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Hybrid-DFT+ V_w method for band structure calculation of semiconducting transition metal compounds: the case of cerium dioxide

Viktor Ivády,^{1,2,*} Adam Gali,^{2,3} and Igor A. Abrikosov^{1,4}

¹*Department of Physics, Chemistry and Biology,
Linköping University, SE-581 83 Linköping, Sweden*

²*Wigner Research Centre for Physics, Hungarian Academy of Sciences,
PO Box 49, H-1525, Budapest, Hungary*

³*Department of Atomic Physics, Budapest University of Technology and Economics,
Budafoki út 8., H-1111 Budapest, Hungary*

⁴*Materials Modeling and Development Laboratory,
National University of Science and Technology 'MISIS', 119049 Moscow, Russia*

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Abstract

Hybrid functionals' non-local exchange-correlation potential contains a derivative discontinuity that improves on standard semi-local density functional theory (DFT) band gaps. Moreover, by careful parameterization, hybrid functionals can provide self-interaction reduced description of selected states. On the other hand, the uniform description of all the electronic states of a given system is a known drawback of these functionals that causes varying accuracy in the description of states with different degrees of localization. This limitation can be remedied by the orbital dependent exact exchange extension of hybrid functionals; the hybrid-DFT+ V_w method [Phys. Rev. B 90, 035146 (2014)]. Based on the analogy of quasi-particle equations and hybrid-DFT single particle equations, here we demonstrate that parameters of hybrid-DFT+ V_w functional can be determined from approximate theoretical quasi-particle spectra without any fitting to experiment. The proposed method is illustrated on the charge self-consistent electronic structure calculation for cerium dioxide where itinerant valence states interact with well-localized $4f$ atomic like states, making this system challenging for conventional methods, either hybrid-DFT or LDA+U, and therefore allowing for a demonstration of the advantages of the proposed scheme.

I. INTRODUCTION

Density functional theory (DFT) with approximate exchange-correlation functionals has proven to be a good compromise between predictive power and computational efficiency¹. On the other hand, to further improve accuracy, one must solve longstanding issues of DFT, such as the missing derivative discontinuity of local and semi-local exchange-correlation functionals²⁻⁴ or self-interaction of the Kohn-Sham particles⁵. The latter error is caused by the non-zero sum of the self-repulsion and self-attraction due to Hartree and exchange-correlation interactions, respectively. Manifestations of the self-interaction are, for example, the over delocalization of the states, the spurious curvature of the total energy curve when generalized to non-integer occupation numbers and the violation of the generalized Koopmans' theorem⁶⁻⁸, in other context, the ionization potential theorem^{4,9,10}. To overcome DFT's self-interaction problem, various methods have been proposed, for instance, self-interaction corrected functionals^{5,11} and Koopmans-compliant functionals¹².

Hybrid functionals that mix local or semi-local DFT exchange potential with the non-local exact exchange potential of single particles¹³ have become popular in several fields of condensed matter physics and quantum chemistry¹⁴. The mixing of the potentials is governed by adjustable parameters that are standardly determined by theoretical considerations or fitting to experimental data sets. From the theoretical point of view, hybrid functionals' success can be attributed to the introduction of derivative discontinuity in the exchange-correlation potential and the partial or complete reduction of self-interaction error¹⁴. Recently, it was shown that by tuning hybrid functionals' internal parameters, self-interaction free description of selected single particle states is possible¹⁵⁻¹⁷. Furthermore, determining hybrid functionals mixing parameter from higher level self-interaction free *ab initio* theory^{6,15,16,18-23} or adjusting the mixing parameter to reproduce experimental band gaps^{24,25} are frequently used strategies nowadays.

Hybrid functionals, on the other hand, are global functionals in the sense that all the electronic states are described uniformly, i.e. by using the same functional parameters. When states of different degrees of localization, such as *sp*-hybridized on one hand and *d* and *f*-orbital related states on the other hand are simultaneously present in the system, uniform treatment of all the states is an inaccurate approximation.²⁶⁻²⁸ We emphasize that such system cannot be described accurately simply by tuning the mixing parameters of hybrid functionals. This issue may arise, for instance, for transition metal related semiconducting materials, consisting of both *s*, *p*, or *sp*-hybridized

and localized $3d$ or $4f$ valence states, as well as for conventional semiconductors and organic molecules that contain transition metal impurities and compounds, respectively. To overcome these limitations, one must go beyond the traditional global hybrid approximation²⁶, for example by locally changing^{29,30} the mixing of the exact and (semi-)local exchange of the generalized Kohn-Sham particles.

As an alternative approach, hybrid-DFT+ V_w method was recently introduced through the unification LDA+ U and hybrid-DFT methods.³¹ Hybrid-DFT+ V_w method, consists of an orbital dependent V_w correction potential and can be considered as an orbital dependent extension of hybrid-DFT, similarly to the case of LDA and LDA+ U methods. It employs hybrid exchange-correlation description for the couplings of delocalized states, while the couplings between the localized states are corrected by the V_w potential. Note that this method exhibits an unknown parameter similarly to LDA+ U method, i.e. the orbitals or bands that are corrected by the V_w potential should be localized and identified prior to the application of the method. On the other hand, the hybrid-DFT+ V_w method should principally well describe systems that simultaneously exhibit charge transfer and Mott insulator properties. Such systems can be properly handled neither by range-separated hybrid density functionals nor by the LDA+ U method. Furthermore, we show that the internal parameter w of the hybrid-DFT+ V_w functional can be determined without fitting to experimental data of the considered system, in contrast to the usual practice of LDA+ U method.

One possible way to obtain w and to make the functional self-interaction corrected is to enforce the fulfillment of the generalized Koopmans' theorem (gKT)^{8,27}. When gKT is fulfilled the energy of the highest occupied Kohn-Sham state ε_{HO} is equal to the negative ionization energy $E_I = E_N - E_{N-1}$, where E_N is the total energy of the N particle system. This means that the considered Kohn-Sham state has a real physical meaning, i.e. it is the negative ionization energy. When both the highest occupied and the lowest unoccupied localized states satisfy the gKT, the energy gap between the two Kohn-Sham states is comparable with experimental band gap. Note, on the other hand, that the system may not be completely self interaction free in this case, since other occupied states of the system may not satisfy gKT simultaneously.

As can be seen above, checking the fulfillment of the gKT requires the calculation of a charged system, to obtain E_{N-1} usually, that unavoidably introduces finite size effects both in the total and the generalized Kohn-Sham energies when periodic boundary condition is applied. Furthermore, the Koopmans' theorem is well-defined for localized states rather than for extended states¹⁰ and thus additional problems arise when the functional is applied to bulk systems. Relying on gKT,

there are only limited possibilities to determine the parameter of hybrid-DFT+ V_w method, thus it limits the method's applicability.

Here, we propose an alternative strategy to determine w without fitting theoretical calculations to any experiment. We discuss the analogy between the quasi-particle equations and the hybrid-DFT single particle equations that allows us to utilize higher level self-interaction free theory, such as the Coulomb hole and screened exchange (COHSEX) within the G_0W_0 approximation³² of the many-body perturbation theory (MBPT), to determine the w parameter. The proposed approach does not rely on the calculation of charged systems, thus it can be applied to both extended and localized systems to obtain a charge self-consistent description $sp-d/f$ mixed systems with affordable computational cost.

As an illustration we calculate the electronic structure of cerium dioxide (CeO_2). Our motivation for choosing this material as a workhorse example was twofold. First of all, cerium dioxide includes p , d and f -electrons close to the Fermi energy^{33,34}, thus it is an ideal model system for our method. Another reason for selecting this material is of its high interest in the field of materials science and engineering. Understanding cerium oxides electronic structure, including CeO_2 and Ce_2O_3 , is very important as these materials are frequently used, for example in automotive exhaust treatment.³⁵ Creation and annihilation of oxygen vacancies play important role in the oxidation processes^{35,36}, thus an accurate characterization of cerium atoms oxidation state and the energetics of oxygen vacancy in CeO_2 is highly desirable. Determination of these parameters requires computationally efficient charge self-consistent first principles methods that can describe both defects and bulk states accurately. We emphasize, that in contrast to the GW COHSEX method, the derived hybrid+ V_w DFT functional can be used to calculate the total energy and forces of the system. By finding the optimal hybrid+ V_w functional for the host CeO_2 solid, the same functional may be applied to explore the energetics of its point defects.

The article is organized as follows: In section II we discuss the theoretical background and introduce our approach. This section includes the discussion of hybrid-DFT single particle and MBPT quasi-particle equations similarity, a short review of the hybrid-DFT+ V_w method, and the introduction of fully theoretical determination of the w parameter. In section III and section IV we describe the details of our computational methods and present our results, respectively. Finally, in section V we summarize our results.

II. THEORY

A. Analogy of generalized Kohn-Sham particles and MBPT quasi-particles

Although hybrid functionals have firm theoretical foundations though the generalized Kohn-Sham schemes³⁷, at the birth of hybrids there were no good theoretical recipes for the determination of the mixing of the exact and local exchange potentials, thus hybrid functionals were often constructed with free parameters that were usually determined by fitting to experimental data sets.¹⁴ Let us consider, for example, the form of the PBE0³⁸ hybrid functional potential:

$$V_{xc}^{\text{PBE0}}(\mathbf{r}, \mathbf{r}') = \alpha V_x^{\text{exact}}(\mathbf{r}, \mathbf{r}') + (1 - \alpha) \delta(\mathbf{r} - \mathbf{r}') V_x^{\text{DFT}}(\mathbf{r}) + \delta(\mathbf{r} - \mathbf{r}') V_c^{\text{DFT}}(\mathbf{r}), \quad (1)$$

where V_x^{exact} , V_x^{DFT} , and V_c^{DFT} are the non-local exact exchange and the local DFT exchange and correlation potentials, respectively, $\delta(\mathbf{r} - \mathbf{r}')$ is the Dirac delta function, and α is the mixing parameter. It is clear that only fraction of the exact exchange interaction, or in other words, exact exchange with a screened Coulomb potential is introduced. To understand how this works, one can consider an analogy between the generalized Kohn-Sham particles and the MBPT quasi-particles. Despite the lack of direct theoretical connection, the equations have similar form thus an analogy can be made.

The MBPT quasi-particle equation can be written as

$$\hat{H}_0 \psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i) \psi_i(\mathbf{r}') d^3 r' = \varepsilon_i \psi_i(\mathbf{r}), \quad (2)$$

where $\psi_i(\mathbf{r})$ is the quasi-particle amplitude, \hat{H}_0 is the Hamiltonian of non-interacting particles, and $\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_i)$ is the non-local and energy dependent quasi-particle self-energy, which can be obtained exactly by Hedin's equations³², but approximated in practice. The most frequently used approximation is the GW approximation³², $\Sigma = iGW$, where G is the Green's function and W is the screened Coulomb interaction. We note that single shot GW method is usually applied in practice, often labeled as G_0W_0 , which means that the Hedin's equations are not solved self-consistently. In the context, GW method refers to G_0W_0 in the rest of the paper. Starting with Eq. (1), the equation of the interacting generalized Kohn-Sham particles can be written in a similar form,

$$\hat{H}_0 \varphi_i(\mathbf{r}) + \int V_{xc}^{\text{PBE0}}(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}') d^3 r' = \varepsilon_i \varphi_i(\mathbf{r}), \quad (3)$$

where φ_i are the general Kohn-Sham particles wavefunctions.

In static or Coulomb hole and screened exchange (COHSEX) approximation³² of the GW self-energy, the self-energy can be written in the form of

$$\Sigma_{\text{COHSEX}}(\mathbf{r}, \mathbf{r}') = \Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}') + \Sigma_{\text{COH}}(\mathbf{r}, \mathbf{r}'), \quad (4)$$

with

$$\Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}') = - \sum_j^{\text{occ.}} \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'), \quad (5)$$

where $W(\mathbf{r}, \mathbf{r}')$ describes the static screened interaction potential of the quasi-particles, and

$$\Sigma_{\text{COH}}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_p(\mathbf{r}, \mathbf{r}'), \quad (6)$$

where $W_p(\mathbf{r}, \mathbf{r}') = W(\mathbf{r}, \mathbf{r}') - v_{ee}(\mathbf{r} - \mathbf{r}')$ and $v_{ee}(\mathbf{r} - \mathbf{r}')$ is the bare Coulomb interaction potential. The screened electron-electron interaction $W(\mathbf{r}, \mathbf{r}')$ is related to the inverse dielectric functions^{39,40}, which in turn is related to the mixing parameter of hybrid functionals.^{20,21,23}

The first term on the right hand side of Eq. (4) describes the static exchange interaction between the quasi-particles. Importantly, this term includes a screened, non-local interaction potential $W(\mathbf{r}, \mathbf{r}')$. The second term describes the interaction with the Coulomb hole, which forms around the electrons due to correlation effects. This interaction is approximated with a local potential, see Eq. (6). The self-energy in the COHSEX approximation shows close similarity to the hybrid functionals' mixed non-local and local exchange-correlation potential. In the PBE0 functional, $\alpha V_x^{\text{ex}}(\mathbf{r}, \mathbf{r}')$ can be considered as an approximation to $\Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}')$, while the semi-local PBE exchange-correlation part given by the second and the third terms in the r.h.s. of Eq. (1) can be viewed as an analogy to $\Sigma_{\text{COH}}(\mathbf{r}, \mathbf{r}')$. Based on this analogy, the following statement can be made: The generalized Kohn-Sham particles are approximations to the quasi-particles, therefore, the generalized Kohn-Sham eigenvalues ε_i can be considered as rough approximations to the quasi-particle energies.^{16,20,21} These arguments were utilized recently to determine the mixing parameter of hybrid functionalism from the screened exchange interaction potential or from the inverse dielectric matrix obtained by approximate MBPT calculation.^{20,21,23} On the other hand, as the hybrid functionals are not directly derived from the quasi-particle equation, the validity of this analogy can only be determined in practical applications.

B. The hybrid-DFT+ V_w method

As we have seen above an analogy can be made between hybrid-DFT and the static COHSEX approximation of many-body perturbation theory. Furthermore, it is well known that LDA+U

method can be connected to the COHSEX approximation as well.^{41,42} Consequently, there is an indirect connection between hybrid-DFT and LDA+U methods. Moreover, a direct mathematical link between the two approaches in the case of localized orbitals was recently revealed in Ref. 31. Here, we shortly reiterate the basic idea of the derivation and introduce the hybrid-DFT+ V_w scheme.

An important difference between the LDA+U and hybrid+DFT approach is that the LDA+U method acts differently on a subspace of correlated orbitals, while hybrids are global exchange-correlation functionals. To be able to make a connection, one can consider the effect of the introduction of the exact exchange potential only on the subset of localized atomic-like orbitals ϕ_m , where m is the projection of the orbital momentum. Furthermore, as LDA+U was introduced as a correction to a local DFT exchange-correlation functional, for the sake of comparison, we express the mixing of the exact and approximate DFT exchange in hybrids as a correction to the DFT potential.

By rearranging the terms in Eq. 1 the PBE0 exchange-correlation potential can be written as:

$$V_{xc}^{\text{PBE0}}(\mathbf{r}, \mathbf{r}') = \alpha (V_x^{\text{ex}}(\mathbf{r}, \mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') V_x^{\text{PBE}}(\mathbf{r})) + \delta(\mathbf{r} - \mathbf{r}') V_{xc}^{\text{DFT}}(\mathbf{r}), \quad (7)$$

where the first and second terms define the potential correction to the DFT exchange-correlation potential V_{xc}^{DFT} . To calculate the correction on the subset of correlated orbitals, we define the on-site occupation matrix

$$\mathbf{n}_{mm'}^\sigma = \sum_i \langle \varphi_i | \phi_m \rangle \langle \phi_{m'} | \varphi_i \rangle. \quad (8)$$

By assuming that an appropriate unitary transformation of the of the atomic orbitals $\phi'_m = \hat{U}^\dagger \phi_m$ diagonalizes the occupation matrix, one can consider only the diagonal elements n_m^σ and rewrite the exact exchange potential as

$$V_x^{\text{ex}}[n_m^\sigma] = - \sum_{m', \sigma} \langle mm' | v_{ee} | m'm \rangle n_{m'}^\sigma. \quad (9)$$

The second term on the right hand side of Eq. (7) corrects for the double counting. To calculate this term, one should determine the restricted effect of the semi-local exchange-correlation functional on the subset of correlated orbitals. As this cannot be made explicitly, an approximation is employed^{31,43,44}, similarly to the one of the LDA+U method. However, in contrast to the LDA+U method, where the screened Hubbard U and Stoner J parameters are used, here the bare interaction strengths, F_0 and J_0 are used to be consistent with the restriction, in which only interactions

among the localized orbitals are taken into account. Thus the screening effect of other delocalized states is not considered. With these in mind, the second term on the right hand side of Eq. (7) can be approximated^{31,43,44} as

$$V_{xc}^{\text{PBE}}[n^{\sigma_m}] = -\frac{F^0 - J^0}{2} - J^0 n_m^{\sigma}. \quad (10)$$

By applying the approximation $\langle mm | v_{ee} | mm \rangle \approx F_0$ and $\langle mm' | v_{ee} | m'm \rangle \approx J_0$ ³¹ the localized orbital-restricted form of the potential correction term in Eq. (7) can be written as

$$\Delta V_m^{\text{PBE0x},\sigma}[\mathbf{n}_m^{\sigma}] = \alpha (F^0 - J^0) \left(\frac{1}{2} - \mathbf{n}_m^{\sigma} \right). \quad (11)$$

The above equations show close similarities to the potential correction terms of the LDA+U method by Dudarev *et al.*⁴⁵. From the mathematically equivalent forms of the corrections, one can deduce that the two methods have the same effect on localized atomic-like orbitals. The difference is only in the strength of the correction. While in the LDA+U method, the correction strength is determined by the effective Hubbard U parameter, which is usually set by hand, in hybrids the magnitude of the correction is determined by the mixing parameter α .

In such systems, where both sp -hybridized and localized d or f -like states are present, a single α parameter most often is not sufficient to provide a suitable description for orbitals of different degrees of localization. To overcome the limitations of the uniform mixing approximation of usual hybrids, the hybrid-DFT+ V_w method was proposed to accomplish this in an orbital dependent fashion^{27,31}. An on-site potential is added to a hybrid functional exchange-correlation potential in the form of Eq. (11) as

$$V_w[\mathbf{n}_m^{\sigma}] = w \left(\frac{1}{2} - \mathbf{n}_m^{\sigma} \right), \quad (12)$$

where w defines now the strength of the on-site potential correction. To achieve improved description

$$w = U_{\text{real}}^{\text{eff}} - U_{\text{hybrid}}^{\text{eff}} = U_{\text{real}}^{\text{eff}} - \alpha (F^0 - J^0), \quad (13)$$

must be satisfied, where $U_{\text{real}}^{\text{eff}}$ is the true effective on-site interaction strength. On the other hand, as $U_{\text{real}}^{\text{eff}}$ is generally unknown, w can also be considered as an adjustable parameter. Note that, the V_w correction can be translated to an orbital dependent adjustment of the mixing parameter α through the formula of

$$\alpha_{\text{loc}} = \alpha + \frac{w}{F^0 - J^0}. \quad (14)$$

Alternatively, one can determine the w parameter through the fulfillment of the theoretical requirements of the exact DFT functional. One of these requirements is the so-called ionization

potential (IP)^{4,9} or, in other context, the generalized Koopmans' theorem (gKT)^{6,8}. According to these theorems the highest occupied Kohn-Sham eigenvalue is equal to the negative ionization energy of the system, and it stays constant under the variation of its occupation number. If these criteria are fulfilled then the functional is approximately self-interaction free, at least for the highest occupied orbital. Standard approximate exchange-correlation functionals do not satisfy gKT, however, there are purpose built functionals that do fulfill it, such as Koopmans-compliant (KC) functionals^{8,12}. In such cases, when a suitable correction potential is known, by adjusting its parameters the gKT can be fulfilled to achieve self-interaction corrected description.

This strategy was applied to determine the w parameter and to calculate the charge transition levels of the correlated impurity systems in Ref. [31] and [27]. In the case of periodic boundary conditions and plane wave basis set, however, this approach suffers from serious limitations due the finite size-effects that cause substantial energy shifts both in the total energy and the KS eigenvalues when the fulfillment of the gKT is investigated. Furthermore, the Koopmans' theorem is valid for states of decaying density (for $r \rightarrow \infty$)¹⁰, and therefore its application for bulk states is not well defined.

C. Calculation of the w potential strength

By utilizing the above described connection between the hybrid-DFT, LDA+U, and the COHSEX approximation of the Hedin's equations³², we propose an alternative method to calculate the w parameter of hybrid-DFT+ V_w scheme.

Following the derivation of Jiang *et al.*⁴², the COHSEX quasi particle shift of PBE single particle energies of localized states, $\Delta\varepsilon_m^{\text{QP}} = \langle \phi_m | \Sigma_{\text{COHSEX}} - v_{xc}^{\text{PBE}} | \phi_m \rangle$, can be written as

$$\Delta\varepsilon_m^{\text{QP}}|_{\text{PBE}} = \Delta V_m \approx \left(\frac{1}{2} - n_m^\sigma \right) U_{\text{COHSEX}}, \quad (15)$$

where $U^{\text{COHSEX}} = \langle \phi_m \phi_m | W(r, r', 0) | \phi_m \phi_m \rangle$. As derived in the previous section, the potential shift due to the mixing of the exact and semi-local exchange, or in other words the ‘‘generalized Kohn-Sham particle shift’’, $\Delta\varepsilon_m^{\text{gKS}} = \langle \phi_m | v_{xc}^{\text{PBE0}} - v_{xc}^{\text{PBE}} | \phi_m \rangle$, can be given as

$$\Delta\varepsilon_m^{\text{gKS}} = \Delta V_m^{\text{PBE0x}} \approx \left(\frac{1}{2} - n_m^\sigma \right) U_{\text{PBE0}}. \quad (16)$$

Assuming $U_{\text{real}} \approx U_{\text{COHSEX}}$, from Eq. (13), (15), and (16) we obtain

$$\begin{aligned} w_{\text{single}} &= \frac{2}{1-2n_m^\sigma} \left(\Delta\varepsilon_m^{\text{QP}} \Big|_{\text{PBE}} - \Delta\varepsilon_m^{\text{gKS}} \right) = \\ &= \frac{2}{1-2n_m^\sigma} \langle \phi_m | \Sigma_{\text{COHSEX}} - v_{xc}^{\text{PBE0}} | \phi_m \rangle = \frac{2}{1-2n_m^\sigma} \Delta\varepsilon_m^{\text{QP}} \Big|_{\text{PBE0}}, \end{aligned} \quad (17)$$

where $\Delta\varepsilon_m^{\text{QP}} \Big|_{\text{PBE0}}$ is the quasi-particle shift of the PBE0 generalized Kohn-Sham particle energies.

In bulk systems the localized atomic-like states often form narrow bands that only slightly hybridize with other states. In such cases, not a single state but a whole band can be corrected by the V_w potential correction. A suitable w can be obtained from the band averaged quasi-particle shift as

$$w_{\text{band}} = \sum_{n\mathbf{k}\sigma} \omega_{\mathbf{k}} \frac{2}{1-2n_{n\mathbf{k}}^\sigma} \Delta\varepsilon_{n\mathbf{k}}^{\text{QP}} \Big|_{\text{PBE0}}, \quad (18)$$

where $\omega_{\mathbf{k}}$ is the weight of \mathbf{k} -point \mathbf{k} in the irreducible Brillouin zone. Note that the above definition does not rely on the variation of the occupation number, thus finite size effects are significantly reduced compared to the previous scheme based on gKT.

III. METHODOLOGY

We demonstrate the application of our *ab initio* charge self-constant method on the band structure calculation of CeO₂. We focus on the electronic structure of CeO₂, in particular on the density of the states (DOS), close to the Fermi-energy, where there are an occupied oxygen *p*-band, an unoccupied cerium *f*-band, and an unoccupied cerium *d*-band.^{33,34} To determine the mixing parameter α and the w potential correction strength we apply the following procedure. First, we adjust w to correct the Ce *f* orbitals position in the *p-d* band gap. The initial value of the w parameter is determined from the band averaged COHSEX quasi-particle shift of the *f*-band through Eq. (18). In the next step, we vary the mixing parameter of the hybrid functional to approach the COHSEX *p-d* band gap. Due to the relaxation of the orbitals, these steps in turn imply small additional adjustment of parameter α and w . Therefore, we cycle these steps to converge the hybrid+ V_w and COHSEX DOS.

In our first principles DFT calculations, we use plane wave basis state of 420 eV cutoff energy and projector augmented wave (PAW) method^{46,47} as implemented in the Vienna Ab initio Simulation Package (VASP)^{48,49}. We combine VASP's hybrid functional and LDA+U implementation to carry out hybrid-DFT+ V_w calculations. For cerium we use a PAW potential that includes a [Kr] 4*d*¹⁰ core. We use a 10 × 10 × 10 Γ -point centered uniform grid to sample the Brillouin

zone. In our hybrid-DFT+ V_w calculations, we use two widespread functionals, the regular PBE0³⁸ and the range separated HSE06^{50,51} hybrid functionals, as base hybrid functional for the method. COHSEX calculations are carried by using VASP’s implementation. For convergent quasi-particle calculations, we include virtual bands up to 90 eV energy and use 170 eV cutoff for the response function calculations. In all calculations, we use HSE06 optimized structure of 5.39355 Å lattice constant.

IV. COMPUTATIONAL RESULTS

The HSE06 DOS compared with the experimental XPS-BIS spectrum^{52,53} is depicted in Fig. 1(a). As can be seen in the figure, HSE06 underestimates the p - f band gap while seems to overestimate the p - d band gap. Furthermore, it reproduces the oxygen p -band’s band width reasonably well, however, the Ce f -band is too narrow, which makes the comparison of theoretical and experimental band gaps difficult, see Table I. Our findings are in reasonably good agreement with previous hybrid functional studies⁵⁴⁻⁵⁶, see Table I. The observable ~ 0.3 eV difference in the band gaps may be attributed to the distinct convergence parameters applied in previous studies.

Starting from HSE06 generalized Kohn-Sham wave functions, the COHSEX DOS improves the p - f and p - d band gaps and the f -band width, while somewhat overestimates the p -band width, see Fig. 1(b). These results suggest that using COHSEX quasi-particle shift to determine the hybrid-DFT+ V_w functional’s internal parameters may improve on the HSE06 results.

By using $\alpha = 0.25$ and $w = 3.7$ eV, hereinafter we name this functional as HSE(0.25)+ V_w (3.7), we obtain an optimal fit of the DOS to the quasi-particle DOS of CeO₂ calculated within COHSEX approximation. The theoretical DOS obtained by HSE(0.25)+ V_w (3.7) functional is compared with the experimental spectra in Fig. 1(c). Due to the V_w correction, the p - d band gap lowers while the position of the f -band increases which brings the HSE(0.25)+ V_w (3.7) results much closer to the experimental data as compared to the original HSE06 results, see Fig. 1(c) and Table I. Interestingly, it turns out that the mixing parameter of HSE06 should not be varied as by correcting the f -band’s position the d -band lowers, due to the interaction of the bands. Similar effect has been reported in LDA+U studies³⁴.

Note that in the example above the range separation parameter μ of the base HSE06 functional is not changed. To understand the effect of range separation on the DOS of CeO₂ in hybrid-DFT+ V_w method, we investigated PBE0 and PBE0 based hybrid-DFT+ V_w methods. In Fig. 2(a),

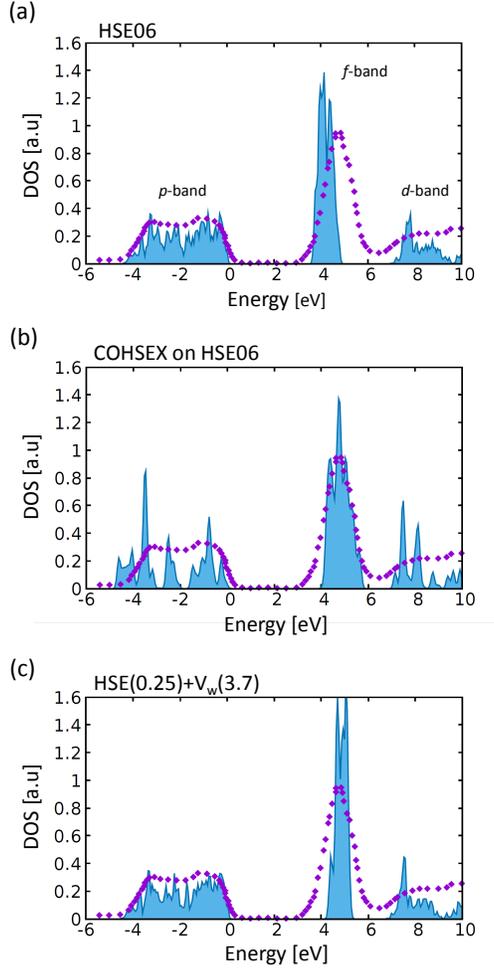


FIG. 1. First principles DOS (filled curve) of cerium dioxide (CeO_2) as obtained by (a) HSE06 functional, (b) COHSEX approximation using HSE06 Kohn-Sham wavefunctions, and (c) HSE(0.25)+ $V_w(3.7)$ method. The experimental XPS-BIS spectra^{52,53} is shown for comparison and is depicted by points. The valence band edge is chosen as the origin of the energy scale in all cases.

one can see the PBE0 DOS. Both the p - f and the p - d band gaps are overestimated, which is consistent with the general trend that PBE0 of $\alpha = 0.25$ tends to overestimate the band gaps of semiconductors⁵⁷. Using PBE0 orbitals, the COHSEX quasi-particle correction improves the electronic structure and the COHSEX DOS agrees well with the experimental spectra, see Fig. 2(b). By using $\alpha = 0.15$ and $w = 5.3$ eV parameters in the PBE0 based hybrid-DFT+ V_w functional we can reproduce the quasi-particle DOS. The resultant DOS can be seen in Fig. 2(c). Interestingly, PBE0(0.15)+ $V_w(5.3)$ DOS is nearly identical with the HSE(0.25)+ $V_w(3.7)$ DOS. The only difference is in position of the f -bands, which is slightly lower in energy. We conclude that the range

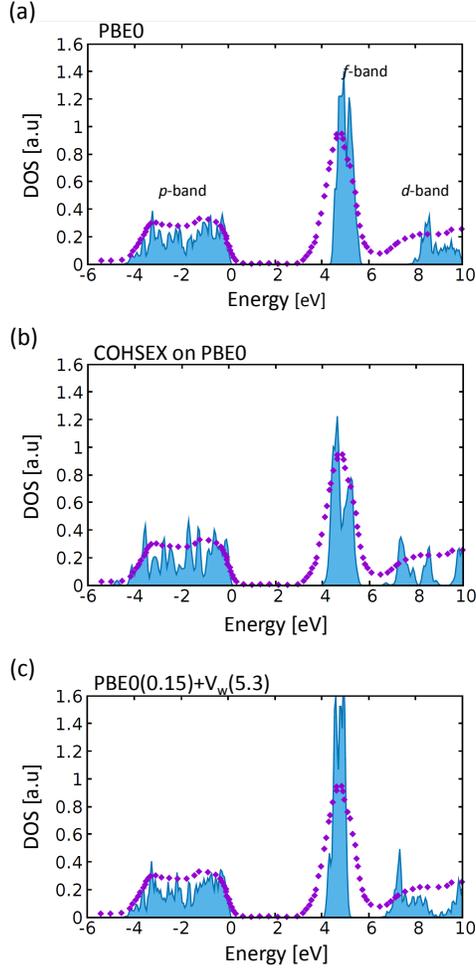


FIG. 2. First principles DOS (filled curve) of cerium dioxide (CeO_2) as obtained by (a) PBE0 functional, (b) COHSEX approximation using PBE0 Kohn-Sham wavefunctions, and (c) PBE0(0.15)+ $V_w(5.3)$ method. The experimental XPS-BIS spectra^{52,53} is shown for comparison and is depicted by points.

separation seems to have minor effect on the final electronic structure, however, the parameters of the hybrid-DFT+ V_w functional do depend on it. One may understand this result by considering the short-range interactions strength of the two functionals. In PBE(0.15) the short-range interaction is more screened than that in HSE(0.25), thus in the former case a larger V_w potential ($w = 5.3$ eV) is required to correct the on-site interaction of the f states.

TABLE I. Theoretical and experimental⁵² p - f and p - d band gaps in the band substructure of CeO₂.

Method	p - f gap	p - d gap
HSE03 ⁵⁴	3.3 - 3.5	7.0
HSE03 ⁵⁵	–	6.96
HSE06 ⁵⁶	3.4	7.2
HSE06	3.64	7.03
COHSEX on HSE06	3.87	6.47
HSE(0.25)+V _w (3.7)	4.22	6.79
PBE0 ⁵⁵	–	7.93
PBE0 ⁵⁶	3.94	8.08
PBE0	4.39	7.77
COHSEX on PBE0	4.07	6.74
PBE0(0.15)+V _w (5.3)	4.12	6.59
Experiment	3 – 3.5	5.5 – 8

V. SUMMARY AND CONCLUSIONS

We have proposed an approach to parameterize the orbital dependent mixing of exact exchange and semi-local exchange in the hybrid-DFT+V_w scheme through the analogy of the COHSEX quasi-particle equations and the hybrid-DFT single particle equations. The computational cost of the proposed method is in the order of a hybrid-DFT functionals demand. We illustrated the application of the method on the band structure calculation of CeO₂, where results achieved by the hybrid-DFT+V_w method improve those of either HSE06 or PBE0 functional calculations. The proposed method should be suitable for charge self-consistent calculations to study, for example, bulk band structure and point defect electronic structure of transition metal related semiconducting materials as well as organic molecules containing transition metal elements.

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* vikiv@ifm.liu.se

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