Screening in orbital-density-dependent functionals

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Electronic-structure functionals that include screening effects, such as Hubbard or Koopmans’ functionals, require to describe the response of a system to the fractional addition or removal of an electron from an orbital or a manifold. Here, we present a general method to incorporate screening based on linear-response theory, and we apply it to the case of the orbital-by-orbital screening of Koopmans’ functionals. We illustrate the importance of such generalization when dealing with challenging systems containing orbitals with very different chemical character, also highlighting the simple dependence of the screening on the localization of the orbitals. We choose a set of 46 transition-metal complexes for which experimental data and accurate many-body perturbation theory calculations are available. When compared to experiment, results for ionization potentials show a very good performance with a mean absolute error of 0.2 eV, comparable to the most accurate many-body perturbation theory approaches. These results reiterate the role of Koopmans’ compliant functionals as simple and accurate quasiparticle approximations to the exact spectral functional, bypassing diagrammatic expansions and relying only on the physics of the local density or generalized-gradient approximation.

I. INTRODUCTION

Accurate prediction of ground- and excited state properties of molecules can be made using quantum chemistry wave-function method or many-body perturbation theory (MBPT) techniques. However such calculations scale unfavorably with the size of the system and become soon computationally untractable. For this reason electronic-structure approaches such as Hartree Fock (HF) or Kohn-Sham density-functional theory (KS-DFT) have often been used as a proxy to classify and understand excitation spectra. However, the eigenvalues of the KS potential have no obvious relationship with the real excited states of the system. One notable exception is the first ionization potential in finite systems, that is exactly reproduced in exact KS-DFT, but usually severely underestimated by standard local or semilocal approximations to the exchange-correlation energy functional. In HF theory, the single-particle energies do have the physical meaning of excitation energies thanks to Koopmans’ theorem, but miss important relaxation effects related to the addition of an electron (or a hole) to the system. These effects can be included in finite systems using e.g. \( \Delta \) self consistent field (\( \Delta \text{SCF} \)) calculations, where the change in the energy associated with an electron addition/removal is calculated via two self-consistent calculations done with \( N \) and \( N+1/N-1 \) electrons. However, it is not straightforward to apply this approach to single-particle energies beyond the frontier ones and its extension to solids poses some issues since the \( \Delta \text{SCF} \) correction, computed with standard density functional approximations, vanishes in the thermodynamic limit.

For these reasons it would be highly desirable to have a functional yielding accurate single particle energies in addition to the well-established accuracy for ground state properties. Failures of standard density functional approximations in reproducing spectral quantities, such as ionization potentials and electron affinities, has been connected to the deviation from piecewise linearity (PWL) of the total energy functional as a function of particle number, and the associated lack of derivative discontinuity at integer particle numbers. First, the deviation from PWL has been suggested as a definition of electronic self-interaction error, and in recently developed functionals, such as DFT-corrected, range-separated, or dielectric-dependent hybrid functionals, PWL has been recognized as a critical feature to address. The criterion of PWL was in particular chosen as a key feature by some of us to introduce the class of Koopmans-compliant (KC) functional. When used to purify approximate standard local or semilocal density functionals, Koopmans’ corrections lead to orbital-density dependent potentials that can be interpreted as an approximation of the spectral potential, i.e. the local and dynamical potential that is necessary and sufficient to describe the local spectral density and, in turn, photoemission spectra. With a relatively small increase of the computational cost this class of functionals delivers accurate spectral properties retaining (in some cases exactly) the good performance of the underlying DFT functional for the ground state total energy. The performance of the KC predictions greatly depends on the correct description of screening/relaxation effects associated to particle number modifications. For simple systems, these effects can be effectively captured by introducing a screening coefficient derived imposing the generalized Koopmans theorem on the frontier orbitals. However, systems with a diverse electronic manifold, like for instance transition-metal compounds, call for a more accurate treatment since the same coefficient cannot equally...
well describe screening when the electron is removed (or added) e.g. from an s- or a d-like orbital. In this work we discuss how to correctly and fully include screening via orbital-dependent coefficients obtained from a linear response theory and thus ultimately from the dielectric screening. We then analyze the performance of the Koopmans-Integral (KI) functional, a standard flavour of the KC class whose definition will be reviewed in Sec. II for a set of 46 transition-metal complexes, and validate the results against GW calculations and experiments.

The paper is organized as follow. In section II we review the basic feature of Koopmans-compliant functionals and we introduce the linear-response approach to screening and relaxation. In section III we compare ionizations potentials for the set of molecules under study, obtained at different level of theory, with experimental data and state-of-the-art many-body perturbation theory calculations, followed by summary and conclusions.

II. METHOD AND COMPUTATIONAL DETAILS

In this section the main features of the KC class of functionals are reviewed with particular emphasis on the KI flavour, and the new scheme to capture screening and relaxation effects based on a linear-response approach is introduced and discussed.

A. Koopmans-compliant functionals

Koopmans-compliant functionals explicitly enforce a generalized criterion of piecewise linearity (PWL) with respect to the fractional removal/addition of an electron from any orbital in approximate DFT functionals. This is done by removing orbital-by-orbital the Slater contribution to the total energy, an approximately quadratic term in the orbital occupation $f_i$, and replacing it with a linear (Koopmans) term. In practice, the Koopmans correction is made up by the product of two equally important terms: (i) an orbital-density dependent corrections $\Pi^a_i$ aiming at correctly describing the addition/removal of an electron in a frozen-orbital or unrelaxed picture (restricted Koopmans theorem), and (ii) a screening factor $\alpha_i$ which takes into account the relaxation of the orbitals as a response to the addition/removal process. In what follows we restrict our attention to the KI energy functional, defined as

$$E^{KI} = E^{DFT} + \sum_i \alpha_i \Pi^a Ki_i,$$

is the unrelaxed KI correction to the DFT energy (see Ref. 23 for a detailed discussion of the KI energy functional and KI orbital-dependent potentials) and $\alpha_i$ the orbital dependent screening factor. Here the orbitals $\{\psi_i\}$ are kept frozen, $\rho_u = \sum_j f_j |\psi_j|^2$ is the total density of the system and $H^{DFT}(s)$ is the approximate KS-DFT Hamiltonian calculated at the unrelaxed density $\rho_u^{i,s} = \sum_{j \neq i} f_j |\psi_j|^2 + s|\psi_i|^2$, where only the explicit dependence on the occupation $s$ is considered [the $f_j$ for $j \neq i$ are typically 1 (or 2 for spin degeneracy)].

At variance with DFT, the variation of the Koopmans-compliant functionals (and ODD functionals in general) leads to local but orbital-dependent Hamiltonians that are in general not invariant under unitary transformations of the electronic wavefunctions. The energy minimization defines a unique set of variational orbitals that are usually very localized or maximally localized Wannier functions. At the minimum, the matrix of Lagrangian multipliers $\Lambda$, associated to the orthogonality constraint, becomes Hermitian and can be diagonalized via a unitary transformation, allowing one to define a second set of canonical orbitals, usually less localized than the variational ones. Although still a debated point, it is a common practice to interpret the eigenvalues of $\Lambda$ as (canonical) orbital energies, as clearly argued for in Ref. 39 and 23.

We note that the KI energy functional at integer occupation numbers preserves the unitary invariance of the underlying DFT functional. The energy minimization is therefore not sufficient to uniquely determine the variational orbitals; at the same time the KI potentials defining the KI eigenvalues depend on the actual representation of the electronic manifold. In previous works we removed this ambiguity by adding to the KI energy functional a vanishingly small Perdew-Zunger (PZ) self-interaction correction, thus interpreting KI as the limit of the KIPZ functional when the PZ correction goes to zero. The small PZ correction breaks the unitary invariance, and leads, through the energy functional minimization, to a set of well defined and typically localized variational orbitals (PZs orbitals in the following) on which the KI corrections are computed. This choice is of course arbitrary, although having a localized set of the
orbitals is a key enabler for the good performance of KC functionals, and a mandatory one when extended systems are considered. This is confirmed also here, by applying the KI corrections on different sets of orbitals with different degrees of localization; beside the set defined by the limiting procedure described above (PZs) we also consider the one represented by the canonical (KS) orbitals of the base DFT functional (usually delocalized over the whole molecule) and other two localized representations given by maximally localized Wannier functions (MLWFs) and by atomic-projected Wannier functions (ProjWFs). The latter are obtained by a projection of the KS states on a set of atomic orbitals that serves as a rough guess for the Wannier function, followed by a symmetric orthonormalization. For the MLWFs, the localization is enforced by using the sum of the quadratic spreads of the wavefunctions as a localization criterion, and searching for the optimal unitary transformation that satisfies that criterion. The use of Wannier functions as a representation to apply the Koopmans’ corrections and restore the missing piecewise linearity of approximate DFT functionals has been shown to give good results for the band gaps of solids. In the following we use the notation $\Pi_0^{KI}$[representation] to indicate the set of orbitals used to compute the KI corrections.

The screening and relaxation effects, naturally associated with the removal/addition of an electron, are accounted for by the multiplicative factor $\alpha_i$ in front of the bare correction $\Pi_i^{KI}$. How to determine this screening is the central goal of this work. In previous applications we showed that a unique (identical for all valence orbitals) screening factor, chosen to enforce the generalized Koopmans’ condition on the frontier orbitals, is sufficient to accurately predict the ionization potentials (IPs) and also photoemission spectra in a variety of molecular systems. A second screening coefficient, derived imposing the Koopmans’ condition on the lowest unoccupied molecular orbital (LUMO), can be attached to all the conduction states, extending the predictive power of KC functionals to electron affinities (EAs). However, a more sophisticated orbital-dependent choice is needed in case of systems with a more diverse electronic manifold.

In the next section we present and discuss this more general, physically sound and orbital-dependent treatment of the screening based on linear-response theory.

### B. Screening in KC functionals

In order to revert the unrelaxed Koopmans’ correction to a fully relaxed one, the screening coefficients can be formally defined as $\alpha_i = \Pi_i^{KI}/\Pi_i$ where $\Pi_i^{KI}$ is the relaxed Koopmans correction defined in Ref. $^{[25]}$. The latter can be written as

$$\Pi_i^{KI}(f_i) = - \{ E^{DFT}[\rho] - E^{DFT}[\rho(f_i=s)=0] \} + f_i \{ E^{DFT}[\rho(f_i=1)] - E^{DFT}[\rho(f_i=0)] \}, \quad (2)$$

where, at variance with Eq. $^{[1]}$, $\rho(f_i=s)$ in this expression corresponds to the fully relaxed density compatible with the condition $f_i = s$. Total energies with the additional constraint on one of the occupation numbers appearing in Eq. $^{(2)}$, could in principle be evaluated by means of constrained-density-functional approach. Applications have been made to e.g. coulomb-interaction parameters to be used in model Hamiltonians or in the context of Hubbard $U$ correction to DFT. Here we follow an alternative route, and evaluate each term in Eq. $^{(2)}$ in a perturbative way introducing a Taylor expansion of the DFT energy with respect to the occupation $f_i$ around some reference occupation $f_{ref}$:

$$E^{DFT}[\rho(f_i=s)] = \sum_n \frac{1}{n!} \frac{d^n E^{DFT}}{d f_i^n} \bigg|_{f=f_{ref}} (s-f_{ref})^n. \quad (3)$$

Substituting in Eq. $^{(2)}$ and stopping at the second order we find:

$$\Pi_i^{KI}(f_i) = \frac{1}{2} f_i(1-f_i) \frac{d^2 E^{DFT}}{d f_i^2} \bigg|_{f_{ref}} + O(f_i^3). \quad (4)$$

Due to Janak’s theorem the second derivative of the energy wrt a given occupation represents also the first derivative of the corresponding eigenvalue. In the following, we will work in the diagonal representation of the KS-DFT Hamiltonian and in the general case of relaxed orbitals, the frozen-orbital case being recovered trivially at the end of the derivation. We have:

$$\frac{d^2 E^{DFT}}{d f_i^2} = -\frac{d \varepsilon_i}{df_i} = \langle \psi_i \big| \frac{d H_{x+c}}{d f_i} \big| \psi_i \rangle = \int d\mathbf{r}d\mathbf{r}' n_i(\mathbf{r}) f_{Hxc}[\rho](\mathbf{r}, \mathbf{r}') \frac{d \rho(\mathbf{r}')}{df_i} \quad (5)$$

where we have used the Hellmann-Feynman theorem in the second identity, and have introduced the orbital density $n_i = |\psi_i|^2$ and the Hartree-exchange-correlation (Hxc) kernel $f_{Hxc} = \delta^2 E_{Hxc}/\delta \rho^2$. The derivative of the charge density with respect to the occupation is made up by two contributions: the first one comes from the explicit dependence of the density on the occupations while the second one comes from the change in the orbitals at
fixed occupation, i.e. at fixed number of particles:
\[
\frac{dp_i(r)}{df_i} = n_i(r) + \int dr' \frac{\delta \rho(r')}{\delta v_{\text{KS}}(r')} \frac{dv_{\text{KS}}(r')}{df_i} = n_i(r) + \int dr' \chi_0(r,r') \frac{dv_{\text{Hxc}}(r')}{df_i}
\]
\[
= n_i(r) + \int dr' [\chi_0 f_{\text{Hxc}}(r,r')] \frac{dp_i(r')}{df_i} \tag{6}
\]
where \(\chi_0 = \delta \rho/\delta v_{\text{KS}}\) is the KS (non-interacting) density-density response function. Equation (6) is a Dyson-like equation for the derivative of the charge density. Its iterative solution can be recast in a compact form introducing the interacting density-density response function \(\chi = \chi_0 + \chi_0 f_{\text{Hxc}}\) to
\[
\frac{dp_i(r)}{df_i} = n_i(r) + \int dr' [\chi f_{\text{Hxc}}(r,r')] n_i(r'). \tag{7}
\]
where it is understood that the response function and the Hxc-kernel are evaluated at \(\rho = \rho^i = f_{\text{KS}}i\). In the frozen orbital approximation the second term on the right hand side of the equation above is exactly zero. Combining Eqs. (7), (5) and (4) we obtain the central result of this paper:
\[
\Pi^{(2)\text{akl}}(f_i) = \frac{1}{2} f_i (1 - f_i) \int drdr' n_i(r) f_{\text{Hxc}}(r,r') n_i(r')
\]
\[
\Pi^{(2)r\text{kl}}(f_i) = \frac{1}{2} f_i (1 - f_i) \int drdr' n_i(r) f_{\text{Hxc}}(r,r') n_i(r') \tag{8}
\]
where we have defined the screened Hxc-kernel \(f_{\text{Hxc}} = (I + f_{\text{Hxc}}\chi) f_{\text{Hxc}} = e^{-1} f_{\text{Hxc}}\). It is important to stress that all the quantities needed to evaluate Eqs. (5), i.e. the orbital density \(n_i(r)\), the Hxc kernel \(f_{\text{Hxc}}\) and the response functions \(\chi_0\) and \(\chi\) are all ground-state properties and, therefore, accessible from the reference ground state calculation (usually the one for the neutral system). Instead, in a finite difference approach, as the one adopted in Refs. [16,47] to compute energy differences when changing the occupation numbers, one needs to ask for the additional requirement to keep fixed the orbital where the electron is added or removed. This is to prevent it from morphing into the highest (partially) occupied orbital, as this would always be the most favorable energetic configuration because of the Aufbau principle. In the linear response approach described above this is not needed since one always refers to single-particle orbitals and energies of the reference calculation, which are fixed by construction.

Even if derived from a simplified treatment based on a second order Taylor expansion, it is formally evident that the inclusion of orbital relaxation leads to a screening of the unrelaxed Koopmans correction. The integrals appearing in Eq. (5) can be interpreted as the effective interaction between the electrons in the orbital \(i\) when all the other orbitals are allowed (second line) or not (first line) to readjust. The connection between the second derivative of the energy with respect to the occupation of a localized orbital and the effective interaction between localized electrons has been also discussed in the context of Hubbard corrections to DFT [60–62]. The value of the static \(U\) parameter to be used in the model Hamiltonian is indeed determined from the constrained variation of the DFT eigenvalue with respect to the occupation number of the localized orbitals [63–65]. The frequency-dependence of the effective interaction has been also computed within the constrained random-phase approximation [24,25] (cRPA) using an expression similar to the second line of Eq. (5) but evaluated at the RPA level, i.e. neglecting the xc-kernel both in the Dyson-like equation defining the response function \(\chi\) and in the dielectric matrix \(\epsilon\). Within this second order expansion the similarity of the Koopmans-compliant functional with the +\(U\) correction in DFT is even more evident and indeed these functionals can be interpreted as a generalization of the DFT+\(U\) approach to the entire electronic manifold (this was the reason, in prims, of their introduction [24,25]). Notwithstanding the apparent similarity, there is a fundamental difference between the two approaches in the fact that KC corrections to DFT aim at describing addition or removal of an electron from the system (charged excitation), while the +\(U\) correction can be interpreted as the energy cost associated to move a fraction of an electron from a localized orbital (or manifold) to the bath represented by the rest of the system (neutral excitation). Then, as argued in Ref. [69], the renormalization of the bare interaction might take place through different screening channels depending on whether the electron is added/removed or continues to stay in the system. In the derivation above, the explicit variation of the particle number is considered [first contribution in Eq. (7)], as KC functionals aim at describing charged excitations, and the screened Koopmans’ correction in Eq. (5) is thus the correct one for such processes. Most importantly, the central results of Eq. (8) are still valid if one substitutes the canonical set of KS orbitals with another set related to the first one by a unitary transformation (see Supporting Information); this is extremely important because the screening coefficients to be used in KC functionals are actually connected to the variational orbitals, i.e. the orbitals that minimize the KC functionals, and these are related by a unitary transformation to the canonical orbitals.

The second line in Eq. (5) could be used as a relaxed Koopmans correction, albeit exact only up to second order. We therefore continue to use the original definition of the screening, and we introduce an orbital-dependent screening coefficient \(\alpha_i\) defined as the ratio between the relaxed and unrelaxed second-order Koopmans correction:
\[
\alpha_i = \frac{\Pi^{(2)r\text{kl}}(f_i)}{\Pi^{(2)\text{akl}}(f_i)} = \frac{\langle n_i f_{\text{Hxc}} | n_i \rangle}{\langle n_i f_{\text{Hxc}} | n_i \rangle} \tag{9}
\]
with \(\langle n_i | A | n_i \rangle = \int dr dr' n_i(r) A(r,r') n_i(r')\). The simplified screening coefficient introduced in previous pub-
dielectric-dependent hybrid functionals

the expression of the mixing parameter in the context of
tion of the screening coefficient in Eq. (9) is similar to
functional perturbation theory (DFPT)

The calculations are performed using Optimized Norm-
Conserving Vanderbilt (ONCV) pseudopotentials
available (only 41 values are available from experiments).

The two methods perform very similarly for each single
molecule (see Fig. 2 and Tab. I in Supporting Informa-
tion); this is not by chance, and highlights the physical
content embedded in the KI corrections: When re-
laxation effects are correctly taken into account the KI
functional reverts the KS eigenvalues into a ΔSCF en-
ergy, inheriting the accuracy of finite-difference DFT
energies. The use of a localized representation leads to a
significant improvement of the performance with a re-
duction of the MAE by a factor 2 over ΔSCF and
KI@KS. The KI@ProjWF and the KI@PZs show very
similar average performance with a MAE comparable to
those from the best GW calculations, i.e. G0W0@PBE0
(MAE 0.21 eV), chosen among ten different prescrip-
tions. We stress here that all the theoretical IPs do
not include relativistic nor zero-point motion effects. As
highlighted in Refs. 72,83 the latter is usually negligi-
ble while the former might be more relevant for this set
of molecules and affect the comparison between theory
and experiment. Comparison between different theor-
etical methods is instead fully consistent since these all
neglect relativistic effects and zero-point motion.

In order to highlight the importance of the orbital-
dependent treatment of the screening we also show the
KI@PZs results obtained using a unique value of the
screening coefficient, i.e. $\alpha_i = \alpha_{cn}$ for all the theoretical methods reported, except for
ΔSCF when the KI is defined as the energy difference
between the neutral molecule and its cation.

C. Computational setup

We apply this complete orbital-dependent scheme to compute the IPs of a set of 46 transition metal com-
plexes first introduced in Ref. 72 for which experimental
as well as many body perturbation theory results are
available (only 41 values are available from experiments).

The calculations are performed using Optimized Norm-
Conserving Vanderbilt (ONCV) pseudopotentials
72,74,75 to model the interaction between nuclei and electrons. In
order to simulate isolated molecules 76 we place these
inside an orthorhombic cell with 22 Bohr of vacuum in each
direction, sufficient to converge total energies and sin-
dense counter-charge corrections.79 The energy cut-off
for the plane-wave expansion is set to 100 Ry (400 Ry
for the charge density). All orbital-density dependent
calculations presented here uses PBE81 to simulate
the xc-energy functional; energy minimizations are per-
formed on the space of complex wavefunctions.

The calculated IP is defined as minus the eigenvalue
of the highest-occupied molecular orbital (HOMO) IP = $-\varepsilon_{ho}$ for all the theoretical methods reported, except for
ΔSCF when the IP is defined as the energy difference
between the neutral molecule and its cation.

III. RESULTS AND DISCUSSION

All the calculated and available experimental IPs
are listed in the Supporting Information. We focus be-
low on the average performance of the KI functional
as estimated by the mean absolute error (MAE), mean
signed error (MSE) and maximum signed error (Max(+),
Max(−)).

A. Performance of the KI functional

In Fig. 1 the absolute difference between calculated
and experimental ionization energies (IPs) is drawn as a
color map. In Tab. 1 the resulting mean absolute error
(MAE), mean signed error (MSE) and maximum signed
error (Max(+), Max(−)) are listed. The PBE results
show the well-known underestimation of the IPs due to
the self-interaction error resulting in a MAE and a maxi-
imum signed error of 3.43 and −5.27 eV, respectively. The
self-interaction correction (SIC) by Perdew and Zunger
(PZ-SIC in the Figures and Tables) over-correction the
PBE results with an almost systematic overestimation of
the IP, while ΔSCF, that usually gives rather good es-
estimation of the frontier orbitals energies, in this case has
a mean absolute error of 0.65 eV which is only slightly
smaller than PZ-SIC. KI corrections computed on top
of the canonical PBE orbitals (KI@KS) show an aver-
age performance that is comparable to that of ΔSCF.

The transition-metal complexes. We also stress here that the

tance of a more advanced treatment of the screening for
transition-metal complexes. We also stress here that the
way of computing a unique screening coefficient, although
conceptually straightforward and appealing, is cumbersome to extend to orbitals different from the frontier ones, and also requires in practice multiple calculations at \( N \) and \( N-1 \) electrons. The linear-response approach introduced here bypasses both these problems in a natural way.

For all our KI calculations, the outlier with the largest error with respect to experimental IP is the CuF molecule. It is highly unlikely that the large deviations observed for this molecule (see Tab. I) comes from effects not included in our calculations. Finite temperature and relativistic effects and/or zero-point motion could account for discrepancy of the order of few tenths of an electron volt. However, it should be also mentioned that the experiment values usually come with an error bar and in this particular case the experimentally measured ionization potential vary from 8.6 to 10.9 eV, making any comparison not particularly significant.

**B. Effect of the localized representation**

It’s interesting to note that despite some inevitable dependence on the choice of the localized representation, there is a substantial equivalence between the KI calculations done on top of the 3 different localized set of orbitals. In Fig. 2 we try to quantify such dependence of the IPs on the underlying representation defining the mean absolute distance (MAD) between two sets \( (a \) and \( b) \) of IPs from different KI calculations as

\[
\text{MAD}_{ab} = \frac{1}{N} \sum_{i=1}^{N} |\text{IP}_a^i - \text{IP}_b^i|, \tag{10}
\]

and plotting it as a color map. We also add the \( \Delta \text{SCF} \) results to highlight again its close relation with KI@KS. The MAD between these two sets of IPs is only 0.08 eV. From the correlation matrix one can also see that KI@PZs and KI@MLW are the second closest pair, reflecting the fact that the PZ localization condition and the MLW one usually lead to very similar sets of orbitals. We also clearly see that calculations on localized sets of orbitals and calculations on KS states (KI@KS and \( \Delta \text{SCF} \)) form two distinct blocks with off-diagonal elements up to 1 eV. The better performance of KI when a localized representation is used with respect to the KI@KS emphasizes what is a key requirement for this class of functionals, i.e. expressing the Koopmans corrections on a localized set of orbitals. While the discrepancy is not dramatic in the case of atoms or small molecules.
molecules, it becomes more and more evident when increasing the size of the system: given the strong connection with the $\Delta$SCF method, KI@KS would experience the same failure of the finite-difference method in the thermodynamic limit\cite{6,7}. Using a localized representation of the electronic manifold to compute the orbital corrections ensures instead a finite correction also in the thermodynamic limit\cite{46}. In addition, there is a strong correlation between screening parameters and orbital localization, e.g. as described by the self-Hartree energies (see Supporting Information). Such correlations would make it easier to apply this approach to large scale calculations, where screening coefficients could be inferred from a few linear-response tests.

Before concluding, we mention two points that are also relevant to the present discussion and worthy of future studies. First, system symmetries are not necessarily reproduced by orbital-density dependent functionals\cite{39,85}, if the corresponding Hamiltonians do not preserve these - hence the symmetry of the localized representation can play an important role, especially in small systems or in the atomic limit. Second, the present discussion makes clear, as is already known for the case of Hubbard functionals\cite{83,87}, that derivatives of the total energy would need to take into account the dependence of the screening coefficients on the varying parameters, e.g. atomic displacements. This dependence is expected to be small or negligible, and in any case these functionals are meant to great enhance the spectral properties, leaving the energetics untouched or slightly improved in strongly self-interacting systems by the screened PZ correction; notably, for the KI class of functionals the potential energy surface is identical to the base functional, and thus such dependence is not relevant.

IV. CONCLUSIONS

In conclusion we have shown how to extend the predictive power of Koopmans-compliant functionals to systems characterized by a complex electronic manifold, such as transition-metal complexes, finding that an orbital-dependent treatment of the screening is crucial to the correct description of spectral properties when orbitals with very different chemical character are considered. A scheme based on a linear-response approach has been introduced and discussed, highlighting the physical content behind the screening coefficient in Koopmans-compliant functionals. We found excellent agreement for the computed value of the ionization potentials with both experiment and state-of-the-art many-body perturbation theory, especially when the orbital dependence of the screening is correctly accounted for and when a localized representation of the electronic manifold is used to enforce the generalized PWL condition of KC functionals. The results on a carefully tested set of 41 transition-metal complexes show mean absolute errors of 0.20, 0.22 and 0.29 eV, respectively, for the KI functional calculated on different localized representations; ten different many-body perturbation theory approaches were in the range 0.21 eV to 1.92 eV, with $G_0W_0@PBE0$ being the most accurate one. These results reiterate the role of Koopmans’ compliant functional as spectral functionals able to simultaneously reproduce electronic spectra and total energies, and as quasiparticle approximations to the exact spectral potential\cite{29,30}.

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