Density-based mixing parameter for hybrid functionals

Miguel A. L. Marques,[1,2] Julien Vidal,[1,2,3] Micael J. T. Oliveira,[1,2] Lucia Reining,[2,3] and Silvana Botti[1,2,3]

[1]*LPMCN, Université "Claude Bernard" Lyon 1 and CNRS, F-69622 Villeurbanne, France*
[2]*European Theoretical Spectroscopy Facility (ETSF)*
[3]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France*

A very popular *ab initio* scheme to calculate electronic properties in solids is the use of hybrid functionals in density functional theory (DFT) that mixes a portion of the Fock exchange with DFT functionals. In spite of its success, a major problem still remains, related to the use of one single mixing parameter for all materials. Guided by physical arguments that connect the mixing parameter to the dielectric properties of the solid, and ultimately to its band gap, we propose a method to calculate this parameter from the electronic density alone. This approach is able to cut significantly the error of traditional hybrid functionals for large and small gap materials, while retaining a good description of the structural properties. Moreover, its implementation is simple and leads to a negligible increase of the computational time.

Density functional theory (DFT) is one of the major achievements of theoretical physics in the last decades. It is now routinely used to interpret experiments or to predict properties of novel materials. The success of DFT relies on the Kohn-Sham (KS) scheme and the existence of good approximations for the unknown exchange and correlation (xc) functional. In the standard KS formulation the xc potential is local and static. Since the original suggestion of the local-density approximation (LDA),[1] a swarm of functionals has been proposed in the literature.[2] In the *ab initio* study of solids, the Perdew, Burke, and Ernzerhof[3] (PBE) parametrization of the xc functional has been, for many years, the default choice for many applications. A good functional must yield ground states properties (like structural parameters), while it is expected that the KS gap and true quasiparticle gap differ by the derivative discontinuity.[4] Indeed, for semiconductors and insulators PBE yields good structural properties and KS band-gap energies that are, at best, half of their experimental value. To obtain both the ground state and quasiparticle energies correctly within one and the same formalism, one can resort to a many-body GW calculation.[5,6] However, GW is, by all measures, an expensive technique with a very unfavorable scaling with the number of atoms in the unit cell. It is therefore unpractical for the study of band structures of large systems and clearly prohibitive regarding total energy calculations even for simple realistic systems.

Much of the computational effort in GW comes from the dynamically screened Coulomb interaction W. It has therefore been crucial to explore to which extent dynamical effects are mandatory, or whether nonlocality is the dominating characteristic. The move from local KS potentials to nonlocal functionals has first been pushed forward in quantum chemistry, where today the so-called hybrid functionals are very popular. These functionals mix a fraction α of the Fock exchange with a combination of LDA and generalized gradient (GGA) functionals. The application of hybrid functionals to the solid state had a slower start.[7,8] The situation changed recently, helped by the wider availability of computer codes that support hybrids[9] and the steady increase of computational power covering the additional cost with respect to a local potential. Besides yielding good structural properties[10] hybrids have

proved to correct, to a large extent, the band-gap problem.[8,11] Another landmark came with the introduction of screened hybrids.[12] These functionals lead to faster calculations and improved band gaps, especially for small band-gap systems. Furthermore, by screening the Coulomb interaction at large distances, they also give access to metals.

The intuition lying behind a hybrid functional is rather clear. While LDA or GGA calculations strongly underestimate the gap, Hartree-Fock calculations overestimate it typically by more than a factor of 2. By changing the mixing α from 0 to 1, one has a continuous change between local KS and Hartree-Fock and an essentially linear variation between the respective gaps. Therefore, to obtain the experimental gap one simply has to use the appropriate mixing parameter. This value can be determined from a fit to a series of systems, and is often set to around $\alpha \sim 0.2$–0.3. This choice gives very good results for a large class of systems, but it usually fails when the gap is very large or very small. But what is the physical meaning of the mixing parameter? To answer this question, it can be instructive to move away from a generalized KS picture,[13] and consider the hybrid as an approximation to the self-energy Σ. In the GW approximation the latter can be written as

$$\Sigma(\boldsymbol{r},\boldsymbol{r}';\omega) = \Sigma_{\mathrm{sX}}(\boldsymbol{r},\boldsymbol{r}') + \Sigma_{\mathrm{rest}}(\boldsymbol{r},\boldsymbol{r}';\omega), \qquad (1)$$

with $\Sigma_{\mathrm{sX}}(\boldsymbol{r},\boldsymbol{r}')$ being the statically screened-exchange (sX) term and $\Sigma_{\mathrm{rest}}(\boldsymbol{r},\boldsymbol{r}';\omega)$ containing the static Coulomb hole and dynamical contributions. If the screening in the sX term is replaced by an effective static dielectric constant $\epsilon_\infty = 1/\alpha$, and Σ_{rest} is modeled by the static and local parts of the hybrid functional,[14] the quasiparticle equation has the same form as the generalized KS equation solved for hybrid functionals.[15] From these arguments we can conclude that the physical value for the mixing parameter α is related to the inverse of the dielectric constant of the material at hand.[16,17] Such a link has also been suggested to explain variations of band gaps with respect to small structural changes.[18]

In Fig. 1 we show that, for a large range of materials, the value of $1/\epsilon_\infty$—obtained with ABINIT[19] using linear response within the PBE approximation—is approximately proportional to the optimal mixing parameter α_{opt}. The latter, calculated with the computer code VASP,[9] is defined as the
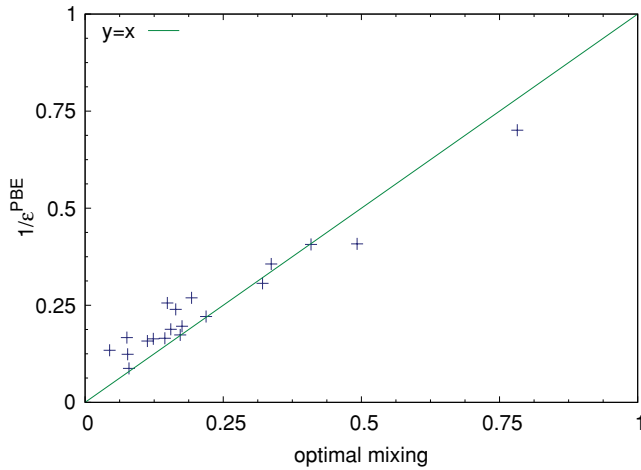
FIG. 1. (Color online) Inverse of the dielectric constant calculated with the PBE functional as a function of the optimal mixing parameter. The line $\alpha_{\text{opt}} = 1/\epsilon_\infty^{\text{PBE}}$ is a guide to the eye.

fraction α of Fock exchange of a PBE0[7] hybrid functional that reproduces the experimental band gap of the material. The correlation is evident, despite the fact that the DFT-PBE calculations systematically overestimate the dielectric constants with respect to the experiment.

In Fig. 2 we display the band gaps calculated using $\alpha = 1/\epsilon_\infty^{\text{PBE}}$ as the mixing parameter of a modified PBE0 hybrid functional (empty squares labeled PBE0ϵ_∞), compared to the experimental data and other theoretical results. In Table I we summarize the calculated band gaps for a series of semiconductors and insulators. We first emphasize that the comparison to the experiment is far from trivial. First, in the calculations we completely ignore the zero point vibrations of the nuclei. This is usually a small correction, but for some cases, like diamond, this can lead to a correction to the band gap of a few tenths of an eV.[20] Of course, the zero point vibrations are routinely subtracted in quantum chemistry benchmarks, but this practice has still to arrive for solids. Second, several of the experiments are optical, including therefore the excitonic binding energy. This quantity usually amounts to a few tens of meV, but excitonic binding energies of 0.5 eV are not unheard

of.[21] Finally, strong polaronic effects can also be expected for some ionic materials. For example, for LiF these effects lead to a shrinkage of the electronic gap that can be as large as 2 eV.[22] In conclusion, we do not believe that, in general, it is scientifically meaningful to compare our calculated values to the experiment to better than 5–10%.

In Table I we can see that the hybrid PBE0 ($\alpha = 1/4$)[7] already improves dramatically the results with respect to a local PBE functional (average error of 47%), bringing the calculated gaps toward the experimental values with an average error of less than 30%. However, this number alone hides the fact that PBE0 gives excellent results for some intermediate band-gap materials, like diamond, BN, AlN, and so on, whereas it fails both for small band-gap materials (like Si or Ge), overestimating their gaps, and for large band-gap materials (like the rare gases) where the gaps are underestimated. This is not surprising: In materials like Si, electrons are delocalized and easily polarizable, leading to a strong screening and small mixing (the optimal mixing is actually $\alpha_{\text{opt}} = 0.12$). For Ne, electrons are localized and screening is basically nonexistent ($\alpha_{\text{opt}} = 0.70$). This effect is captured by the dependence on the dielectric constant of the mixing $\alpha = 1/\epsilon_\infty$. Such a calculation decreases overall the error by almost a factor of 2. The remaining error is dominated by the large underestimation of the gap for materials like Si, Ge, or GaAs. This points to the fact that, to predict good gaps approaching the metallic limit, one needs a finite amount of the Fock exchange that is not accounted for by the simple $1/\epsilon_\infty$ model for the mixing, as can be seen in Fig. 1.

The ϵ_∞-dependent mixing is hence physically motivated and can yield good band gaps. However, the procedure to obtain it (i.e., the calculation of the dielectric constant) is fairly cumbersome and therefore often unpractical. The best option would be to find an estimator of the dielectric constant from quantities readily available from the ground state. To obtain such a relation, we first observe that there is a strong correlation between the electronic dielectric constant of the material and the energy gap.[23] Of course, it is not desirable to have a functional depending explicitly on the band gap of the material, so the question is if one can find an estimator of this quantity based solely on reduced densities.
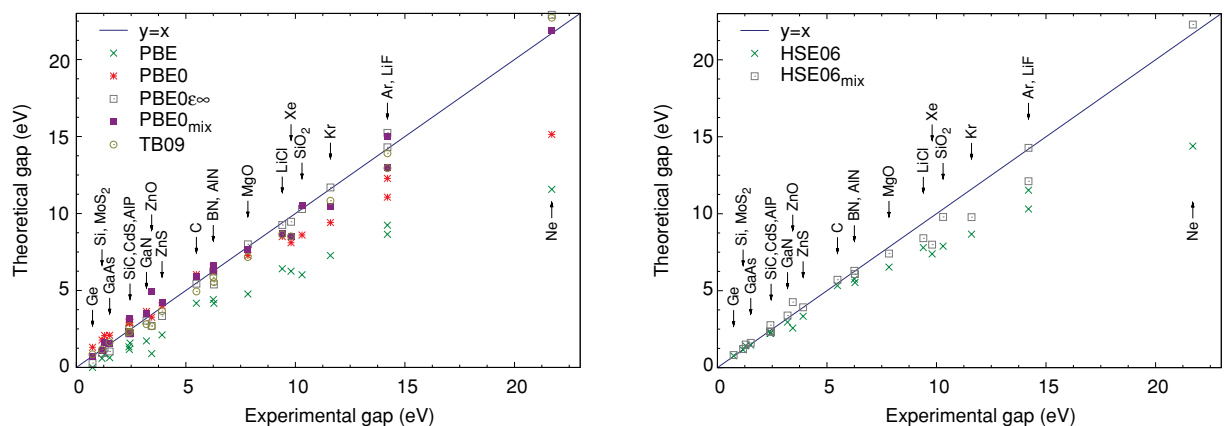

FIG. 2. (Color online) Electronic band gaps calculated as differences of generalized KS eigenvalues for a series of semiconductors and insulators. All calculations were performed at the experimental lattice constant. The symbols labeled PBE0$_{\epsilon_\infty}$, PBE0$_{\text{mix}}$, and HSE06$_{\text{mix}}$ are the results obtained with the hybrid functionals proposed in this article. TB09 results come from Ref. 28.

TABLE I. Electronic band gaps calculated as differences of generalized KS eigenvalues for a series of semiconductors and insulators. All calculations were performed at the experimental lattice constant. The column labeled HF + c denotes Hartree-Fock including PBE correlation. The columns $PBE0_{\epsilon_\infty}$, $PBE0_{mix}$, and $HSE06_{mix}$ present the results obtained with the hybrid functionals proposed in this article. The columns TB09 and G_0W_0 are from Ref. 28.

	exp.	PBE	HF + c	PBE0	$PBE0\epsilon_\infty$	$PBE0_{mix}$	HSE06	$HSE06_{mix}$	TB09	G_0W_0
Ne	21.70	11.57	26.14	15.14	22.95	21.88	14.39	22.29	22.72	19.59
Ar	14.20	8.65	18.45	11.06	14.35	12.98	10.31	12.11	13.91	13.28
Kr	11.60	7.27	16.04	9.41	11.75	10.48	8.67	9.78	10.83	
Xe	9.80	6.25	13.79	8.10	9.53	8.48	7.39	7.99	8.52	
C	5.48	4.17	12.05	6.06	5.48	5.92	5.33	5.71	4.93	5.50
Si	1.17	0.59	6.00	1.78	0.98	1.07	1.16	1.21	1.17	1.12
Ge	0.74	0.00	5.49	1.31	0.32	0.68	0.77	0.82	0.85	0.66
LiF	14.20	9.24	21.55	12.26	15.27	14.99	11.53	14.28	12.94	13.27
LiCl	9.40	6.41	14.94	8.50	9.28	8.69	7.80	8.41	8.64	
MgO	7.83	4.77	15.24	7.27	8.06	7.67	6.53	7.41	7.17	7.25
SiC	2.40	1.34	8.18	2.95	2.28	2.33	2.24	2.36	2.28	2.27
BN	6.25	4.41	13.06	6.50	6.25	6.60	5.75	6.29	5.85	6.10
GaN	3.20	1.72	10.29	3.64	3.07	3.52	2.96	3.39	2.81	2.80
GaAs	1.52	0.63	6.81	2.09	1.04	1.56	1.47	1.61	1.64	1.30
AlP	2.45	1.58	7.40	2.93	2.24	2.23	2.27	2.32	2.32	2.44
ZnS	3.91	2.11	10.06	4.00	3.38	4.25	3.34	3.92	3.66	3.29
CdS	2.42	1.17	8.56	2.87	2.25	3.15	2.23	2.76	2.66	2.06
AlN	6.28	4.16	12.94	6.25	5.39	6.29	5.53	6.08	5.55	5.83
SiO_2	10.30	6.02	16.75	8.63	9.10	10.53	7.89	9.79		
MoS_2	1.29	0.87	7.90	2.09	1.25	1.63	1.42	1.50		
ZnO	3.44	0.90	11.21	3.26	2.74	4.90	2.57	4.26	2.68	2.51
Δ (%)	–	47.32	250.23	29.42	16.53	14.37	16.92	10.36	9.85	11.25

In fact, several density-functional estimators of a "local gap" have been proposed in the past years. For example, Gutle *et al.*[24] proposed to use the quantity $G = \frac{1}{8}|\nabla n|^2/n^2$ to define the gap locally. Their arguments for the use of this quantity were based on the asymptotic expansion of the function G for finite systems (G will reduce to the ionization energy) and on the observed piecewise exponential behavior of the density.[25] More recently, the quantity $|\nabla n|/n$ was used to model a position-dependent screening function in the so-called "local-hybrid" functionals.[12,26] Also the von Weizsäcker kinetic energy density $\tau_W = |\nabla n|^2/8n$ has been used to define a "local band gap" and inserted into a "local-hybrid" functional that turns off the exact-exchange term when this local gap has metallic character.[27]

To obtain a global estimator of the band gap of the material, and therefore of its static dielectric constant, one can average the local estimator over the unit cell. We will follow the idea contained in the meta-GGA of Tran and Blaha (TB09)[28] and define the quantity

$$\bar{g} = \frac{1}{V_{cell}} \int_{cell} d^3r \sqrt{\frac{|\nabla n(\boldsymbol{r})|}{n(\boldsymbol{r})}}, \qquad (2)$$

where the integral is over the unit cell of volume V_{cell}. We note that the quantity $\bar{g}$ is very similar to the average involved in the calculation of the c_{TB09} parameter of TB09 and is quite stable regardless of which theory is used to evaluate the density. In fact, we verified that using as input either a PBE or a Hartree-Fock density leads to only minor differences in

its value. Our basic hypothesis is that the mixing parameter can be written as a function of the parameter $\bar{g}$. From the theoretical argumentation one can only conclude that $\bar{g}$ can be approximately written as a function of $\frac{|\nabla n(\boldsymbol{r})|}{n(\boldsymbol{r})}$. The relative powers in the numerator and denominator of $\frac{|\nabla n(\boldsymbol{r})|}{n(\boldsymbol{r})}$ should be fixed in such a way that in the asymptotic limit $\bar{g}$ converges to a finite number that can be related to the ionization energy of the system. Within these constraints, there is still some freedom to choose the functional dependence of $\bar{g}$. We have numerically tested different possible functional forms. The form of Eq. (2) gave slightly better results than the one used by Tran and Blaha[28] and that is the reason why we preferred it. Note that, in the end, the only difference between our mixing coefficient and the one of the TB09 functional is that, in our case, the square root is inside the integral while in TB09 it is outside.

To proceed we need to specify the local part of the hybrid. We chose to use the PBE0 form[7] which is the basis for the screened hybrid of Heyd, Scuseria, and Ernzerhof (HSE).[12] As we expected, there is a clear correlation between the value of α_{opt} and $\bar{g}$. It can be quite well fitted by the simple function $\alpha(\bar{g})$ (with $\bar{g}$ in atomic units)

$$\alpha = -1.00778 + 1.10507 \, \bar{g}. \qquad (3)$$

Analyzing the resulting gaps displayed in Fig. 2 and Table I (labeled $PBE0_{mix}$) we realize that fixing the mixing parameter according to Eq. (3)[29] reduces the mean average error to about 14%, much better than PBE0 (29%) and slightly better than the HSE06 (17%).[30] Furthermore, in contrast with PBE0

and HSE06, our density-dependent mixing describes equally well small, medium, and large gap systems. The largest errors arise for d-electron materials like ZnO where our recipe overestimates the mixing parameter and therefore the electronic gap. This is due to the fact that localized d states give too large contributions to the mixing through strong density variations. A possible solution would be finding a more pertinent density-estimator for those d states.

In view of the success of screened hybrids in improving the accuracy of PBE0, we applied our construction also to the HSE06 functional.[30] In this case, the physical interpretation of the mixing parameter as an inverse screening is considerably more complicated, as screening is already present to some extent in the range separation. Following our protocol, we arrived at the following fit for the mixing parameter

$$\alpha = 0.121\,983 + 0.130\,711\,\bar{g}^4. \tag{4}$$

We remark on the different power of $\bar{g}$ in the expression. This is due to the fact that the screening already present in HSE06 decreases considerably the strength of the Hartree-Fock term, increasing the values of $\alpha_{\rm opt}$ required to reproduce the experimental band gap of small-gap systems. This is actually the cause of the success of HSE06: for example, for Si $\alpha_{\rm opt}$ is now 0.24, which is very close to the actual mixing of HSE06 ($\alpha = 1/4$). Results for band gaps using HSE06 and our mixing scheme (labeled HSE06$_{\rm mix}$) are shown in Fig. 2 and Table I. Our mixing scheme brings down the HSE06 error from around 17% to 10%, achieving an error of the same order of magnitude as the one incurred by the G_0W_0 (11%) approximation and the TB09 meta-GGA (10%).[28]

We want now to compare our approach to the the TB09 meta-GGA. The physical interpretation of our functional implies that the mixing parameter should take values between 0 and 1, while in TB09 the corresponding parameter $c_{\rm TB09}$ is larger than 1. This difference stems from the fact that the TB09 functional is a purely local potential. Therefore, the band gap defined in terms of total energy differences should be equal to the difference of the KS eigenvalues plus the derivative discontinuity of the xc potential. It is known that the Becke-Johnson potential[31] (upon which the TB09 functional has been constructed) reproduces to a very good extent the derivative discontinuity of the exact exchange for molecular chains.[32] Therefore it is reasonable to expect that the DFT band gap with the TB09 functional, after adding the derivative discontinuity, would actually become much larger than the experiment, and possibly even larger than the Hartree-Fock gap since $c_{\rm TB09}$ is always larger than 1, in agreement with what was proved by Grüning *et al.*[33] Of course, the aim of TB09 is to obtain the gaps simply as eigenvalue differences and therefore require $c_{\rm TB09} > 1$ to compensate for the underestimation of the eigenvalue gap in the Becke-Johnson functional.[34] In this sense, it is similar in spirit to the pragmatic Xα approach.[35]

From Fig. 2 it is clear that the average error of TB09 is comparable to ours. On the one hand, a meta-GGA is clearly much lighter from the computational point of view than any hybrid functional. However, TB09 is an approximation for the xc *potential* and is thus incapable of yielding total energies (in contrast to our approach). In fact, it can be proved that TB09 is not the functional derivative of any energy

functional and therefore violates serious constraints like the zero-force theorem.[36] As a consequence, such functionals do not allow to calculate structural properties. Our approach, instead, can also be used to calculate total energies and structural properties. We tested our functionals and found that they give relaxed geometries as good as the standard PBE0 and HSE06 (with lattice constants better than 0.7% for the cubic semiconductors considered here). Moreover, we mention that the TB09 meta-GGA also inherited some of the problems of the Becke-Johnson functional[31] on which it is based (for example, TB09 is not gauge invariant).[37]

It is clear that the averaging procedure in Eq. (2) is only meaningful for bulk systems and will fail for finite systems, slabs, interfaces, supercells with defects, and so on. This issue can be fixed by converting the global $\bar{g}$ (and thus the uniform screening) into a local function function $\bar{g}(\mathbf{r})$ (i.e., transforming the functional in a local hybrid). It is, however, doubtful if strictly local or semilocal information, like the density, its gradient, or even the kinetic energy density, is sufficient to determine a useful $\bar{g}(\mathbf{r})$. In fact, according to the previous discussion, $\bar{g}(\mathbf{r})$ is mimicking an energy gap or a dielectric constant. These are not local quantities, but can be estimated by taking averages over large enough volumes. We therefore propose to define

$$\bar{g}(\mathbf{r}) = \frac{1}{\sqrt{2\pi\sigma^2}} \int d^3 r' \, e^{-\frac{(\mathbf{r}-\mathbf{r}')^2}{2\sigma^2}} \frac{|\nabla n(\mathbf{r}')|}{n(\mathbf{r}')}, \tag{5}$$

where σ should be large enough to allow for a proper estimation of the dielectric properties, but small enough to sample only the local environment. This length scale should somehow be related to the screening parameter ω that defines the separation range in screened hybrids and that is related to a characteristic distance $2/\omega$ at which the short-range interactions become negligible. Assuming that this happens at distances of 2σ, we find that $\sigma \sim 5$ Å. Note that Eq. (5) has the form of a convolution and can therefore be trivially handled by current DFT codes by using fast Fourier transforms. As all the systems studied here have small unit cells, we expect that using the local form (5) will not change the results obtained with Eq. (2).

In conclusion, we proposed a scheme to calculate dynamically the mixing parameter of hybrid functionals depending on the density of the system. In this way, the average error on the values of the energy gap are considerably reduced with respect to the original hybrid functionals. The resulting band gaps are roughly of the same quality as those obtained using a GW approach or the meta-GGA of Tran and Blaha. Moreover, this method assures also an excellent description of the structural properties. These improvements are obtained with no increase of computational time with respect to a fixed mixing parameter hybrid functional calculation.

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] G. E. Scuseria and V. N. Staroverov, in: *Theory and Applications of Computational Chemistry: The First Forty Years*, edited by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria, (Elsevier, Amsterdam, 2005), pp. 669–724.

[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).

[4] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982); J. P. Perdew and M. Levy, *ibid.* **51**, 1884 (1983); L. J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983); Phys. Rev. B **32**, 3883 (1985).

[5] L. Hedin, Phys. Rev. **139**, A796 (1965).

[6] W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys. **54**, 1 (2000).

[7] M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).

[8] E. N. Brothers, A. F. Izmaylov, J. O. Normand, V. Barone, and G. E. Scuseria, J. Chem. Phys. **129**, 011102 (2008).

[9] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11169 (1996).

[10] J. Paier, M. Marsman, and G. Kresse, J. Chem. Phys. **127**, 024103 (2007).

[11] J. Paier, M. Marsman, and G. Kresse, Phys. Rev. B **78**, 121201 (2008); J. Hafner, J. Comput. Chem. **29**, 2044 (2008).

[12] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003); **124**, 219906(E) (2006).

[13] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Phys. Rev. B **53**, 3764 (1996).

[14] F. Gygi and A. Baldereschi, Phys. Rev. Lett. **62**, 2160 (1989).

[15] Note that this is similar to the sX LDA method [see, e.g. D. M. Bylander and L. Kleinman, Phys. Rev. B **41**, 7868 (1990)], where Sigma is replaced by a Thomas-Fermi-screened exchange part of the LDA xc functional.

[16] A. Alkauskas, P. Broqvist, and A. Pasquarello, Phys. Status Solidi (b), doi:10.1002/pssb.201046195.

[17] S. J. Clark and J. Robertson, Phys. Rev. B **82**, 085208 (2010).

[18] J. Vidal, S. Botti, P. Olsson, J-F. Guillemoles, and L. Reining, Phys. Rev. Lett. **104**, 056401 (2010).

[19] X. Gonze, G.-M. Rignanese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, Ph. Ghosez, M. Veithen, J.-Y. Raty, V. Olevano, F. Bruneval, L. Retenir, R. W. Godby, G. Onida, D. R. Hamann, and D. C. Allan, Z. Kristallogr. **220**, 558 (2005).

[20] M. Cardona, Sci. Technol. Adv. Mater. **7**, S60 (2006).

[21] R. Laskowski, N. E. Christensen, P. Blaha, and B. Palanivel, Phys. Rev. B **79**, 165209 (2009).

[22] J. Vidal, F. Trani, F. Bruneval, and M. A. L. Marques, and S. Botti, Phys. Rev. Lett. **104**, 136401 (2010).

[23] V. Fiorentini and A. Baldereschi, Phys. Rev. B **51**, 17196 (1995).

[24] C. Gutle, A. Savin, J. B. Krieger, and J. Chen, Int. J. Quantum Chem. **75**, 885 (1999).

[25] G. Sperber, Int. J. Quantum Chem. **5**, 189 (1971); W. P. Wang and R. G. Parr, Phys. Rev. A **16**, 891 (1977); M. Kohout, A. Savin, and H. Preuss, J. Chem. Phys. **95**, 1928 (1991).

[26] A. V. Krukau, G. E. Scuseria, J. P. Perdew, and A. Savin, J. Chem. Phys. **129**, 124103 (2008).

[27] J. Jaramillo, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 1068 (2003).

[28] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009).

[29] Note that, in principle, there is a contribution to the potential due to the variation of the mixing parameter α with the density. In these calculations we have neglected this term. However, we believe this to be a very good approximation due to the robustness of $\bar{g}$ to the actual details of the calculation of the density.

[30] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006). Note that a local-hybrid functional is a nonlocal functional.

[31] A. D. Becke and E. R. Johnson, J. Chem. Phys. **124**, 221101 (2006).

[32] R. Armiento, S. Kümmel, and T. Körzdörfer, Phys. Rev. B **77**, 165106 (2008).

[33] M. Grüning, A. Marini, and A. Rubio, J. Chem. Phys. **124**, 154108 (2006).

[34] F. Tran, P. Blaha, and K. Schwarz, J. Phys. Condens. Matter **19**, 196208 (2007).

[35] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[36] A. P. Gaiduk and V. N. Staroverov, J. Chem. Phys. **131**, 044107 (2009); A. Karolewski, R. Armiento, and S. Kummel, J. Chem. Theory Comput. **5**, 712 (2009).

[37] E. Räsänen, S. Pittalis, and C. R. Proetto, Phys. Rev. B **81**, 195103 (2010).