Self-consistent generalized Kohn-Sham local hybrid functionals of screened exchange: Combining local and range-separated hybridization

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(Received 9 June 2008; accepted 18 August 2008; published online 29 September 2008)

We present local hybrid functionals that incorporate a position-dependent admixture of short-range (screened) nonlocal exact [Hartree-Fock-type (HF)] exchange. We test two limiting cases: screened local hybrids with no long-range HF exchange and long-range-corrected local hybrids with 100% long-range HF exchange. Long-range-corrected local hybrids provide the exact asymptotic exchange-correlation potential in finite systems, while screened local hybrids avoid the problems inherent to long-range HF exchange in metals and small-bandgap systems. We treat these functionals self-consistently using the nonlocal exchange potential constructed from Kohn-Sham orbital derivatives. Generalized Kohn-Sham calculations with screened and long-range-corrected local hybrids can provide accurate molecular thermochemistry and kinetics, comparable to existing local hybrids of full-range exchange. Generalized Kohn-Sham calculations with existing full-range local hybrids provide results consistent with previous non-self-consistent and “localized local hybrid” calculations. These new functionals appear to provide a promising extension of existing local and range-separated hybrids. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2980056](https://doi.org/10.1063/1.2980056)]

I. INTRODUCTION

Density functional theory (DFT) has become the pre-dominant method for predicting the electronic structures of molecules and condensed systems.¹ DFT's accuracy and computational efficiency strongly depend on the approximation used for the exchange-correlation (XC) functional

$$E_{XC} = \int d^3\mathbf{r} e_{XC}(\mathbf{r}). \quad (1)$$

Semilocal functionals approximate $e_{XC}(\mathbf{r})$, the XC energy density at point $\mathbf{r}$, using ingredients obtained from the occupied Kohn-Sham (KS) spinorbitals $\{\phi_{i\sigma}(\mathbf{r})\}$ ($\sigma = \uparrow, \downarrow$) in an infinitesimal region around $\mathbf{r}$. The local spin density approximation (LSDA) uses the electron spin-density

$$\rho_{\sigma}(\mathbf{r}) = \sum_i |\phi_{i\sigma}(\mathbf{r})|^2, \quad (2)$$

generalized gradient approximations (GGAs) use the density and density gradient, and meta-GGAs incorporate the kinetic energy density

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_{i\sigma}(\mathbf{r})|^2, \quad (3)$$

and/or density Laplacian.² Some of the most accurate XC functionals are “hybrids” incorporating a fraction of exact [Hartree-Fock-type (HF)] exchange.³ Mixing HF exchange and semilocal DFT exchange is formally justified by adiabatic connection arguments^{3,4} and is thought to simulate some nondynamical correlation effects.^{5–12}

There has been substantial recent interest^{13–23} in local hybrid functionals containing a position-dependent admixture of HF exchange

$$E_{XC}^{Lh} = E_C^{DFT} + \sum_{\sigma} \int d^3\mathbf{r} [f_{\sigma}(\mathbf{r}) e_{X\sigma}^{HF}(\mathbf{r}) + (1 - f_{\sigma}(\mathbf{r})) e_{X\sigma}^{DFT}(\mathbf{r})]. \quad (4)$$

Here E_C^{DFT} is the energy obtained from a semilocal correlation functional and $e_{X\sigma}^{DFT}(\mathbf{r})$ is the σ -spin exchange energy density predicted by a semilocal exchange functional. The HF exchange energy density (in the conventional gauge^{13,22}) is constructed from the occupied KS spinorbitals as

$$e_{X\sigma}^{HF}(\mathbf{r}_1) = -\frac{1}{2} \sum_{ij} \phi_{i\sigma}^*(\mathbf{r}_1) \phi_{j\sigma}(\mathbf{r}_1) \int d^3\mathbf{r}_2 \frac{\phi_{j\sigma}^*(\mathbf{r}_2) \phi_{i\sigma}(\mathbf{r}_2)}{r_{12}}, \quad (5)$$

($r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$). A local hybrid's performance is governed by the choice of mixing function $f_{\sigma}(\mathbf{r})$ and the choice of semilocal density functional. The general local hybrid form was suggested by Burke *et al.*¹³ as early as 1998, but specific forms of $f_{\sigma}(\mathbf{r})$ were not proposed or implemented until later.^{2,14} Jaramillo *et al.*¹⁴ proposed and implemented a local hybrid with

$$f_{\sigma}(\mathbf{r}) = \frac{\tau_{W\sigma}(\mathbf{r})}{\tau_{\sigma}(\mathbf{r})}, \quad (6)$$

$$\tau_{W\sigma}(\mathbf{r}) = \frac{|\nabla \rho_{\sigma}(\mathbf{r})|^2}{8\rho_{\sigma}(\mathbf{r})}. \quad (7)$$

This mixing function incorporates no HF exchange in regions of constant density (e.g., the uniform electron gas,

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where semilocal exchange is exact). It incorporates 100% HF exchange in one-electron regions where HF exchange is the exact XC functional. Unfortunately, its thermochemical performance is rather poor.¹⁴ Later, Kaupp and co-workers^{16,17,20} showed that parametrized mixing functions including

$$f_{\sigma}(\mathbf{r}) = \alpha \frac{\tau_{W\sigma}(\mathbf{r})}{\tau_{\sigma}(\mathbf{r})}, \quad (8)$$

(where α is an empirical parameter) can provide accurate thermochemistry and reaction barriers in local hybrids of LSDA exchange. We recently presented a density matrix similarity metric that shows promise for constructing local hybrids of LSDA and GGA exchange.^{19,21}

There has also been substantial recent interest^{24–50} in range-separated hybrid functionals incorporating different fractions of HF exchange at different electron-electron separations. Range-separated hybrids partition the Coulomb operator into short-range (SR) and long-range (LR) components

$$\frac{1}{r_{12}} = \underbrace{\frac{\text{erfc}(\omega r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}} \quad (9)$$

and include different fractions of HF exchange in each range.²⁵ The parameter ω in Eq. (9) controls the range separation. The error function is chosen for computational convenience, as the screened electron-electron repulsion integrals can be evaluated analytically in Gaussian basis sets. Long-range-corrected (LC) functionals incorporating 100% LR HF exchange yield the exact asymptotic exchange-correlation potential in finite systems.⁴⁴ These functionals improve properties such as polarizabilities of long chains,^{30,40} charge transfer and Rydberg excitations,³⁶ nonlinear optical properties,³⁹ and dissociation of two-center three-electron bonds.^{40,43} They can provide accurate molecular thermochemistry and kinetics,^{41,43} and have been extended to multideterminant treatments of LR correlation.^{27,34} Conversely, screened hybrids incorporating only SR HF exchange avoid the problems inherent to LR HF exchange in continuous systems. (The long-range exchange is exactly cancelled by LR correlation in the uniform electron gas,⁵¹ and approximately cancelled by LR correlation in metals and narrow-bandgap semiconductors. Calculations combining long-range HF exchange with a semilocal approximation for correlation have formal and computational problems in such systems.^{44,52,53}) The screened hybrid of Heyd, Scuseria, and Ernzerhof (HSE) (Refs. 31 and 42) combines the range-separated²⁸ Perdew-Burke-Ernzerhof⁵⁴ (PBE) GGA with 25% SR HF exchange. It accurately treats many properties of molecules and solids,^{32,33} providing generalized KS (see below) band energy differences that accurately reproduce semiconductor band gaps.^{33,37} It also avoids the formal and computational problems inherent to LR HF exchange in solids. The observation that both screened and LC hybrids can accurately treat molecular thermochemistry⁴¹ led to recent work on “middle-range” hybrids.^{45,50}

Most existing range-separated hybrid functionals use a universal range-separation parameter ω and a constant fraction of HF exchange in each range. Despite its successes, this approach has clear limitations. Several investigators have discussed the importance of more flexible approximations such as system-dependent range separation.^{24,26,38,46,49}

In this work, we present a new combination of the local and range-separated approximations. Our “local admixture of screened exchange” partitions the exchange energy as in Eq. (9), with a *universal* range-separation parameter ω and a *position-dependent* admixture of SR HF exchange. This approximation complements the position-dependent ω recently proposed in Ref. 49. We consider two limiting cases: LC local hybrids

$$E_{\text{XC}}^{\text{LC-Lh}} = E_X^{\text{LR-HF}} + E_C^{\text{DFT}} + \sum_{\sigma} \int d^3\mathbf{r} [f_{\sigma}(\mathbf{r}) e_{X\sigma}^{\text{SR-HF}}(\mathbf{r}) + (1 - f_{\sigma}(\mathbf{r})) e_{X\sigma}^{\text{SR-DFT}}(\mathbf{r})], \quad (10)$$

and screened local hybrids

$$E_{\text{XC}}^{\text{SC-Lh}} = E_X^{\text{LR-DFT}} + E_C^{\text{DFT}} + \sum_{\sigma} \int d^3\mathbf{r} [f_{\sigma}(\mathbf{r}) e_{X\sigma}^{\text{SR-HF}}(\mathbf{r}) + (1 - f_{\sigma}(\mathbf{r})) e_{X\sigma}^{\text{SR-DFT}}(\mathbf{r})]. \quad (11)$$

The SR HF exchange energy density $e_{X\sigma}^{\text{SR-HF}}(\mathbf{r})$ in Eqs. (10) and (11) is obtained by replacing $1/r_{12}$ with $\text{erfc}(\omega r_{12})/r_{12}$ in Eq. (5) (see Sec. II). The SR semilocal exchange energy density $e_{X\sigma}^{\text{SR-DFT}}(\mathbf{r})$ is obtained from model exchange holes as in standard range-separated hybrids.^{28,30,35,47,48} LC local hybrids incorporate 100% asymptotic HF exchange, regardless of the choice of mixing function. (Mixing functions incorporating 100% asymptotic HF exchange by construction were proposed in Refs. 14, 17, and 19–21.) These functionals will be valuable for calculations on finite systems, where HF exchange provides the exact asymptotic exchange-correlation potential. Screened local hybrids incorporate only SR HF exchange, regardless of the choice of mixing function. They will be essential for local hybrid treatments of metals and narrow-bandgap semiconductors, due to the aforementioned problems of LR HF exchange in such systems.^{52,53}

In this work, we test screened and LC local hybrids that use Eq. (8) to locally admix SR HF exchange. These functionals contain two empirical parameters: The maximum fraction of SR HF exchange α in Eq. (8), and the universal range-separation parameter ω in Eq. (9).

The local, range-separated, and local-range-separated hybrids discussed above are all special cases of XC functionals that depend explicitly on the KS spinorbitals. Self-consistent implementations of such functionals typically follow one of two routes. The first route is to calculate the KS local XC potential

$$v_{\text{XC}\sigma}(\mathbf{r}) = \frac{\delta E_{\text{XC}}}{\delta \rho_{\sigma}(\mathbf{r})}, \quad (12)$$

using the optimized effective potential method^{55–59} (OEP) or approximations such as KLI (Ref. 60) or LHF/CEDA.^{61,62} Such calculations yield high quality one-particle spectra^{57,58} and are useful for predicting properties such as NMR chemi-

cal shifts,^{63–65} but have formal and computational problems in finite basis sets.^{66–69} The second route is to calculate the nonlocal XC potential that may be defined in terms of functional derivatives with respect to the spinorbitals

$$\hat{v}_{XC\sigma}\phi_{i\sigma}(\mathbf{r}) \leftarrow \frac{\delta E_{XC}}{\delta \phi_{i\sigma}^*(\mathbf{r})}. \quad (13)$$

Equation (13) contributes to the Fock-like Hamiltonian matrix in a finite KS orbital basis set $\{\mu(\mathbf{r})\}$ with matrix elements

$$V_{\mu\nu,\sigma}^{XC} = \int d^3\mathbf{r} \mu^*(\mathbf{r}) \hat{v}_{XC\sigma} \nu(\mathbf{r}). \quad (14)$$

This generalized Kohn-Sham (GKS) approach is outside of the KS formalism, but is a rigorous generalized DFT in its own right.^{70,71} GKS appears to be behind the success of the HSE screened hybrid for semiconductor band gaps.^{31,33,37,72} GKS is also typically simpler to implement and more computationally tractable than OEP approximations. Most existing density functional codes use GKS implementations of hybrid and meta-GGA functionals.

Local hybrid functionals were implemented self-consistently within the LHF/CEDA approximation to OEP by Arbuznikov, Kaupp, and Bahmann (AKB) in 2006.¹⁵ This self-consistent “localized local hybrid” (LLH) method was later extended and applied in calculations of nuclear shielding constants.¹⁸ The implementation is computationally demanding, requiring two separate resolutions of the identity to construct the averaged local potential entering the LLH equations. Most subsequent thermochemical tests of local hybrids have been performed non-self-consistently.^{16,17,19–21,23}

In this work, we present self-consistent GKS calculations using the screened and LC local hybrid functionals defined in Eqs. (10) and (11). Section II derives the necessary nonlocal GKS exchange potentials. Section III gives details of our implementation and calculations. Section IV presents thermochemical tests of screened and LC local hybrids. Section IV also compares our GKS approach to published non-self-consistent and LLH treatments of existing local hybrids of full-range (FR) HF exchange. Section V presents our conclusions.

II. GKS LOCAL HYBRID EXCHANGE POTENTIALS

Here we derive matrix elements of the GKS exchange potential for FR, screened, and LC local hybrid functionals. The derivation closely follows the “functional derivatives with respect to the orbitals” which were obtained by AKB as an intermediate step in the LLH of Refs. 15 and 18. We generalize the derivation to screened exchange and complex orbitals and use partial integration to remove quantities such as $\nabla|\nabla\rho|$ and $\nabla\tau$ [see Eq. (28) of Ref. 15 and Eq. (17) of Ref. 18]. The resulting equations can also be derived following the procedure of Pople *et al.*⁷³ by first expanding the KS orbitals in a basis set, then taking the derivative of Eq. (15) with respect to the expansion coefficients (not shown). Extensions to more general hyper-GGA forms are presented. We note that although the authors of Refs. 15 and 18 did not

report GKS calculations using the nonlocal exchange potentials constructed from their functional derivatives, they could have done so had they wished.

We begin with the σ -spin exchange energy of a local hybrid of FR HF exchange from Eq. (4),

$$E_{X\sigma}^{\text{Lh}} = \int d^3\mathbf{r}_1 [f_{\sigma}(\mathbf{r}_1) e_{X\sigma}^{\text{HF}}(\mathbf{r}_1) + (1 - f_{\sigma}(\mathbf{r}_1)) e_{X\sigma}^{\text{DFT}}(\mathbf{r}_1)]. \quad (15)$$

(The remainder of this section suppresses spin labels for conciseness. KS orbitals, electron and exchange energy densities, mixing functions, and associated quantities are assumed to be σ spin. The straightforward extension to screened and LC local hybrids is presented below.) We construct the HF exchange energy density by applying a resolution of the identity (RI) to Eq. (5) and symmetrizing, following Della Sala and Görling⁶¹

$$\begin{aligned} e_X^{\text{HF}}(\mathbf{r}_1) &= -\frac{1}{4} \sum_{ij} \phi_i^*(\mathbf{r}_1) \int d^3\mathbf{s} \delta(\mathbf{r}_1 - \mathbf{s}) \phi_j(\mathbf{s}) \int d^3\mathbf{r}_2 \\ &\quad \times \frac{\phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2)}{|\mathbf{s} - \mathbf{r}_2|} + \text{c.c.} \\ &= -\frac{1}{4} \sum_{ij} \sum_{\alpha\beta} \phi_i^*(\mathbf{r}_1) \alpha(\mathbf{r}_1) S_{\alpha\beta}^{-1} \int d^3\mathbf{s} \int d^3\mathbf{r}_2 \\ &\quad \times \frac{\beta^*(\mathbf{s}) \phi_j(\mathbf{s}) \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2)}{|\mathbf{s} - \mathbf{r}_2|} + \text{c.c.} \end{aligned} \quad (16)$$

Here $\{\alpha(\mathbf{r})\}$ is the RI basis set, $S_{\alpha\beta}^{-1}$ is its inverse overlap matrix, and “c.c.” denotes the complex conjugate of the displayed expression. We assume in what follows that the KS orbital basis set $\{\mu(\mathbf{r})\}$ is used for the RI. Given a spin density matrix $\mathbf{P}$ defined in terms of the occupied KS spinorbitals as

$$\sum_i \phi_i(\mathbf{r}_1) \phi_i^*(\mathbf{r}_2) = \sum_{\mu\nu} \mu(\mathbf{r}_1) P_{\mu\nu} \nu^*(\mathbf{r}_2), \quad (17)$$

the HF exchange energy density of Eq. (16) becomes

$$e_X^{\text{HF}}(\mathbf{r}_1) = \frac{1}{2} \sum_{\mu\nu} \mu(\mathbf{r}_1) Q_{\mu\nu} \nu^*(\mathbf{r}_1), \quad (18)$$

$$\mathbf{Q} = \frac{1}{2} (\mathbf{S}^{-1} \cdot \mathbf{K} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{K} \cdot \mathbf{S}^{-1}), \quad (19)$$

where

$$K_{\mu\nu} = - \sum_{\lambda\eta} P_{\lambda\eta} (\mu\lambda|\eta\nu), \quad (20)$$

$$(\mu\lambda|\eta\nu) = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\mu^*(\mathbf{r}_1) \lambda(\mathbf{r}_1) \eta^*(\mathbf{r}_2) \nu(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (21)$$

We assume that the local hybrid mixing function $f(\mathbf{r})$ and the exchange energy density $e_X^{\text{DFT}}(\mathbf{r})$ are real semilocal functions of $\phi_i(\mathbf{r})$, $\nabla\phi_i(\mathbf{r})$, and their complex conjugates. (Extensions to the nonlocal mixing functions of Refs. 19 and 21 will be treated in future work.) $e_X^{\text{HF}}(\mathbf{r})$ is a nonlocal function of $\phi_i(\mathbf{r}')$ and $\phi_i^*(\mathbf{r}')$, but not a function of $\nabla\phi_i(\mathbf{r}')$ or $\nabla\phi_i^*(\mathbf{r}')$. Given this, the functional derivative of Eq. (15) becomes

$$\frac{\delta E_X^{\text{Lh}}}{\delta \phi_i^*(\mathbf{r})} = (\hat{v}^{\text{Lh}(1)} + \hat{v}^{\text{Lh}(2)} + \hat{v}^{\text{Lh}(3)}) \phi_i(\mathbf{r}), \quad (22)$$

$$\hat{v}^{\text{Lh}(1)} \phi_i(\mathbf{r}) = \int d^3 \mathbf{r}_1 f(\mathbf{r}_1) \frac{\partial e_X^{\text{HF}}(\mathbf{r}_1)}{\partial \phi_i^*(\mathbf{r})}, \quad (23)$$

$$\hat{v}^{\text{Lh}(2)} \phi_i(\mathbf{r}) = e_{\text{diff}} \frac{\partial f(\mathbf{r})}{\partial \phi_i^*(\mathbf{r})} - \nabla \cdot \left[e_{\text{diff}} \frac{\partial f(\mathbf{r})}{\partial (\nabla \phi_i^*(\mathbf{r}))} \right], \quad (24)$$

$$\hat{v}^{\text{Lh}(3)} \phi_i(\mathbf{r}) = (1 - f(\mathbf{r})) \frac{\partial e_X^{\text{DFT}}(\mathbf{r})}{\partial \phi_i^*(\mathbf{r})} - \nabla \cdot \left[(1 - f(\mathbf{r})) \frac{\partial e_X^{\text{DFT}}(\mathbf{r})}{\partial (\nabla \phi_i^*(\mathbf{r}))} \right]. \quad (25)$$

Here

$$e_{\text{diff}} = e_X^{\text{HF}}(\mathbf{r}) - e_X^{\text{DFT}}(\mathbf{r}). \quad (26)$$

The nonlocal operator $\hat{v}^{\text{Lh}(1)}$ is obtained by substituting Eq. (16) into Eq. (23),

$$\begin{aligned} \hat{v}^{\text{Lh}(1)} \nu(\mathbf{r}) = & -\frac{1}{4} \sum_j \sum_{\alpha\beta} \left(f(\mathbf{r}) \alpha(\mathbf{r}) S_{\alpha\beta}^{-1} \int d^3 \mathbf{s} \int d^3 \mathbf{r}_2 \frac{\beta^*(\mathbf{s}) \phi_j(\mathbf{s}) \phi_j^*(\mathbf{r}_2) \nu(\mathbf{r}_2)}{|\mathbf{s} - \mathbf{r}_2|} + \int d^3 \mathbf{r}_1 f(\mathbf{r}_1) \nu(\mathbf{r}_1) \alpha^*(\mathbf{r}_1) \right. \\ & \times (S_{\alpha\beta}^{-1})^* \int d^3 \mathbf{s} \frac{\beta(\mathbf{s}) \phi_j^*(\mathbf{s}) \phi_j(\mathbf{r})}{|\mathbf{s} - \mathbf{r}|} + \int d^3 \mathbf{r}_1 f(\mathbf{r}_1) \phi_j^*(\mathbf{r}_1) \alpha(\mathbf{r}_1) S_{\alpha\beta}^{-1} \int d^3 \mathbf{s} \frac{\beta^*(\mathbf{s}) \nu(\mathbf{s}) \phi_j(\mathbf{r})}{|\mathbf{s} - \mathbf{r}|} + \int d^3 \mathbf{r}_1 f(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \alpha^*(\mathbf{r}_1) \\ & \left. \times (S_{\alpha\beta}^{-1})^* \int d^3 \mathbf{r}_2 \frac{\phi_j^*(\mathbf{r}_2) \nu(\mathbf{r}_2) \beta(\mathbf{r})}{|\mathbf{r}_2 - \mathbf{r}|} \right). \end{aligned} \quad (27)$$

Matrix elements of this operator are obtained from Eq. (14) as

$$\begin{aligned} V_{\mu\nu}^{\text{Lh}(1)} = & -\frac{1}{4} \sum_{\alpha\beta} \left(\left[\int d^3 \mathbf{r} \mu^*(\mathbf{r}) f(\mathbf{r}) \alpha(\mathbf{r}) \right] S_{\alpha\beta}^{-1} \left[\sum_j \int d^3 \mathbf{s} \int d^3 \mathbf{r}_2 \frac{\beta^*(\mathbf{s}) \phi_j(\mathbf{s}) \phi_j^*(\mathbf{r}_2) \nu(\mathbf{r}_2)}{|\mathbf{s} - \mathbf{r}_2|} \right] \right. \\ & + \left[\sum_j \int d^3 \mathbf{r} \int d^3 \mathbf{s} \frac{\mu^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{s}) \beta(\mathbf{s})}{|\mathbf{s} - \mathbf{r}|} \right] S_{\beta\alpha}^{-1} \left[\int d^3 \mathbf{r}_1 \alpha^*(\mathbf{r}_1) f(\mathbf{r}_1) \nu(\mathbf{r}_1) \right] \\ & + \sum_{\lambda\eta} P_{\lambda\eta} \left[\int d^3 \mathbf{r}_1 \eta^*(\mathbf{r}_1) f(\mathbf{r}_1) \alpha(\mathbf{r}_1) \right] S_{\alpha\beta}^{-1} \left[\int d^3 \mathbf{s} \int d^3 \mathbf{r} \frac{\mu^*(\mathbf{r}) \lambda(\mathbf{r}) \beta^*(\mathbf{s}) \nu(\mathbf{s})}{|\mathbf{s} - \mathbf{r}|} \right] \\ & \left. + \sum_{\lambda\eta} \left[\int d^3 \mathbf{r} \int d^3 \mathbf{r}_2 \frac{\mu^*(\mathbf{r}) \beta(\mathbf{r}) \eta^*(\mathbf{r}_2) \nu(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}|} \right] S_{\beta\alpha}^{-1} \left[\int d^3 \mathbf{r}_1 \alpha^*(\mathbf{r}_1) f(\mathbf{r}_1) \lambda(\mathbf{r}_1) \right] P_{\lambda\eta} \right), \end{aligned} \quad (28)$$

where $(S_{\alpha\beta}^{-1})^* = S_{\beta\alpha}^{-1}$ and Eq. (17) is invoked. Simplification yields the matrix representation of the operator

$$\mathbf{V}^{\text{Lh}(1)} = \frac{1}{4} (\mathbf{f} \cdot \mathbf{S}^{-1} \cdot \mathbf{K} + \mathbf{K} \cdot \mathbf{S}^{-1} \cdot \mathbf{f}) + \frac{1}{2} \tilde{\mathbf{K}}, \quad (29)$$

where the matrix $\mathbf{f}$ is given by

$$\mathbf{f}_{\mu\nu} = \int d^3 \mathbf{r} \mu^*(\mathbf{r}) f(\mathbf{r}) \nu(\mathbf{r}), \quad (30)$$

and the matrix $\tilde{\mathbf{K}}$ is obtained by replacing $\mathbf{P}$ with $(\mathbf{P} \cdot \mathbf{f} \cdot \mathbf{S}^{-1} + \mathbf{S}^{-1} \cdot \mathbf{f} \cdot \mathbf{P})/2$ in Eq. (20). For a global hybrid of FR HF exchange, where $f(\mathbf{r})$ equals a constant α , the matrix $\mathbf{f}$ is α times the KS orbital basis overlap matrix $\mathbf{S}$, and $\mathbf{V}^{\text{Lh}(1)} = \alpha \mathbf{K}$, as expected.

Matrix elements of $\hat{v}^{\text{Lh}(2)}$ and $\hat{v}^{\text{Lh}(3)}$ are obtained in the usual way.^{73,74} $\hat{v}^{\text{Lh}(2)}$ is

$$\begin{aligned} \hat{v}^{\text{Lh}(2)} \nu(\mathbf{r}) = & e_{\text{diff}} \left(\nu(\mathbf{r}) \frac{\partial f(\mathbf{r})}{\partial \rho(\mathbf{r})} + 2[\nabla \rho(\mathbf{r}) \cdot \nabla \nu(\mathbf{r})] \frac{\partial f(\mathbf{r})}{\partial G(\mathbf{r})} \right) \\ & - \nabla \cdot \left[e_{\text{diff}} \left(2[\nabla \rho(\mathbf{r})] \nu(\mathbf{r}) \frac{\partial f(\mathbf{r})}{\partial G(\mathbf{r})} \right. \right. \\ & \left. \left. + \frac{1}{2} [\nabla \nu(\mathbf{r})] \frac{\partial f(\mathbf{r})}{\partial \tau(\mathbf{r})} \right) \right], \end{aligned} \quad (31)$$

where $G(\mathbf{r}) = |\nabla \rho(\mathbf{r})|^2$. Its matrix elements are obtained from Eq. (14), using a partial integration to remove terms in e.g., ∇e_{diff} and $\nabla \tau$ resulting from the second and third lines of Eq. (31),

$$\begin{aligned}
V_{\mu\nu}^{\text{Lh}(2)} = & \int d^3\mathbf{r} e_{\text{diff}} \left(\mu^*(\mathbf{r}) \nu(\mathbf{r}) \frac{\partial f(\mathbf{r})}{\partial \rho(\mathbf{r})} \right. \\
& + 2[\nabla \rho(\mathbf{r}) \cdot \nabla (\mu^*(\mathbf{r}) \nu(\mathbf{r}))] \frac{\partial f(\mathbf{r})}{\partial G(\mathbf{r})} \\
& \left. + \frac{1}{2} [\nabla \mu^*(\mathbf{r}) \cdot \nabla \nu(\mathbf{r})] \frac{\partial f(\mathbf{r})}{\partial \tau(\mathbf{r})} \right). \quad (32)
\end{aligned}$$

A similar derivation gives

$$\begin{aligned}
V_{\mu\nu}^{\text{Lh}(3)} = & \int d^3\mathbf{r} (1 - f(\mathbf{r})) \left(\mu^*(\mathbf{r}) \nu(\mathbf{r}) \frac{\partial e_X^{\text{DFT}}(\mathbf{r})}{\partial \rho(\mathbf{r})} \right. \\
& + 2[\nabla \rho(\mathbf{r}) \cdot \nabla (\mu^*(\mathbf{r}) \nu(\mathbf{r}))] \frac{\partial e_X^{\text{DFT}}(\mathbf{r})}{\partial G(\mathbf{r})} \\
& \left. + \frac{1}{2} [\nabla \mu^*(\mathbf{r}) \cdot \nabla \nu(\mathbf{r})] \frac{\partial e_X^{\text{DFT}}(\mathbf{r})}{\partial \tau(\mathbf{r})} \right). \quad (33)
\end{aligned}$$

GKS exchange potentials for screened and LC local hybrids are obtained by replacing the FR exchange energy densities in Eq. (15) with the corresponding SR quantities. The SR DFT exchange energy density and its derivatives are obtained from DFT exchange hole models in the usual way.^{28,30,35,47,48} The SR HF exchange terms are obtained by evaluating the two-electron integrals in Eq. (21) with the SR interaction in Eq. (9), and using these integrals to construct the $\mathbf{K}$ and $\tilde{\mathbf{K}}$ matrices entering Eq. (29). The LR exchange energy density, which in the present work does not include local hybridization, contributes to the GKS exchange potential in the usual way.

This derivation is readily extended to more general hyper-GGAs.² To illustrate, we consider a hyper-GGA for exchange

$$E_X^{\text{HGGA}} = \int d^3\mathbf{r} e_X^{\text{HGGA}}(\mathbf{r}, [\rho(\mathbf{r}), G(\mathbf{r}), \tau(\mathbf{r}), \{e_{X,a}^{\text{HF}}(\mathbf{r})\}]),$$

where $\{e_{X,a}^{\text{HF}}(\mathbf{r})\}$ are the set of HF exchange energy densities evaluated with modified electron-electron interactions $\{h_a(|\mathbf{r}-\mathbf{r}'|)\}$, and the exchange energy density is a functional of all the quantities in square brackets. (Here a indexes the different modified interactions.) Matrix elements of the GKS exchange potential become

$$V_{\mu\nu}^{\text{HGGA}} = \sum_a V_{\mu\nu,a}^{\text{HGGA}(1)} + V_{\mu\nu}^{\text{HGGA}(2)}. \quad (34)$$

The nonlocal operators $V_{\mu\nu,a}^{\text{HGGA}(1)}$ are obtained from Eq. (29) by replacing $f(\mathbf{r})$ with $\partial(e_X^{\text{HGGA}}(\mathbf{r}))/\partial(e_{X,a}^{\text{HF}}(\mathbf{r}))$ in Eq. (30), and evaluating $\mathbf{K}$ and $\tilde{\mathbf{K}}$ with the modified electron-electron interaction $h_a(|\mathbf{r}-\mathbf{r}'|)$. The other operator is obtained by replacing e_X^{DFT} with e_X^{HGGA} and setting $f(\mathbf{r})=0$ in Eq. (33).

III. COMPUTATIONAL DETAILS

We have implemented the expressions in Sec. II into the development version of the GAUSSIAN electronic structure program.⁷⁵ The implementation is restricted to using the KS orbital basis set for the RI used to construct the HF exchange energy density and its derivatives. Accordingly, all calculations use fully uncontracted Gaussian atomic orbital (AO)

TABLE I. Definition of the five local hybrid functionals investigated in this work. “FR,” “SC,” and “LC” denote full-range, screened, and long-range-corrected local hybrids. ω (bohr⁻¹) is the range-separation parameter of Eq. (9).

	ω	$f(\mathbf{r})$
FR-Lh-BPW91 ^a	...	τ_W/τ
FR-Lh-LSDA ^b	...	$0.48\tau_W/\tau$
SC-Lh-LSDA	0.11	$0.55\tau_W/\tau$
LC-Lh-LSDA	0.18	$0.44\tau_W/\tau$
SC-Lh-PBE	0.11	$0.25\tau_W/\tau$

^aReference 14 and 15.

^bReference 16.

basis sets of augmented-triple-zeta or larger size.^{15,22,76}

We test five local hybrid functionals: two previously proposed FR local hybrids, screened and LC LSDA local hybrids, and a screened PBE local hybrid. Details of the functionals are presented in Table I. The functionals hybridize the BPW91,^{77–79} LSDA (Vosko-Wilk-Nusair correlation functional V of Ref. 80), range-separated LSDA,³⁵ and range-separated²⁸ PBE (Ref. 54) exchange functionals. The SC-Lh-PBE screened local hybrid is an extension of the HSE06 (Refs. 31 and 42) screened hybrid. We selected the HSE06 $\omega=0.11$ bohr⁻¹ for screened local hybrids, as this value has been shown to provide a reasonable balance between accuracy and computational efficiency in screened hybrid calculations on solids.⁴² The remaining empirical parameters of our screened and LC local hybrids were fitted to the small AE6 and BH6 sets of atomization energies and hydrogen transfer reaction barrier heights.⁸¹

We test these functionals for heats of formation ($\Delta_f H_{298}^0$) of the G2-1 (54 molecules),^{82,83} G2/97 (147 molecules),⁸⁴ and G3/99 (222 molecules) (Ref. 85) data sets;⁸⁶ hydrogen-transfer reaction barrier heights of the HTBH38/04 set and non-hydrogen-transfer reaction barrier heights of the NHTBH38/04 set;^{87,88} bond lengths of the T-96R set;^{89,90} and atomization energies and barrier heights of the small AE6 and BH6 test sets.⁸¹ Geometries and experimental values for the HTBH38/04 and NHTBH38/04 sets are from Ref. 88. Those for the AE6 and BH6 sets are from Ref. 81. Experimental values for the T-96R set are from Ref. 89. Be₂ was omitted from the T-96R set due to its van der Waals bond. Si₂ was omitted from the G2-1, G2/97, G3/99, and T-96R sets due to convergence issues. $\Delta_f H_{298}^0$ calculations use equilibrium B3LYP/6-31G(2df,p) geometries and zero-point energies with a frequency scale factor of 0.9854, as recommended in Ref. 91. Self-consistent GKS calculations with the HSE06 screened hybrid,^{31,42} the LC- ω PBE long-range-corrected hybrid,⁴³ and the PBE GGA (Ref. 54) and its global hybrid (PBEh) (Refs. 92 and 93) are included for comparison. Open-shell systems are treated spin unrestricted. Errors are calculated as theory-experiment.

IV. RESULTS

Table II presents mean (ME) and mean absolute (MAE) errors in heats of formation $\Delta_f H_{298}^0$ for the G2 and G3 sets of small and medium-sized molecules. Calculations use the uncontracted 6-311++G(3df,3pd) basis set following Refs. 19

TABLE II. Mean and mean absolute errors (kcal/mol) in $\Delta_f H_{298}^0$. Uncontracted 6-311++G(3df,3pd) basis set. Self-consistent GKS calculations unless noted otherwise.

Functional	G2-1		G2/97		G3/99	
	ME	MAE	ME	MAE	ME	MAE
FR-Lh-LSDA, post-LSDA	-1.2	3.6	-1.9	3.7	-1.2	3.4
FR-Lh-LSDA	-1.6	3.8	-2.6	4.2	-2.1	3.9
SC-Lh-LSDA	0.2	4.3	1.2	4.3	2.9	5.0
LC-Lh-LSDA	-1.4	3.6	-1.7	3.9	-0.5	3.9
HSE06	1.8	3.0	-1.0	4.0	-2.5	5.0
LC- ω PBE	2.0	3.5	-0.5	3.8	-1.0	4.3

and 21. Non-self-consistent “post-LSDA” calculations use orbitals from an LSDA global hybrid with 10% HF exchange, as in Ref. 20. Non-self-consistent calculations with the full-range local hybrid FR-Lh-LSDA agree with the results in Refs. 20 and 21, modulo small differences due to the computational setup. This functional’s thermochemical performance is slightly degraded in self-consistent calculations, possibly because it was parametrized post-LSDA.¹⁶ The LC local hybrid gives very accurate thermochemistry, comparable to the FR local hybrid and the LC- ω PBE LC functional. The thermochemical performance of the screened local hybrid SC-Lh-LSDA is somewhat inferior, though still comparable to the HSE06 screened hybrid. The results overall indicate that both screened and LC local hybrids of LSDA exchange can provide good thermochemical performance.

Table III presents errors in reaction barrier heights of the HTBH38/04 and NHTBH38/04 test sets,^{87,88} evaluated for the functionals in Table II. Calculations use the large uncontracted aug-cc-pVQZ basis. Again, the non-self-consistent results for the FR local hybrid agree with Refs. 20 and 21 modulo differences in basis set and orbitals. This functional’s performance is again slightly degraded in self-consistent calculations. Both screened and LC local hybrids give accurate reaction barriers, with results comparable to the FR local hybrid. It is especially notable that the SC-Lh-LSDA screened local hybrid provides comparable thermochemistry and significantly improved reaction barriers relative to the HSE06 screened hybrid. Though the results are not quite comparable to recent middle-range hybrids,^{45,50} we feel that they are encouraging.

While local hybrids have been tested non-self-consistently for the bond lengths of radical cation

dimers,^{14,19,20} we are not aware of published tests for conventional covalent bond lengths. Table IV presents errors in bond lengths of the T-96R test set,⁸⁹ evaluated using the uncontracted aug-cc-pVQZ basis set. All of the tested hybrid functionals are reasonably accurate for predicting bond lengths. The local hybrids tend to overestimate bond lengths relative to PBEh or HSE06, with unsigned errors comparable to the LC hybrid LC- ω PBE.

Previous investigations have suggested that semilocal functions such as τ_W/τ and the density gradient can be used to construct accurate FR local hybrids of LSDA exchange, but not of GGA exchange.^{20,21} (While the nonlocal density matrix similarity metrics presented in Ref. 21 yield improved GGA local hybrids, they are still not comparable to the best LSDA local hybrids.) Unfortunately, it appears that the performance of τ_W/τ in local hybrids of GGA exchange is not improved by hybridizing screened versus FR HF exchange. Table V compares our SC-Lh-PBE screened local hybrid of PBE exchange to its “parent” screened hybrid HSE06.^{31,42} The table includes mean absolute errors (kcal/mol) in the small AE6 atomization energy and BH6 reaction barrier height test sets. Calculations are performed self-consistently in the uncontracted 6-311++G(3df,3pd) basis set. The SC-Lh-PBE screened local hybrid gives thermochemistry and barrier heights that are significantly worse than HSE06. In contrast, as in Tables II and III, the SC-Lh-LSDA screened local hybrid of LSDA exchange is comparable to HSE06 for atomization energies and better than HSE06 for reaction barrier heights.

The remainder of this section compares our self-consistent GKS method to the non-self-consistent and “localized local hybrid” (LLH) results obtained by AKB in

TABLE III. Mean and mean absolute errors (kcal/mol) in reaction barrier heights. Uncontracted aug-cc-pVQZ basis set. Self-consistent GKS calculations unless noted otherwise.

Functional	HTBH38/04		NHTBH38/04	
	ME	MAE	ME	MAE
FR-Lh-LSDA, post-LSDA	-1.7	2.3	-1.2	2.5
FR-Lh-LSDA	-2.1	2.6	-1.5	2.6
SC-Lh-LSDA	-1.3	2.1	-0.9	2.2
LC-Lh-LSDA	-1.6	2.2	-0.5	2.3
HSE06	-4.3	4.3	-3.2	3.6
LC- ω PBE	-0.2	1.3	1.6	2.6

TABLE IV. Mean and mean absolute errors (angstrom) in bond lengths of the T-96R data set. Self-consistent GKS calculations, uncontracted aug-cc-pVQZ basis set.

Functional	ME	MAE
FR-Lh-LSDA	0.0079	0.0131
SC-Lh-LSDA	0.0076	0.0132
LC-Lh-LSDA	0.0064	0.0125
PBE	0.0172	0.0174
PBEh	0.0001	0.0089
HSE06	0.0006	0.0089
LC- ω PBE	-0.0068	0.0125

TABLE V. Mean absolute errors (kcal/mol) in AE6 atomization energies and BH6 barrier heights for the SC-Lh-PBE screened local hybrid of PBE exchange, its “parent” screened hybrid HSE06, and the SC-Lh-LSDA screened local hybrid of LSDA exchange. Self-consistent GKS calculations, uncontracted 6-311++G(3df,3pd) basis set.

Functional	AE6	BH6
SC-Lh-PBE	5.9	6.0
HSE06	4.9	4.9
SC-Lh-LSDA	4.8	2.4

Ref. 15. Results are presented for the FR-Lh-BPW91 local hybrid of FR HF exchange (Table I). The calculations in Ref. 15 used the contracted cc-pVQZ AO basis set (g functions excluded) for the KS orbitals and the corresponding uncontracted basis for the RI. Our calculations use the uncontracted cc-pVQZ basis set (including g functions) for both KS orbitals and RI. Table VI compares non-self-consistent (post-BPW91) and self-consistent atomic total energies. Our post-BPW91 total energies are ~ 1 mH above AKB, a small difference that is consistent with the difference in KS orbital basis. Our self-consistent GKS energies are ~ 2.5 mH below AKB’s LLH energies. This is as expected: our uncontracted KS orbital basis has additional variational freedom, and OEP and approximate OEP calculations on many-electron systems generally give total energies somewhat above GKS (Refs. 57 and 94; see, however, Ref. 66). Table VII compares atomization energies [E (atoms)– E (molecule), kcal/mol]. The table presents results from the BPW91 GGA, and from post-BPW91 and self-consistent calculations with the FR-Lh-BPW91 local hybrid. Geometries are from the CCCBDB website,⁹⁵ other details are as in Table VI. Our BPW91 and post-BPW91 local hybrid atomization energies are within ~ 0.2 kcal/mol of AKB, consistent with the aforementioned difference in KS orbital basis. Our self-consistent GKS local hybrid atomization energies are within ~ 1 kcal/mol of AKB’s LLH results.⁹⁶

TABLE VI. Total atomic energies (hartree) from local hybrid FR-Lh-BPW91 (Table I), evaluated post-BPW91 or self-consistently. Current GKS implementation vs LLH of AKB (Ref. 15). Other details are in the text.

	post-BPW91		GKS This work	LLH AKB
	This work	AKB		
H	–0.5060	–0.5060	–0.5066	–0.5066
Li	–7.4842	–7.4854	–7.4866	–7.4862
Be	–14.6542	–14.6553	–14.6572	–14.6563
C	–37.8427	–37.8438	–37.8470	–37.8452
N	–54.5962	–54.5974	–54.6004	–54.5988
O	–75.0817	–75.0829	–75.0868	–75.0845
F	–99.7561	–99.7574	–99.7615	–99.7592
Na	–162.2932	–162.2947	–162.2984	–162.2956
Si	–289.3866	–289.3876	–289.3927	–289.3887
P	–341.2847	–341.2856	–341.2905	–341.2864
S	–398.1364	–398.1373	–398.1430	–398.1382
Cl	–460.1743	–460.1752	–460.1809	–460.1761

V. CONCLUSIONS

We have presented an extension of local hybrid functionals to a local admixture of screened nonlocal HF exchange. We treat these functionals self-consistently in the generalized KS approximation. The self-consistent implementation contains only standard quantities, and should be readily implemented into existing quantum chemistry codes. Self-consistent GKS calculations using existing local hybrids of FR HF exchange give reasonable results compared to published localized local hybrid and non-self-consistent calculations. Self-consistent GKS calculations using screened and LC local hybrids of LSDA exchange give accurate molecular thermochemistry and kinetics, comparable to the corresponding FR local hybrids.

The success of our SC-Lh-LSDA screened local hybrid of LSDA exchange is particularly encouraging. This functional, like previous screened hybrids incorporating a constant fraction of SR^{31,42} or middle-range^{45,50} HF exchange, should be readily applicable in calculations on solids.^{33,37} In contrast, we expect that local hybrids of FR HF exchange will inherit the computational difficulties of global hybrids in calculations on metals and narrow-bandgap semiconductors. Local admixture of even a small fraction of FR HF exchange will naively require evaluating the entire HF exchange operator ($\mathbf{K}$ in Eqs. (18) and (29)), giving a computational cost comparable to a global hybrid. For completeness, we note that local hybrids of FR HF exchange could perhaps avoid this problem with a mixing function that includes *no* HF exchange in small-bandgap systems, or by using the real-space mixing function to determine which elements of the FR $\mathbf{K}$ matrix to evaluate. We suggest that local hybridization of screened exchange is a more promising approach. It uses existing integral screening routines for generating the SR $\mathbf{K}$ matrix, and can readily incorporate a large fraction of screened HF exchange where necessary.

Inspection of the equations in Sec. II suggests that a self-consistent GKS local hybrid calculation in a given basis set will have a computational cost on the order of a GKS global hybrid calculation in that basis set. However, like all local hybrid calculations to date, those presented here require large, uncontracted basis sets for the RI. Implementations combining a large, uncontracted RI basis with a contracted KS orbital basis should further reduce the computational expense.

ACKNOWLEDGMENTS

This work was supported by a training fellowship from the National Library of Medicine to the Keck Center for Interdisciplinary Bioscience Training of the Gulf Coast Consortium (NLM Grant Nos. 5T15LM07093), NSF CHE-0807194, and the Welch Foundation (C-0036). The authors thank Edward N. Brothers and Thomas M. Henderson for useful discussions.

TABLE VII. Atomization energies (kcal/mol) from the BPW91 GGA and the FR-Lh-BPW91 local hybrid (“Lh”) of Table I. Results evaluated post-BPW91 or self-consistently. Current GKS implementation vs LLH of AKB (Ref. 15). “ $|\Delta E|$ ” is the absolute difference between the atomization energies calculated in this work vs those of AKB. Other details are in the text.

	BPW91			post-BPW91 Lh			GKS Lh	LLH Lh	$ \Delta E $
	This work	AKB	$ \Delta E $	This work	AKB	$ \Delta E $	This work	AKB	
H ₂	105.9	105.9	0.0	104.2	104.2	0.0	104.4	104.4	0.0
LiH	53.4	53.5	0.1	49.7	49.6	0.1	51.0	50.8	0.2
CH ₄	416.2	416.2	0.0	402.7	402.5	0.2	404.1	402.7	1.4
C ₂ H ₂	407.9	407.8	0.1	378.3	378.0	0.3	379.9	378.5	1.4
C ₂ H ₄	563.5	563.4	0.1	533.8	533.5	0.3	536.2	534.0	2.2
NH ₃	297.2	297.2	0.0	278.6	278.5	0.1	279.9	278.6	1.3
H ₂ O	230.3	230.3	0.0	215.3	215.2	0.1	216.0	215.3	0.7
OH	107.9	107.9	0.0	99.0	98.9	0.1	99.5	99.1	0.4
HF	139.8	139.7	0.1	130.3	130.2	0.1	130.7	130.4	0.3
HCN	319.9	319.7	0.2	279.1	279.0	0.1	281.2	279.8	1.4
SiH ₄	311.7	312.0	0.3	301.2	301.5	0.3	305.9	303.5	2.4
PH ₃	236.8	236.8	0.0	219.5	219.7	0.2	222.8	220.8	2.0
H ₂ S	179.3	179.4	0.1	167.3	167.4	0.1	168.6	167.8	0.8
HCl	104.9	104.9	0.0	98.7	98.8	0.1	99.2	98.9	0.3
Li ₂	17.5	17.8	0.3	16.3	16.0	0.3	16.9	16.6	0.3
LiF	136.8	136.9	0.1	125.8	125.7	0.1	127.6	127.3	0.3
Be ₂	8.3	8.3	0.0	-1.1	-1.3	0.2	0.5	-0.9	1.4
CO	264.0	263.8	0.2	227.9	227.6	0.3	229.5	228.4	1.1
N ₂	237.3	237.0	0.3	188.5	188.5	0.0	190.3	188.9	1.4
NO	166.5	166.2	0.3	117.8	117.6	0.2	119.8	118.4	1.4
O ₂	138.6	138.3	0.3	89.4	89.4	0.0	91.1	90.2	0.9
F ₂	49.6	49.5	0.1	6.8	6.8	0.0	8.1	7.2	0.9
PN	150.8	150.7	0.1	109.0	109.0	0.0	111.4	110.2	1.2
CS	174.2	174.1	0.1	144.5	144.5	0.0	146.1	145.2	0.9
SO	134.9	134.8	0.1	100.3	100.3	0.0	102.4	101.6	0.8
SO ₂	265.5	265.1	0.4	199.7	199.4	0.3	203.7	201.9	1.8
ClF	68.0	67.6	0.4	40.7	40.5	0.2	42.3	41.2	1.1
NaCl	92.2	91.7	0.5	94.1	93.6	0.5	95.0	94.3	0.7
SiCl ₂	204.4	204.2	0.2	188.8	188.8	0.0	190.7	189.9	0.8
SiCl ₄	371.1	370.6	0.5	355.3	355.2	0.1	357.1	356.2	0.9
SiS	145.1	145.1	0.0	129.8	129.8	0.0	131.2	130.8	0.4
P ₂	117.5	117.3	0.2	93.9	93.8	0.1	95.7	94.8	0.9
P ₄	294.7	294.1	0.6	248.5	248.4	0.1	252.7	249.7	3.0
PCl ₃	234.1	233.6	0.5	204.4	204.3	0.1	207.3	205.4	1.9
PS	108.3	108.0	0.3	86.9	86.8	0.1	88.8	87.6	1.2
S ₂	110.1	109.8	0.3	89.0	89.0	0.0	90.3	89.7	0.6
S ₂ Cl ₂	208.1	207.3	0.8	166.3	166.4	0.1	170.0	167.4	2.6
Cl ₂	61.4	61.1	0.3	46.6	46.7	0.1	47.4	47.0	0.4
Average			0.2			0.1			1.1

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