) of exact exchange typically improve electronic structure calculations over semi-local approximations [1], in particular with regard to the position of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Attempts to rationalize \(\alpha\) theoretically have led to values of 1/4 [2, 3] or 0.5 [4], where \(\alpha\) is kept constant for all systems. In a more pragmatic approach \(\alpha\) was fit to experimental data [5] in order to obtain a more realistic description of the electronic structure and thereby introducing a system dependent choice of \(\alpha\). A material dependent parametrization of the XC functional can also be obtained by considering the cohesive properties of a system, which then leads to a greatly improved description of point defects in the material [6]. However, fitting to experimental values is theoretically unsatisfying as it introduces an empirical parameter and it relies on the accuracy and existence of experimental data. In general it has been shown that \(\alpha\) should be system dependent by its relation to the inverse of the dielectric function [7]. For finite systems, an ab initio way of accessing \(\alpha\) has recently been proposed [8, 9] by employing the difference in self-consistent field calculations (\(\Delta\) SCF) approach.

On the other hand, the \(GW\) approximation [10] within the framework of many-body perturbation theory is a powerful method for calculating spectral properties and is applicable to both finite and periodic systems. In practice the \(GW\) spectrum is often obtained from a single shot calculation [11] (also referred to as \(G_0W_0\)) based on DFT reference states \(\psi_{n\sigma}\) with orbital energies \(\epsilon_{n\sigma}\),

\[
\epsilon_{G_0W_0}^{n\sigma} = \epsilon_{n\sigma} + \langle \psi_{n\sigma} | \Sigma^{G_0W_0} - v^{xc} | \psi_{n\sigma} \rangle.
\]

(1)

The indices \(n\) and \(\sigma\) label the main quantum numbers and spin states respectively, \(v^{xc}\) is the DFT exchange correlation potential and \(\Sigma\) is the self-energy within the \(G_0W_0\) approximation which itself depends on \(\psi_{n\sigma}\) and \(\epsilon_{n\sigma}\). Since performed in a post-processing manner, \(G_0W_0\) only corrects for the quasi particle (QP) levels while leaving the wavefunctions and thus also the electron density fixed at the underlying DFT density. Furthermore, the QP correction itself depends on the starting point [12] by Eq. (1), and this dependence can be pronounced [13, 14]. Therefore an appropriate choice of the underlying XC functional is of importance for both, the electron density and the QP levels.

In this paper we propose a scheme that obtains the \(G_0W_0\) starting point by optimizing the fraction of exact exchange within the framework of hybrid DFT. This lifts the ambiguity in the choice of \(\alpha\) and obtains a generalized Kohn-Sham (GKS) potential that is consistent with the QP self-energy. We consider the PBE hybrid functional (PBEh) with the exchange energy \(E^X\) being regarded as a function of \(\alpha\),

\[
E^X = \alpha E^{EX} + (1-\alpha)E^{PBE}, \quad \alpha \in [0, 1],
\]

(2)

where \(E^{PBE}\) and \(E^{EX}\) denote PBE exchange and exact exchange energies, respectively. In order to stress the \(\alpha\) dependence in the exchange part we introduce the notation PBEh(\(\alpha\)) for the corresponding functional. For example \(\alpha = 0\) corresponds to the PBE and \(\alpha = 0.25\) to the PBE0 functional. It should be noted that for \(\alpha = 1\), that is for full exact exchange, the GKS equation does not reduce to the Hartree-Fock equation as there is still a PBE contribution to the correlation energy. Instead of fixing \(\alpha\) globally we consider it as a system dependent parameter (that in principle depends on the electron density by the Hohenberg-Kohn theorem). For a given system we then chose \(\alpha\) by minimizing the QP correction to the HOMO-level according to Eq. (1)

\[
\alpha^* = \arg \min_{\alpha} |\langle \psi_H(\alpha) | \Sigma^{G_0W_0}(\alpha) - v^{xc}(\alpha) | \psi_H(\alpha) \rangle|,
\]

(3)

where the index \(H\) denotes the HOMO level and the dependence of the XC potential, the KS-orbitals and the self-energy on \(\alpha\) has been taken into account explicitly. In exact DFT the HOMO level of a finite system can be rigorously assigned to the IP [15, 16], and therefore the self-energy correction to the HOMO is strictly
proximation plus Hubbard U tendency between DFT and perspective Eq. (3) also reduces the SIE. As a side node DFT is obeyed as closely as possible. Hence, from a DFT perspective, the correspondence between HOMO and IP in exact DFT is minimized. For almost all systems we considered, we found $\alpha^*$ values for which the KS and the QP HOMO-levels can be matched implying a vanishing QP correction.

Our scheme - choosing $\alpha$ by minimizing the $G_0W_0$ perturbation to the generalized KS Hamiltonian - is conceptually similar to the QP self-consistent GW (QSGW) theory as proposed by Schilfgaarde et al. [17]. However, in our scheme the choice of the optimum potential is restricted to a subset that emerges from hybrid KS DFT. As a consequence, the corresponding ground state energy is still variational with respect to the density, unlike in QSGW.

We apply the scheme to the TTF/TCNQ dimer, a prototypical donor/acceptor system in the field of organic electronics [18–20]. It was shown that standard semilocal and hybrid XC functionals can fail drastically [21, 22] in describing their electronic structures. First we consider the individual molecules. We adopt the notation ”method@functional”, for example $G_0W_0@PBE$ corresponds to a $G_0W_0$ calculation with PBE reference states. Figure 1(a,b) shows the KS and QP HOMO levels as a function of $\alpha$. The calculations were performed using the all-electron FHI-aims code [23, 24] based on numeric atom-centered orbitals, with a tier 3 basis set for the $G_0W_0$ calculations. The geometry of the individual molecules was optimized in PBE and a tier 2 basis set using a quasi-newton method with a convergence criterion of $10^{-3}$ eV/Å for the residual maximum force component.

We obtain $\alpha^* = 0.8$ for both TTF and TCNQ. Similar values for $\alpha$ were reported [25] for benzene ($\alpha = 0.7$), bithiophene ($\alpha = 0.6$) and benzoquinone ($\alpha = 0.5$) by minimizing the many electron SIE [26]. These are all much higher than $\alpha = 0.25$ used in the PBE0 functional.

Experimentally, the ionization potential (IP) of TTF obtained by photoelectron spectroscopy is 6.70 eV [27]. For different $G_0W_0$ starting points the TTF IPs are (these values are compared with the experimental value): (6.14 eV, 9.1%) for $G_0W_0@PBE$, (6.40 eV, 4.7%) for $G_0W_0@PBE0$, and (6.66 eV, 0.6%) for $G_0W_0@PBEh(\alpha^*)$. TCNQ has an experimental IP of 9.61 eV [28]. In comparison, the calculated IPs read: (8.88 eV, 8.2%) for $G_0W_0@PBE$, (9.21 eV, 4.3%) for $G_0W_0@PBE0$, and (9.70 eV, 1.0%) for $G_0W_0@PBEh(\alpha^*)$. In both cases, the IP obtained by $G_0W_0@PBEh(\alpha^*)$ is in excellent agreement with the experimental value, otherwise it tends to be underestimated. Coupled cluster calculations including single, double and perturbative triple excitations (CCSD(T)) predict an electron affinity (EA) of 3.22 eV [29] for TCNQ. We find TCNQ EAs of (4.06 eV, 26.1%) for $G_0W_0@PBE$, (3.95 eV, 22.7%) for $G_0W_0@PBE0$, and (3.73 eV, 15.8%) for $G_0W_0@PBEh(\alpha^*)$. All $G_0W_0$ results give too high EAs as compared to CCSD(T). However, the lowest error is obtained for $G_0W_0@PBEh(\alpha^*)$, even though the LUMO level is not explicitly taken into account in Eq. (3).
electron transfer in the long range limit which induces to their description of electron transfer, as also shown in PBE and PBE0 in the long range limit can be traced back to the energetic ordering. In line with Ref. [21], for $\alpha > 0.3$ the level alignment of the TTF-TCNQ frontier orbitals qualitatively agrees with experiment (CCSD(T)) for which $\Delta$ is positive. In particular both, PBE ($\alpha = 0$) and PBE0 ($\alpha = 0.25$) are below the critical $\alpha$ value of 0.3 and therefore have an artificial contribution to electron transfer. On the other hand PBEh($\alpha^*$) has a level alignment that is consistent with experiment (CCSD(T)) and a vanishing QP correction to $\Delta$. As a consequence the tuned PBEh functional is free from spurious asymptotic electron transfer (for details see Ref. [22]).

We also examined the performance of the proposed scheme for a subset of the G2 test set for ionization energies [31], consisting of 50 atoms and molecules for which experimental geometries and vertical IPs are available [32]. All calculations were carried out for experimental geometries using the tier 4 FHI-aims basis [23] augmented with diffuse functions from aug-cc-pV5Z. Following Eq. (3) we obtain $\alpha^*$ values $\geq 0.7$. A compilation of the results can be found in the supplementary mate-

At this point we note that Fig. 1 (a) and (b) imply that for a given system there is only one $\alpha$ that satisfies Eq. (3). This raises the question whether a unique solution can also be found for the HSE [30] family of XC functionals, which additionally depends on the inverse screening length $\omega$. Figure 1 (c) and (d) shows the optimum ($\alpha, \omega$) values if Eq. (3) is generalized to the HSE family of XC functionals. For both, TTF and TCNQ, we find that several choices of ($\alpha, \omega$) satisfy the optimization requirement and hence the solution is in general not unique. For solids this could be exploited to reduce the computational cost by working at higher screening parameters $\omega$ and therefore more short-ranged exact exchange. However, $\omega = 0$ (that is the PBEh family of XC functionals) gives the best compromise in describing the location of both, the HOMO and the LUMO level.

Next, we evaluate the impact of $\alpha$ in describing dipole moments and the electron transfer for the TTF/TCNQ dimer. We chose our geometry (right side of Fig. 2) by cutting out a dimer of an interface of TTF and TCNQ [38]. Figure 2 (a) shows the absolute value of the dipole moment as a function of the distance. At the interface equilibrium distance ($d_0$) the dipole moment differs significantly between PBE, PBE0 and PBEh($\alpha^*$). In particular the dipole moment for PBE and PBE0 does not vanish for long distances, as it should since in the long range limit the total dipole moment should be given by the individual molecules which have both zero net dipole moments. Only the PBEh($\alpha^*$) functional reproduces the correct asymptotic limit. The unphysical behaviour of PBE and PBE0 in the long range limit can be traced back to their description of electron transfer, as also shown in Fig. 2 (b); both PBE and PBE0 predict non vanishing electron transfer in the long range limit which induces non-vanishing dipole moments.

In order to proceed we consider the limit of infinite molecular separation. In this limit electron transfer between the molecules is determined by the ratio of the EA of TCNQ and the IP of TTF. However, the CCSD(T) and $G_0W_0$ EA of TCNQ is smaller than the IP of TTF, and thus does not allow for interaction free electron transfer. This indicates that both, PBE and PBE0 fail to describe the ground state density for this system. Within the framework of KS DFT the total electron density is built up by occupying orbitals with respect to their energetic ordering. It is thus the relative alignment of the TCNQ-LUMO and the TTF-HOMO that determines electron transfer between the two molecules in this limit. Fig. 3 illustrates the difference of the GKS LUMO of TCNQ and the HOMO of TTF, $\Delta$, as a function of $\alpha$. For $\alpha < 0.3$ the TCNQ-LUMO level is located below the TTF-HOMO level. Thus, TCNQ will receive a certain amount of charge just by occupying orbitals with respect to the energetic ordering. In line with Ref. [21], for $\alpha > 0.3$ the level alignment of the TTF-TCNQ frontier orbitals qualitatively agrees with experiment (CCSD(T)) for which $\Delta$ is positive. In particular both, PBE ($\alpha = 0$) and PBE0 ($\alpha = 0.25$) are below the critical $\alpha$ value of 0.3 and therefore have an artificial contribution to electron transfer. On the other hand PBEh($\alpha^*$) has a level alignment that is consistent with experiment (CCSD(T)) and a vanishing QP correction to $\Delta$. As a consequence the tuned PBEh functional is free from spurious asymptotic electron transfer (for details see Ref. [22]).

We also examined the performance of the proposed scheme for a subset of the G2 test set for ionization energies [31], consisting of 50 atoms and molecules for which experimental geometries and vertical IPs are available [32]. All calculations were carried out for experimental geometries using the tier 4 FHI-aims basis [23] augmented with diffuse functions from aug-cc-pV5Z. Following Eq. (3) we obtain $\alpha^*$ values $\geq 0.7$. A compilation of the results can be found in the supplementary mate-
TABLE I. Mean absolute error (MAE) in meV of different total energy methods for the S22 database [34]. The errors are relative to results obtained by CCSD(T) extrapolated to the complete basis set limit [35].

<table>
<thead>
<tr>
<th>Method</th>
<th>H-bonds</th>
<th>Dispersion</th>
<th>Mixed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>51</td>
<td>198</td>
<td>87</td>
<td>116</td>
</tr>
<tr>
<td>PBEh((\alpha^*))</td>
<td>36</td>
<td>164</td>
<td>55</td>
<td>89</td>
</tr>
<tr>
<td>(EX+cRPA)@PBE</td>
<td>55</td>
<td>34</td>
<td>24</td>
<td>37</td>
</tr>
<tr>
<td>(EX+cRPA)@PBEh((\alpha^*))</td>
<td>21</td>
<td>54</td>
<td>24</td>
<td>34</td>
</tr>
</tbody>
</table>

FIG. 4. (Color online) Mean absolute percentage error (MAPE) of theoretical IPs obtained from the \(G_0W_0\) (left) and (generalized) KS (right) HOMO levels with respect to experimental vertical IPs for 50 molecules of the G2 test set.
The choice of this geometry is motivated by a recent experiment in which it was shown that the TTF/TCNQ interface exhibits metallic conduction [18] although the individual crystals are large band-gap semiconductors. The mutual crystal interface distance was optimized on the PBE level of theory including van der Waals corrections [39]. We define the distance between the TTF and TCNQ crystals $d_0$ as the distance between the planes spanned by the Hydrogen atoms of TTF and the Nitrogen atoms of TCNQ (right hand side of Fig. 2) for which we obtain $d_0 = 2.1 \text{ Å}$.