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Influence of the exchange screening parameter on the performance of screened hybrid functionals

Aliaksandr V. Krukau, Oleg A. Vydrov, Artur F. Izmaylov, and Gustavo E. Scuseria[a)]
Department of Chemistry, Rice University, Houston, Texas 77005-1892

This work reexamines the effect of the exchange screening parameter ω on the performance of the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional. We show that variation of the screening parameter influences solid band gaps the most. Other properties such as molecular thermochemistry or lattice constants of solids change little with ω. We recommend a new version of HSE with the screening parameter $\omega = 0.11$ bohr^{-1} for further use. Compared to the original implementation, the new parametrization yields better thermochemical results and preserves the good accuracy for band gaps and lattice constants in solids. © *2006 American Institute of Physics.*
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I. INTRODUCTION

Applications of Kohn-Sham density functional theory to solids mostly employ semilocal approximations to the exchange-correlation energy, such as the functional of Perdew, Burke, and Ernzerhof (PBE).[1] However, semilocal functionals have some important shortcomings. For instance, they systematically underestimate band gaps with respect to experiment.[2–4] Also, semilocal functionals overestimate electron delocalization effects and therefore fail for many d- and f-element compounds.[5] Recent studies[6–11] have shown that hybrid density functionals, which include a portion of Hartree-Fock (HF) exchange, partially solve these problems. However, HF exchange drastically increases the computational demand for calculations in periodic systems.

An efficient alternative to conventional hybrids is the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE).[12–16] In HSE, the spatial decay of the HF exchange interaction is accelerated by substitution of the full $1/r$ Coulomb potential with a screened one. This enables a substantial lowering of the computational cost for calculations in extended systems. The HSE functional partitions the Coulomb potential for exchange into short-range (SR) and long-range (LR) components:

$$\frac{1}{r} = \underbrace{\frac{1 - \mathrm{erf}(\omega r)}{r}}_{\text{SR}} + \underbrace{\frac{\mathrm{erf}(\omega r)}{r}}_{\text{LR}},$$

(1)

where the screening parameter ω defines the separation range. The exchange-correlation energy is then calculated as

$$E_{xc}^{HSE} = a E_x^{HF,SR}(\omega) + (1-a) E_x^{PBE,SR}(\omega)$$
$$+ E_x^{PBE,LR}(\omega) + E_c^{PBE},$$

(2)

where $E_x^{HF,SR}$ is the short-range HF exchange, $E_x^{PBE,SR}$ and $E_x^{PBE,LR}$ are the short-range and long-range components of the PBE exchange functional obtained by integration of the model PBE exchange hole,[13,17] and E_c^{PBE} is the PBE correlation energy. The parameter $a = 1/4$ is the HF mixing constant derived from perturbation theory.[18] Note that HSE may be viewed as an adiabatic connection functional,[18] but only in the short-range portion of the potential. There is no long-range HF exchange in HSE, only short-range HF. For $\omega = 0$, HSE reduces to the hybrid functional PBEh [also known as PBE0 (Ref. 19) or PBE1PBE (Ref. 20) in the literature], and for $\omega \to \infty$, HSE becomes identical with PBE.[21] HSE with a finite value of ω can be regarded as an interpolation between these two limits. A comparative study of HSE and PBEh performance for solids was recently published.[22]

The value of the screening parameter was originally selected based on molecular tests[12] and yielded excellent band gaps for solids.[15,16] However, the screening parameter $\omega = 0.15$ bohr^{-1} quoted in our previous publications[11–16] is not the one used in the code. Because of interpretation errors, $\omega/\sqrt{2}$ was used instead of ω in the Hartree-Fock part of the code, whereas $2^{1/3}\omega$ was used in the PBE part both for short and long ranges (see recent Erratum to Ref. 12). There is no *a priori* reason to use different screening parameters for PBE and HF exchange. Moreover, HSE is exact in the uniform electron gas limit only when $\omega_{HF} = \omega_{PBE}$.

In this work, we reexamine how the choice of the screening parameter ω affects the HSE performance when both screening parameters are the same. Note that in previous publications[12–16] only the influence of screening parameter on enthalpies of formation was discussed.[12] To avoid confusion, we will here refer to the previous HSE version with $\omega_{HF} = 0.15/\sqrt{2}$ and $\omega_{PBE} = 0.15 \times 2^{1/3}$ as HSE03. The current version with $\omega_{HF} = \omega_{PBE}$ will here be denoted HSE06.

II. COMPUTATIONAL DETAILS

The HSE functional is implemented in the development version of the GAUSSIAN suite of programs.[23] The details of the implementation have been described in previous papers.[12–14] For the $E_x^{HF,SR}$ calculation, we use the new integral screening algorithm,[24] which allows us to achieve computational efficiency comparable to that of standard pure

a)Electronic mail: guscus@rice.edu

TABLE I. Total nonrelativistic energies of atoms (a.u.) using the aug-cc-pV5Z basis set.

Functional ω	PBEh 0.00	HSE06 0.05	HSE06 0.11	HSE06 0.15	HSE06 0.20	PBE ∞	HSE03[a]	Exact[b]
H	−0.501	−0.502	−0.502	−0.501	−0.501	−0.500	−0.511	−0.500
He	−2.895	−2.897	−2.896	−2.896	−2.896	−2.893	−2.918	−2.904
Li	−7.467	−7.469	−7.469	−7.469	−7.469	−7.462	−7.498	−7.478
Be	−14.637	−14.639	−14.639	−14.639	−14.639	−14.630	−14.679	−14.667
B	−24.620	−24.624	−24.623	−24.623	−24.622	−24.612	−24.675	−24.654
C	−37.807	−37.812	−37.812	−37.811	−37.811	−37.798	−37.876	−37.845
N	−54.546	−54.553	−54.552	−54.552	−54.551	−54.535	−54.629	−54.589
O	−75.023	−75.031	−75.031	−75.030	−75.029	−75.015	−75.119	−75.067
F	−99.682	−99.692	−99.692	−99.691	−99.690	−99.676	−99.792	−99.775
Ne	−128.871	−128.883	−128.883	−128.882	−128.881	−128.866	−128.995	−128.938

[a]$\omega_{HF}=0.15/\sqrt{2}$ and $\omega_{PBE}=0.15\times2^{1/3}$ (Erratum to Ref. 12).
[b]Reference 31.

density functional calculations. We use the mixing parameter $a=1/4$, ultrafine integration grid, and high accuracy criterion for self-consistent field convergence everywhere. Molecular calculations are carried out with the $6\text{-}311++G(3df,3pd)$ basis set unless otherwise specified. Throughout this work we also employ the following convention: deviation =theory−experiment. Tables that show detailed results for individual atoms, molecules, and solids are available through EPAPS depository.[25]

Calculations for solids are done with our periodic boundary-condition code.[26] The basis sets for solids, as well as references for experimental values of lattice constants and band gaps are in the supplementary information. The reciprocal space integration is performed with at least 12 k points in each dimension for the pure density functionals and at least 24 k points in each dimension for the HSE hybrid functional. The self-consistent field procedure is repeated until an accuracy of 10^{-8} hartree in the total energy per unit cell is achieved. All band gaps are reported at the optimized lattice constants.

TABLE II. Summary of deviations from experiment of standard enthalpies of formation ($\Delta_f H_{298}^0$). The $6\text{-}311++G(3df,3pd)$ basis set is used. All values are in kcal/mol.

Functional ω	PBEh 0.00	HSE06 0.05	HSE06 0.11	HSE06 0.15	HSE06 0.20	PBE ∞	HSE03
			G2-1 test set (55 molecules)				
ME	1.28	1.98	1.92	1.79	1.52	−6.65	1.28
MAE	2.86	3.12	3.11	3.07	2.98	8.16	2.75
Max (+)	9.8	10.3	10.2	10.2	9.7	10.8	9.5
Max (−)	−5.9	−5.9	−6.0	−5.9	−5.9	−28.9	−7.1
			G2/97 test set (148 molecules)				
ME	−2.42	−0.63	−0.69	−0.91	−1.39	−16.07	−2.00
MAE	4.87	3.85	3.87	3.96	4.19	16.87	4.39
Max (+)	21.3	22.2	22.1	22.1	22.1	10.8	19.7
Max (−)	−19.8	−15.1	−15.3	−15.9	−17.2	−50.5	−18.3
			G3/99 test set (223 molecules)				
ME	−4.73	−1.99	−2.05	−2.35	−3.00	−21.69	−4.45
MAE	6.66	4.81	4.84	5.00	5.38	22.22	6.57
Max (+)	21.3	22.2	22.1	22.1	22.1	10.8	20.0
Max (−)	−35.6	−27.5	−27.8	−29.0	−31.4	−79.7	−35.5

III. RESULTS AND DISCUSSION

A. Atoms and molecules

In previous work,[13] it was observed that HSE03 total energies were consistently lower than the PBEh ones. Table I shows atomic total energies for first- and second-row elements, obtained with the aug-cc-pV5Z basis set. Here we see that most of the differences between HSE03 and PBEh total energies are due to the use of two different ω values for HF and PBE exchange in HSE03. For all atoms in Table I, HSE06 yields total energies that differ from the PBEh values by only 2 mhartree/electron or less.

We have used the G3/99 (Ref. 27) test set of 223 standard enthalpies of formation, 88 ionization potentials (IPs), and 58 electron affinities (EAs) to study the influence of screening parameter ω on these properties. The molecular geometries and zero-point energies were obtained at the B3LYP/6-31G($2df,p$) level using a frequency scaling factor of 0.9854. Table II presents results for enthalpies of formation with the G3/99 test set and its two subsets: G2-1 (55 molecules) and G2/97 (148 molecules). We see that HSE06 improves on HSE03 for all the values of ω considered, reducing both mean error (ME) and mean absolute error (MAE) for the G3/99 test set.

IPs and EAs are calculated as the differences of total energies between charged and neutral species at 0 K. The HSE03 values of IPs and EAs show a systematic shift of 0.23−0.25 eV with respect to the PBEh values.[13] Tables III and IV demonstrate that HSE06 does not have such a shift. This leads to the conclusion that the systematic error for IPs and EAs exhibited by HSE03 originates from the use of two different screening parameters for HF and PBE exchange.

In order to test the influence of the screening parameter on calculated bond lengths and barrier heights, we have used the T-96R (Ref. 28) and BH42/04 (Refs. 29 and 30) test sets, respectively. For barrier heights, the forward and reverse activation barriers are compared to the best estimates.[30] The geometries for all systems in the BH42/04 test set, optimized at the QCISD level of theory, were taken from Ref. 30. Tables V and VI show that for $0\leq\omega\leq0.20$, the MAE for both bond lengths and barrier heights does not change significantly.

TABLE III. Summary of deviations from experiment of ionization potentials with G3/99 test set (Ref. 27). The 6-311++G($3df,3pd$) basis set is used. All values are in eV.

Functional	PBEh	HSE06	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.00	0.05	0.11	0.15	0.20	∞	
ME	−0.064	−0.063	−0.068	−0.073	−0.076	−0.105	0.188
MAE	0.199	0.200	0.202	0.203	0.202	0.235	0.224
Max (+)	1.61	1.61	1.60	1.59	1.56	1.11	1.88
Max (−)	−0.67	−0.67	−0.68	−0.69	−0.70	−1.01	−0.41

TABLE IV. Summary of deviations from experiment of electron affinities with G3/99 test set (Ref. 27). The 6-311++G($3df,3pd$) basis set is used. All values are in eV.

Method	PBEh	HSE06	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.00	0.05	0.11	0.15	0.20	∞	
ME	−0.027	−0.024	−0.026	−0.025	−0.022	0.061	0.195
MAE	0.165	0.165	0.165	0.163	0.160	0.118	0.206
Max (+)	1.09	1.10	1.09	1.08	1.05	0.78	1.33
Max (−)	−0.39	−0.37	−0.37	−0.37	−0.36	−0.29	−0.11

TABLE V. Summary of deviations from experiment for bond lengths of the T-96R test set (Ref. 28). The 6-311++G($3df,3pd$) basis set is used. All values are in Å.

Method	PBEh	HSE06	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.00	0.05	0.11	0.15	0.20	∞	
ME	−0.0006	−0.0004	−0.0001	0.0003	0.0011	0.0153	−0.0023
MAE	0.0097	0.0096	0.0094	0.0094	0.0092	0.0159	0.0089
Max (+)	0.063	0.064	0.057	0.059	0.062	0.055	0.039
Max (−)	−0.052	−0.050	−0.050	−0.049	−0.048	−0.013	−0.050

TABLE VI. Summary of deviations from experiment for barrier heights of the BH42/04 test set (Refs. 29 and 30). The 6-311++G($3df,3pd$) basis set is used. All values are in kcal/mol.

Method	PBEh	HSE06	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.00	0.05	0.11	0.15	0.20	∞	
ME	−4.7	−4.6	−4.7	−4.9	−5.2	−9.6	−4.6
MAE	4.7	4.6	4.7	4.9	5.2	9.6	4.6
Max (−)	−7.7	−7.4	−7.7	−8.0	−8.7	−20.3	−7.8

TABLE VII. Statistics for lattice constant errors (Å).

Method	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.11	0.15	0.20	∞	
		All solids (25 solids)			
ME	0.024	0.026	0.028	0.053	0.014
MAE	0.028	0.030	0.032	0.057	0.029
Max (+)	0.101	0.099	0.094	0.123	0.060
Max (−)	−0.015	−0.015	−0.015	−0.026	−0.059
		Metals (8 solids)			
ME	0.037	0.036	0.037	0.038	0.013
MAE	0.039	0.039	0.039	0.050	0.044
Max (+)	0.094	0.099	0.094	0.083	0.060
Max (−)	−0.010	−0.010	−0.010	−0.026	−0.059
		Semiconductors and insulators (17 solids)			
ME	0.018	0.021	0.024	0.061	0.014
MAE	0.024	0.026	0.029	0.061	0.021
Max (+)	0.062	0.068	0.077	0.123	0.057
Max (−)	−0.015	−0.015	−0.015	None	−0.015

TABLE VIII. Statistics for band gap errors (eV).

Method	HSE06	HSE06	HSE06	PBE	HSE03
ω	0.11	0.15	0.20	∞	
	Semiconductors and insulators (13 solids)				
ME	−0.12	−0.28	−0.44	−1.07	−0.07
MAE	0.21	0.32	0.46	1.07	0.19
Max (+)	0.43	0.29	0.17	None	0.46
Max (−)	−0.82	−1.03	−1.27	−2.88	−0.72

B. Solids

In this work, the performance of the HSE functional for solids is assessed with a test set of 25 metals, semiconductors, and insulators. This is the test set from Ref. 14 with four additional semiconducting solids (AlAs, AlP, BAs, and Ge). We were not able to converge calculations with $\omega < 0.11$ in a reasonable amount of computer time, so only calculations with $\omega \geq 0.11$ are reported.

The band gaps and lattice constants for individual solids can be found in Tables S7 and S8 of the supplementary information.[25] We see that the increase of ω yields longer lattice constants for the semiconductors and transition metals. On the other hand, for the alkaline metals and insulating ionic solids, the increase of screening parameter ω makes the lattice constant smaller (Li, K) or does not change it appreciably (Na, LiCl, LiF, NaCl, NaF).

The statistics for lattice constants is presented in Table VII. It can also be deduced that, on average, HSE06 tends to give somewhat longer lattice constants than HSE03. The ME for lattice constants of semiconductors with HSE06 is therefore larger than the ME with HSE03 (Table VII).

Even a small increase of ω substantially lowers the calculated band gap (Table S8 in Ref. 25), but the absolute value of the decrease is system dependent. Table VIII presents a statistical analysis of the errors for the band gaps of 13 semiconductors and insulators. In the range $0.11 \leq \omega \leq 0.20$, the smaller ω is, the closer the calculated band gaps and lattice constants are to the experiment. However, for $\omega < 0.11$, calculations become significantly more expensive computationally. Therefore, HSE06 with $\omega = 0.11$ represents a reasonable compromise between computational cost and quality of the results. Also note that HSE06 with $\omega = 0.11$ gives results that are similar to HSE03 results. This suggests that the calculated band gap depends mainly on ω_{HF} and not on ω_{PBE}.

IV. CONCLUSIONS

In our original implementation, the HSE03 functional[13] showed some unexpected problems. In particular, the total energies with this screened hybrid functional were substantially lower than those with its unscreened counterpart. Also, a systematic shift in calculated IPs and EAs was reported.[13] Results in this paper strongly suggest that these problems are related to the different screening parameters ω_{HF} and ω_{PBE} used in our original implementation by mistake. Here, we present a new version of HSE functional, for which these problems disappear.

For all studied properties except band gaps, HSE06 results have minor dependence on the screening constant. However, the screening parameter ω strongly influences the calculated band gaps. The results presented here suggest that HSE06 with the parameters $a = 0.25$ and $\omega = 0.11$ bohr^{-1} predicts enthalpies of formation, ionization potentials, and electron affinities somewhat better than HSE03, while preserving the good accuracy for band gaps and lattice constants in solids.

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