Range-Separated Exchange Functionals with Slater-Type Functions

Michael Seth* and Tom Ziegler

Department of Chemistry, University of Calgary, University Drive 2500, Calgary, AB T2N-1N4, Canada

S *Supporting Information*

ABSTRACT: An implementation of range-separated density functionals utilizing the Yukawa potential and Slater-type functions is described. The density-functional part of the range-separated regime is straightforward. The exact exchange part makes use of established methods for evaluating exchange integrals over Slater-type functions but still requires new one- and two-center integrals. Equations for the one-center integrals are derived. The two-center integrals are evaluated through a combination of new equations and techniques taken from procedures for evaluating two-center Coulomb integrals over Slater-type functions. In a first application, the performance of range-separated functionals in the prediction of transition metal thermochemistry is evaluated using a database of average ligand removal energies. The range-separated functionals perform better than a GGA parent and similarly to commonly used hybrid and meta-hybrid functionals. The results were relatively insensitive to the chosen value of the attenuation parameter.

1. INTRODUCTION

Density functional theory (DFT) has become the most common theoretical framework used in the prediction of the properties of solids and isolated molecules. An important step in the development of DFT was the recognition that the admixture of a suitable portion of exact (Hartree−Fock type) exchange with a fraction of the exchange obtained from a local (semilocal) density functional resulted in improved predictions for many properties.[1−3] These types of hybrid functionals are often described as "global" hybrids because the ratio of exact to DFT exchange is the same at all points in space.

One way to go beyond global hybrids is to utilize range-separated functionals. In a range-separated calculation, the regions of electron−electron interaction are divided into "long" and "short" range parts by dividing the Coulomb operator into two pieces:

$$\frac{1}{r_{12}} = SR + LR = \frac{w(\gamma, r_{12})}{r_{12}} + \frac{1 - w(\gamma, r_{12})}{r_{12}} \tag{1}$$

where r_{12} is the interelectronic distance $|\vec{r}_1 - \vec{r}_2|$ and w is some kind of continuous switching function that goes to 1 as r_{12} goes to zero and to zero as r_{12} becomes large. The parameter γ determines how rapidly the switching occurs. This type of division has been introduced by a number of groups to combine DFT and wavefunction theory.[4−21] These methodologies generally, but not exclusively, modify the exchange part of the DFT functional and add exact exchange as the wave-function contribution.

Range separation has been applied in a number of ways. Exact exchange at short-range and DFT exchange at long-range have been found to be useful in the description of periodic systems,[12,13] while range-separated functionals for molecules typically treat the short-range interaction with DFT and the long-range interaction with exact exchange.[5,8] As described so far, range-separated functionals attenuate one type of interaction at short-range and the other at long-range. More complicated approaches have been described where both exact and DFT exchange contribute significantly at short and/or long

range. Scuseria and co-workers have taken the approach one step further by introducing a third, "middle", region.[22]

These more sophisticated types of range-separated functionals cannot be described by eq 1 but require a more general form such as

$$\frac{1}{r_{12}} = DFT + HF = \frac{\alpha + \sum_i \beta_i w_i(\gamma_i, r_{12})}{r_{12}} + \frac{\delta + \sum_j \varepsilon_j w_j(\gamma_j, r_{12})}{r_{12}} \tag{2}$$

where α, β_i, δ, and ε_j are constants.

Range-separated functionals have been shown to provide improved results over global hybrids in a number of areas.[9−11,15,16,20,23−27] In particular, reaction barriers and excitation energies involving significant distances such as Rydberg and charge-transfer excitations have been shown to be more accurately predicted by range-separated functionals that are mainly DFT exchange at short-range and exact exchange at long-range.[9,10,20,25−27]

An aspect that has been found to be problematic is the fact that no one attenuation parameter γ has proved to be universal. A value of γ that is optimal for thermochemistry is typically not optimal for charge-transfer excitations.[25,28] Attempts to improve this situation have considered the parameter γ not as a universal constant but as a local parameter that may depend on the density and perhaps the gradient of the density.[4,29−34] This idea appears promising but has yet to be explored fully.

The most common type of switching function w is the complementary error function erfc[7,8,12,14] or erfc plus additional functions such as Gaussians.[10,11] The error function is attractive for practical reasons as integrals involving the error function and Gaussian basis functions are reasonably straightforward to compute. An alternative to the error function is the exponential function $\exp(-\gamma r_{12})$, which in combination with the $1/r_{12}$ operator

gives the Yukawa potential.[4,6,17−19,21] The Yukawa potential seems like a natural choice as a screened Coulomb potential. Although range-separated functionals are easier to implement in Gaussian-based codes when the switching function is erfc, it has been shown that the Yukawa potential can be used in combination with Gaussian functions by making use of Slater-type geminals.[18,35,36] Early calculations utilizing this implementation suggest that the Yukawa potential may give superior results to the Coulomb potential screen by erfc.[18,19] Range-separated functionals that utilize the Yukawa potential have also been combined with valence plane wave and localized core basis functions in a periodic DFT code.[21]

In this paper, we outline how to construct range-separated functionals in combination with Slater-type basis sets. We will consider the Yukawa potential as the screened Coulomb potential because the error function provides no particular computational advantage in combination with Slater orbitals. The formalism will be general and may be used in combination with eq 2 with the restriction that w is an exponential function. We will consider γ to be constant for a given system.

The rest of the paper will be as follows. We will first present the theoretical background including the evaluation of DFT exchange and exact exchange with Slater-type functions in combination with the Yukawa potential. In the second part of the paper, we will present applications of the implementation to the binding energy of ligands in transition metal complexes.

2. THEORY

The Yukawa potential between electrons has the form

$$V^Y = \frac{e^{-\gamma r_{12}}}{r_{12}} \tag{3}$$

This potential is a screened Coulomb potential that decays to zero at a rate dependent on the value of r_{12} and the size of the parameter γ.

2.1. The Exchange Functional with the Yukawa Potential. In the majority of modern range-separated calculations, only the exchange part of the functional is modified, and it is assumed that the correlation part is unchanged. The Coulomb term in the energy is also assumed to be unscreened. We will follow this practice here. The exchange energy of the homogeneous electron gas with the electrons interacting via the Yukawa potential has been known for a long time:[37,38]

$$E_X^Y[\rho] = -\frac{1}{2} \sum_\sigma \int K \rho_\sigma^{4/3} F(a_\sigma) \, dr \tag{4}$$

$$K = 3\left(\frac{3}{4\pi}\right)^{1/3} \tag{5}$$

$$F(a_\sigma) = \left[1 - \frac{8}{3}a_\sigma\left(\arctan\frac{1}{a_\sigma} + \frac{a_\sigma}{4} \right.\right.$$
$$\left.\left. - \frac{a_\sigma}{4}(a_\sigma^2 + 3)\ln\left(1 + \frac{1}{a_\sigma^2}\right) \right) \right] \tag{6}$$

$$a_\sigma = \frac{\gamma}{2k_\sigma} \tag{7}$$

$$k_\sigma = 3\rho_\sigma^{1/3}\left(\frac{\pi}{K}\right)^{1/2} \tag{8}$$

where ρ is the electron density and σ stands for α or β spin.

Two approaches have been proposed to deal with gradient-corrected functionals in combination with range-separated functionals. Hirao and co-workers suggested using the exchange energy of the homogeneous electron gas with K modified to correspond to the chosen gradient-corrected exchange functional.[8] The formalism of Hirao and co-workers makes use of the complementary error function to screen the Coulomb potential. Ten-no and Akinaga have successfully applied the same approach to range-separated functionals that utilize the Yukawa potential.[18] Scuseria and co-workers have advocated a more theoretically rigorous approach where the hole function corresponding to a given gradient corrected functional is integrated with the attenuated potential to obtain the energy density functional.[12,13,39] It is not yet clear whether it is necessary to use the more sophisticated methodology described in the latter work. Some studies have found that a proper description of the exchange hole did lead to significant improvements,[39,40] while another found little difference between results obtained by the two methods.[28]

In the present case, we chose to go with the simpler form suggested by the Hirao and Ten-no groups. We therefore evaluate the DFT part of the exchange energy using eq 4 with K replaced with the appropriate K_σ^{GGA} if a gradient corrected exchange functional is used.

K_σ^{GGA} depends on the definition of the particular GGA under consideration and is defined by the following expression for the energy of a generic GGA

$$E_X^{GGA}[\rho] = -\frac{1}{2} \sum_\sigma \int K_\sigma^{GGA}(\rho_\sigma, |\nabla\rho_\sigma|)\rho_\sigma^{4/3} \, dr$$

It should be noted that eq 4 becomes numerically unstable for very small densities (large values of a_σ). Equations appropriate for this regime can be found in the Supporting Information.

2.2. Integrals of Slater-Type Functions over the Yukawa Potential. In order to evaluate conventional exact exchange, it is necessary to evaluate integrals of the type

$$(\mu\nu|\kappa\lambda) = \int\int \chi_\mu(\vec{r}_{1A}) \, \chi_\nu(\vec{r}_{1B}) \, \frac{1}{r_{12}}\chi_\kappa(\vec{r}_{2C}) \, \chi_\lambda(\vec{r}_{2D})$$
$$\times \, d\vec{r}_{1A} \, d\vec{r}_{2A} \tag{9}$$

where χ is a basis function, the subscript 1 and 2 indicate electrons 1 and 2, and the subscript capital letters refer to the center of the coordinate system that defines a given vector. When χ is a Slater-type function, the three- or four-center integrals are extremely difficult to evaluate.

A way to get around this difficulty was suggested recently.[41−43] The troublesome integrals were avoided by first fitting the density produced by each pair of basis functions

$$|\mu\nu) \approx \sum_i c_{\mu\nu i}|f_i) \tag{10}$$

where f_i is a fit function and $c_{\mu\nu i}$ a real coefficient. For more details concerning the fitting procedures, see our recent publications.[42,43] All two-electron integrals are transformed into linear combinations of one- or two-center integrals.

$$(\mu\nu|\kappa\lambda) \approx \sum_{ij} c_{\mu\nu i}c_{\kappa\lambda j}(f_i|f_j) \tag{11}$$

In our implementation, the fit functions f_i are themselves Slater-type functions. One-center integrals over Slater-type functions can be evaluated analytically.[44] A number of methodologies for evaluating two-center integrals over Slater-type functions have been developed, such as the ζ-function method of Barnett and Coulson,[45−47] making use of a transformation to elliptical coordinates[48,49] and the shift operator approach of Fernández Rico and co-workers.[50−52]

We will follow a similar procedure to that just described for the calculation of multicenter exchange integrals over Slater-type functions to evaluate the equivalent integrals over the Yukawa potential. Before proceeding, we should note the alternative approach to calculating these integrals using series expansion techniques that have been presented by Guseinov.[53]

The fitting process is identical to that of the integrals involving the unscreened Coulomb potential, so we begin with integrals over fit functions:

$$(f_i|f_j)^Y = \int \int \chi_{nlm\sigma}^{\zeta_i}(\vec{r}_{1A}) \frac{e^{-\gamma r_{12}}}{r_{12}} \chi_{n'l'm'\sigma'}^{\zeta_j}(\vec{r}_{2B})\, d\vec{r}_{1A} \\ d\vec{r}_{2A} \tag{12}$$

Here, χ is a real spherical Slater function

$$\chi_{nlm}^{\zeta} = N_{nlm} r^{n-1}\, e^{-\zeta r}\, P_l^{|m|}(\cos\theta) \begin{cases} \cos m\phi, & m \geq 0 \\ \sin m\phi, & m < 0 \end{cases} \tag{13}$$

where n, l, and m are the standard atomic quantum numbers; r, θ, and ϕ are spherical coordinates; N is a normalization constant; and $P_l^{|m|}$ is an associated Legendre polynomial.

In order to carry out the integration, we expand the Yukawa potential following[54] eq 7.98

$$\frac{e^{-\gamma r_{12}}}{r_{12}} = -\gamma \sum_{l=0}^{\infty} (2l+1)\, j_l(i\gamma r_{<A})\, h_l^{(1)}(i\gamma r_{>A}) \\ \times P_l(\cos\theta_A) \tag{14}$$

where θ_A is the angle between $\vec{r}_{1A}$ and $\vec{r}_{2A}$, j_l and $h_l^{(1)}$ are spherical Bessel functions of the first and third kinds,[54,55] i is $(-1)^{1/2}$, and $r_{<A}$ ($r_{>A}$) is the lesser (greater) of r_{1A} and r_{2A}.

This expansion is the same as that of the standard Coulomb potential but with the term

$$-\gamma(2l+1)\, j_l(i\gamma r_{<A})\, h_l^{(1)}(i\gamma r_{>A}) \tag{15}$$

replacing

$$\frac{r_{<A}^l}{r_{>A}^{l+1}} \tag{16}$$

The Coulomb and Yukawa potentials therefore have the same angular dependence. The part of the integration over the angles θ and ϕ is thus unchanged when going from the Coulomb to the Yukawa potential, and we shall focus on the integration over r.

2.2.1. One-Center Integrals. If $A = B$, then the integration is straightforward, if somewhat tedious. The integral can be divided into angular and radial parts:

$$(f_i^{nlm\zeta_i}|f_j^{n'l'm'\zeta_j})_{AA}^Y = \delta_{ll'}\delta_{mm'}\, R_{nn'l}^{\zeta_i\zeta_j\gamma}\, A_{lm} \tag{17}$$

with A_{lm} representing the integral over angular terms and any normalization constants. The radial part is

$$R_{nn'l}^{\zeta_i\zeta_j\gamma} = (-1)^{l+1}(2l+1)\left(\frac{1}{(\zeta_i^2 - \gamma^2)^{n+1}}\right.$$

$$\times \sum_{m'=0}^{l} \frac{(2\gamma)^{l-m'}(l+m')!}{(l-m')!m'!}\left(\frac{(n'-m')! R_{nl}^{(1)\zeta_i\gamma}}{(\zeta_j + \gamma)^{n'-m'+1}}\right.$$

$$\left.+ \frac{R_{nn'lm'}^{(2)\zeta_i\zeta_j\gamma}}{(\zeta_i + \zeta_j + 2\gamma)^{n'-m'+1}}\right)$$

$$+ \sum_{m=0}^{l} \frac{(2\gamma)^{l-m}(l+m)!(n-m)!}{(l-m)!m!}$$

$$\left.\times \sum_{k=0}^{n-m} \frac{R_{n'kl}^{(3)\zeta_i\zeta_j}}{k!(\zeta_i + \gamma)^{n-m-k+1}}\right) \tag{18}$$

$$R_{nl}^{(1)\zeta_i\gamma} = \sum_{m=0}^{l} \frac{(l+m)!(n-m)!}{2^{l+m+1}(l-m)!m!}$$

$$\times \sum_{j=0}^{m} \sum_{i=l+m+1-2j}^{n-m+1} ((-1)^{l+m+j+1}$$

$$+ (-1)^{i+j}) \times \binom{m}{j}\binom{n-m+1}{i}\zeta_i^{n+m-2j-i+1}$$

$$\times \gamma^{2j+i-l-m-1} \tag{19}$$

$$R_{nn'lm'}^{(2)\zeta_i\gamma} = \frac{1}{(\zeta_i + \zeta_j + 2\gamma)^n}\sum_{m=0}^{l}(-1)^{l-m}$$

$$\times \frac{(l+m)!(n-m)!}{m!(l-m)!}\sum_{k=0}^{n-m}\frac{(n'-m'+k)!}{k!}$$

$$\times \sum_{q=0}^{n-k}\sum_{p=0}^{m+k}\sum_{i=0}^{n-m-k+1}(-1)^p$$

$$\times \binom{n-k}{q}\binom{m+k}{p}\binom{n-m-k+1}{i}$$

$$\times (\zeta_i + \zeta_j)^{n-k-q} 2^{q-m-l-1}\zeta_i^{n+m+k-i-2p+1}$$

$$\times \gamma^{i-m+2p+q-l-1} \times \left(\left(1 + (-1)^{l-m+1+i}\right)\right.$$

$$\left.+ \sum_{j=1}^{n'-m'+k+1}\binom{n'-m'+k+1}{j}\frac{(2\gamma)^j}{(\zeta_i + \zeta_j)^j}\right)_i$$

$$-m + 2p + q - l - 1 + j \geq 0 \tag{20}$$

$$R_{n'kl}^{(3)\zeta_i\zeta_j} = \frac{1}{(\zeta_i + \zeta_j + 2\gamma)^{n'+k+1}}$$

$$\times \sum_{m=0}^{l} (-1)^{l-m+1} \frac{(n' + k - m)!(l + m)!}{m!(l - m)!}$$

$$\times \sum_{i=m+l+1}^{n'+k+1} \binom{n' + k + 1}{i} \frac{(2\gamma)^{i-m-l-1}}{(\zeta_i + \zeta_j)^{i-m}}$$

$$(21)$$

where the terms $\binom{a}{b}$ are binomial coefficients. The forms of eqs 18−21 are complicated by the series expansions of the spherical Bessel functions and the need to avoid expansions that are numerically unstable for small values of γ. Equation 18 is undefined when $\gamma = \zeta_i$. An alternative expression, that can be employed if it is necessary to choose that $\gamma = \zeta_i$, can be derived if needed.

While we only quote the final result here, more information on the derivation of eqs 18−21 is given in the Supporting Information.

2.2.2. Two-Center Integrals. We now consider the case where the two fit functions are on different centers. This analysis follows that presented by Barnett for integration of a bare Coulomb interaction over Slater-type functions on two centers.[47]

Since we only have two rather than four functions, the present case is a simplified form of Barnett's $(aa|bb)$ integrals. The difference between the Yukawa potential and bare Coulomb potential cases appears in the radial integral over the first electron. For the Coulomb potential, this integral is eq 26 in ref 47.

$$I_{nl}(\zeta_i, r_{2A}) = \int_0^\infty r_{1A}^n\, e^{-\zeta_i r_{1A}} \frac{r_{<A}^l}{r_{>A}^{l+1}}\, dr_{1A}$$

$$(22)$$

while for the Yukawa potential it is

$$I_{nl}^Y(\zeta_i, r_{2A}, \gamma) = -\gamma(2l + 1) \int_0^\infty r_{1A}^n\, e^{-\zeta_i r_{1A}} j_l(i\gamma r_{<A})$$

$$\times h_l^{(1)}(i\gamma r_{>A})\, dr_{1A}$$

$$(23)$$

Note that we use the symbol I for this term rather than j as in ref 47 to avoid confusion with the spherical Bessel function of the first kind. Performing the integration in eq 23 gives

$$I_{nl}^Y(\zeta_i, r_{2A}, \gamma) = (2l + 1) \sum_{m=0}^{l} \frac{(l + m)!}{m!(l - m)!2^{m+1}\gamma^m i^l}$$

$$\times (2j_l(i\gamma r_{2A}) \frac{\Gamma(n - m + 1, (\zeta_i + \gamma)r_{2A})}{(\zeta_i + \gamma)^{n-m+1}}$$

$$+ h_l^{(1)}(i\gamma r_{2A})(\frac{\gamma(n - m + 1, (\zeta_i + \gamma)r_{2A})}{(\zeta_i + \gamma)^{n-m+1}}$$

$$+(-1)^{l-m+1}\frac{\gamma(n - m + 1, (\zeta_i - \gamma)r_{2A})}{(\zeta_i - \gamma)^{n-m+1}}))$$

$$(24)$$

where $\Gamma(n,x)$ and $\gamma(n,x)$ (not to be confused with the attenuation parameter γ) are the upper and lower incomplete γ functions,[56] respectively.

Equation 24 is numerically unstable for small values of γ but can be converted into a form that is stable in this case (see the Supporting Information). The case where $\gamma = \zeta_i$ is also problematic here. Although it appears that eq 24 could be imaginary because of the factor i^l, a second factor of i^l will come from the remaining Bessel functions leading to the real number i^{2l}.

The rest of the integration of two-center, two-electron terms with Slater-type functions proceeds in the same way as the bare Coulomb case. The modified radial integral over the first electron $I_{nl}^Y(\zeta_i, r_{2A}, \gamma)$ must be substituted for the $I_{nl}(\zeta_i, r_{2A})$ ($j_{nj,lj}(\kappa_2, t)$ in the notation of ref 47) in eq 45 of ref 47.

3. EXAMPLE CALCULATIONS

In our lab, we are interested in the properties of transition metal compounds with a particular focus on organometallics. The performance of range separated functionals in the prediction of thermochemistry has been tested against a number of sets of benchmark data.[10,23,25] These tests have generally focused on compounds limited to main group elements, and validation studies involving transition metal thermochemistry and range-separated functionals appear to be very rare.[20,57] As a first application of our implementation, we have tested the performance of range-separated functionals with the Yukawa potential and Slater-type orbitals against the benchmark set developed by Johnson and Becke.[58] This data set is made up of the average ligand binding energies of 32 first row transition metal compounds. A number of different bonding situations commonly encountered in organometallic complexes are included.[58] This test set therefore should provide a good test of the ability of a functional to describe the thermochemistry of a range of transition metal complexes.

3.1. Computational Details. The formulas described in the previous section were implemented in a development version of the ADF program.[59−64] The DFT part of the range separated functionals was evaluated using a modified version of the functional automatic differentiation code of Ekström et al.[65] that has been interfaced with ADF. Automatic differentiation considerably simplifies the calculation of functional derivatives of the range-separated functionals that are needed for the evaluation of the exchange-correlation potential and higher derivatives such as the kernel.

The exact exchange part of the range-separated functional was straightforward to implement within the existing exact exchange routines of ADF.

The benchmark set of Johnson and Becke consists of experimental mean ligand-removal enthalpies of 32 neutral first-row transition metal compounds. The mean ligand removal enthalpy is defined as

$$\bar{E}_L = \frac{nE(L) + mE(M) - E(M_mL_n)}{n + m - 1}$$

$$(25)$$

where M is a metal atom, L is a ligand, and m and n are integers. The benchmark set is made up of seven Ti complexes, seven Cr complexes, five Mn complexes, five Fe complexes, and two each that include Co, Ni, Cu, and Zn.

Ligand-removal enthalpies were calculated with 11 functionals: BP,[66,67] LCY-BP, BLYP,[66,68] LCY-BLYP, PBE,[69] LCY-PBE, B3LYP,[3] CAMY-B3LYP,[16,18] PBE0,[70,71] TPSSh,[72] and M06.[73] The standard functionals were included for

comparison purposes. Although many of these functionals were included in Johnson and Becke's original study,[58] the energies with these functionals were recalculated to ensure that basis set effects could be eliminated. The LCY functionals are range-separated in the sense proposed by Hirao and co-workers[8] but ultilizing an exponential function to switch between DFT and exact exchange. The Coulomb operator is divided into two regions with DFT at short-range and exact exchange at long-range. The DFT (exact exchange) varies from 0% (100%) at large values of r_{12} to 100% (0%) at small values. CAMY-B3LYP is the Yukawa form of CAM-B3LYP[16] with $\alpha = 0.19$ and $\beta = 0.46$ but with the Yukawa potential rather than the Coulomb potential attenuated by the complementary error function. These range-separated functionals were first suggested by Tenno and Akinaga,[18] and we make use of their recommended attenuation parameters (0.75 a_0^{-1} for LCY-BP, LCY-BLYP, and LCY-PBE and 0.34 a_0^{-1} for CAMY-B3LYP, where a_0 is the Bohr radius). We also examined the performance of these functionals as a function of γ (see section 3.2).

A valence triple-ζ basis set augmented by two polarization functions was used for all atoms. The polarization functions consist of a pd set for H, a df set for all main group elements, and a pf set for all transition metals. The 1s core was frozen for C, O, N, and F; the 1s2s2p core was frozen for Cl and the transition metals; and the 1s2s3s3p3d core was frozen for Br. This basis set is fairly large but is still smaller than that used by Johnson and Becke. We prefer to utilize this type of basis set, as it is more consistent with the sets of functions that could be used in calculations involving larger transition metal complexes.

Relativistic effects were not included, as was the case in the earlier study.[58] Geometries and thermal corrections were taken from ref 58, and the same methodology for treating transition metals with several unpaired electrons as that described in ref 58 was used.

3.2. Results and Discussion. An analysis of our results is presented in Table 1. Tables that include all of the mean ligand removal energies that are summarized in Table 1 can be found in the Supporting Information.

The results for the standard functionals BP, BLYP, PBE, B3LYP, PBE0, and TPSSh are similar to those obtained by Johnson and Becke.[58] The errors in this work are slightly higher, probably because of differences is the chosen basis sets. The meta-hybrid M06 is new to this work and provides results similar in quality to the other meta-hybrid TPSSh and slightly inferior to the hybrids B3LYP and PBE0.

The range-separated functional forms of the BP, BLYP, and PBE functionals with $\gamma = 0.75$ all provide improved results over their GGA equivalents. The average sizes of the errors are reduced, the maximum errors are reduced, and the errors are more evenly distributed around zero. CAMY-B3LYP with $\gamma = 0.34$ is a small improvement over B3LYP. Overall, with the standard values of γ, the range-separated functionals provide results similar or perhaps slightly superior to those obtained with commonly used hybrids and meta-hybrids.

In addition to calculations utilizing the suggested values of γ from ref 18, further sets of calculations were performed with a range of γ values. For LCY-BP, LCY-BLYP, and LCY-PBE, γ was varied between 0.50 a_0^{-1} and 1.0 a_0^{-1} with a step size of 0.05 a_0^{-1} while for CAMY-B3LYP it was varied between 0.05 a_0^{-1} and 0.50 a_0^{-1} also with a step size of 0.05 a_0^{-1}. The calculations that gave the lowest MAE are listed in Table 1.

In the case of LCY-BP, LCY-BLYP, and LCY-PBE, the best values of γ are fairly similar to the recommended value, and

Table 1. Analysis of Errors in Mean Calculated Mean Ligand-Removal Energies As Compared with Experimental Results[a]

	γ	MAE	ME	MaxE	
BP		11.1	10.2	22.3	(CrO_3)
BP[b]		9.4	8.6	20.6	(TiO_2)
BLYP		7.46	5.0	20.0	(CrO_3)
BLYP[b]		6.3	3.4	13.6	(CrO_3)
PBE		12.8	12.3	25.3	(CrO_3)
PBE[b]		10.9	10.4	21.2	(TiO_2)
B3LYP		3.7	−2.9	−18.4	($Fe(C_5H_5)_2$)
B3LYP[b]		4.3	−4.1	−19.6	($Fe(C_5H_5)_2$)
PBE0		4.9	1.3	20.9	($FeH_2(CO)_4$)
PBE0[b]		2.7	−1.3	−15.8	(CrO_3)
TPSSh		6.3	5.4	20.6	($Fe(C_2H_4)(CO)_4$
TPSSh[b]		4.5	3.1	−9.5	(CuF)
M06		5.9	2.4	23.1	(CuF)
LCY-BP	0.75	5.0	4.2	9.7	($Zn(CH_3)_2$)
LCY-BP	0.90	3.5	0.5	−15.7	(CrO_3)
LCY-BLYP	0.75	3.2	−1.2	−9.3	(TiO_2)
LCY-BLYP	0.70	2.9	0.1	−6.6	(TiO_2)
LCY-PBE	0.75	4.7	3.8	9.9	($Zn((CH_2CH_3)_2)$)
LCY-PBE	0.90	3.3	0.1	−15.6	(CrO_3)
CAMY-B3LYP	0.34	3.4	−1.5	−14.9	($Fe(C_5H_5)_2$)
CAMY-B3LYP	0.30	3.2	−1.1	−14.4	($Fe(C_5H_5)_2$)
CAMY-B3LYP	0.10	3.1	−1.2	−15.2	($Fe(C_5H_5)_2$)

[a]All energies in kcal/mol. MAE: mean absolute error. ME: mean error. MaxE: maximum error. [b]Results by Johnson and Becke.[58]

optimization of γ leads to small but significant improvements. Overall, the performance of the LCY functionals is similar to that of the global hybrid functionals and perhaps slightly better when γ is optimized. BLYP was the best of the standard GGA functionals, and LCY-BLYP has the lowest MAE of all the LCY functionals. The performance of CAMY-B3LYP as a function of γ is a little different from that of the LCY functionals. Two minima were found in the calculated MAE of the mean ligand-removal energies between $\gamma = 0.05$ and $\gamma = 0.50$. One at 0.30 a_0^{-1} is close to the value recommended by Ten-no and Akinaga,[18] while the other is rather different at 0.10 a_0^{-1}. Results for both of these γ values are presented in Table 1. The quality of the results obtained with CAMY-B3LYP is rather insensitive to the value of γ. For values of γ between 0.05 a_0^{-1} and 0.34 a_0^{-1}, the largest MAE obtained is 3.5 kcal/mol and the smallest is 3.1 kcal/mol. Thus, any value of γ between 0.05 a_0^{-1} and 0.35 a_0^{-1} will do a reasonable job of predicting ligand-removal energies with CAMY-B3LYP. A wide range of "good" values of γ is an advantage, as it suggests that it should be possible to find a value of γ that can simultaneously predict ligand-removal energies and other properties of interest such as excitation energies.

The assessment of range-separated functionals as equal or perhaps slightly superior to the most commonly used global hybrid functionals is similar to the conclusions obtained in other studies when considering the thermochemistry of molecules composed of main group elements.[10,23,25] A previous study that included transition metal compounds found that a range-separated functional (M11) did slightly worse than the equivalent functional without range separation in the calculation of thermochemical properties of transition metal compounds that can be described as "single reference".[20]

4. CONCLUSIONS

In this article, we presented details of an implementation of range-separated functionals in combination with Slater-type basis functions. The Yukawa potential was chosen as the form of the attenuated Coulomb interaction. On the DFT side, the exchange functionals in the presence of the Yukawa potential do not depend on the choice of basis set and therefore follow the form presented previously.[18] An analytical formula for one-center integrals valid for almost all values of γ was presented. The evaluation of two-center integrals follows closely the ζ-function approach for calculating two-center Coulomb integrals with Slater-type functions presented by Barnett and Coulson.[45−47] We therefore only describe modifications to this procedure that are needed to evaluate two-center integrals over the Yukawa potential. We were unable to derive universal equations for these integrals but present here and in the Supporting Information equations that cover almost all values of γ. Combined with the atomic-orbital pair fitting procedure described in refs 42 and 43, these integrals allow calculations with range-separated functionals and Slater-type functions to be performed for any molecule that can be studied using a global hybrid functional.

As a first application of our implementation, we considered the performance of several range-separated functionals in the mean-ligand removal energy data set of Johnson and Becke. The addition of exact exchange at large values of r_{12} led to significant improvements in the performance of all GGAs considered here. The performance was not distinctly superior to that of common global hybrids. CAMY-B3LYP also performed slightly better than B3LYP and PBE0. It thus appears that range-separated functionals can be expected to perform as well or perhaps a little better than global hybrids in the prediction of the thermochemistry of transition metal complexes. The quality of the results obtained was fairly insensitive to the value of the γ parameter. This is a particularly advantageous property as it increases the chance of finding a single value of γ that is suitable for many if not all properties of interest, a task that has proven to be challenging thus far.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

More detail on the derivations described here and the full set of average ligand-removal energies that are summarized in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: (403)220 7176. Fax: (403)289 9488. E-mail: mseth@ucalgary.ca

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(2) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.
(3) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.
(4) Bylander, D. M.; Kleinman, L. *Phys. Rev. B* **1990**, *41*, 7868−7871.
(5) Savin, A. On degeneracy, near-degeneracy and density functional theory. In *Recent Developments and Applications of Modern Density Functional Theory*; Seminario, J. M., Ed.; Elsevier: Amsterdam, 1995; pp 327−357.
(6) Savin, A.; Flad, H.-J. *Int. J. Quantum Chem.* **1995**, *56*, 327−332.
(7) Leininger, T.; Stoll, H.; Werner, H.-J.; Savin, A. *Chem. Phys. Lett.* **1997**, *275*, 151−160.
(8) Iikura, H.; Tsuneda, T.; Tanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540−3544.
(9) Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2004**, *120*, 8425−8433.
(10) Song, J.-W.; Tokura, S.; Sato, T.; Watson, M. A.; Hirao, K. *J. Chem. Phys.* **2007**, *127*, 154109.
(11) Song, J.-W.; Watson, M. A.; Hirao, K. *J. Chem. Phys.* **2009**, *131*, 144108.
(12) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207−8215.
(13) Heyd, J.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 1187−1192.
(14) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 234109.
(15) Henderson, T. M.; Janesko, B. G.; Scuseria, G. E. *J. Phys. Chem. A* **2008**, *112*, 12530−12542.
(16) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51−57.
(17) Baer, R.; Neuhauser, D. *Phys. Rev. Lett.* **2005**, *94*, 043002.
(18) Akinaga, Y.; Ten-no, S. *Chem. Phys. Lett.* **2008**, *462*, 348−351.
(19) Akinaga, Y.; Ten-no, S. *Int. J. Quantum Chem.* **2009**, *109*, 1905−1914.
(20) Pavarti, R.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2011**, *2*, 2810−2817.
(21) Tran, F.; Blaha, P. *Phys. Rev. B.* **2011**, *83*, 235118.
(22) Henderson, T. M.; Izmaylov, A. F.; Scuseria, G. E.; Savin, A. *J. Chem. Phys.* **2007**, *127*, 221103.
(23) Song, J.-W.; Hirowasa, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2007**, *126*, 154105.
(24) Caricato, M.; Trucks, G. W.; Frisch, M. J.; Wiberg, K. B. *J. Chem. Theory Comput.* **2011**, *7*, 456−466.
(25) Peach, M. J.; Cohen, A. J.; Tozer, D. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4543−4549.
(26) Lange, A. W.; Rohrdanz, M. A.; Herbert, J. M. *J. Phys. Chem. B* **2008**, *112*, 6304−6308.
(27) Silverstein, D. W.; Jensen, L. *J. Chem. Phys.* **2010**, *132*, 194302.
(28) Nguyen, K. A.; Day, P. N.; Pachter, R. *J. Chem. Phys.* **2011**, *135*, 074109.
(29) Pollet, R.; Savin, A.; Leininger, T.; Stoll, H. *J. Chem. Phys.* **2002**, *116*, 1250−1258.
(30) Toulouse, J.; Colonna, F.; Savin, A. *J. Chem. Phys.* **2005**, *122*, 014110.
(31) Baer, R.; Livshits, E.; Neuhauser, D. *Chem. Phys.* **2006**, *329*, 266−275.
(32) Livshits, E.; Baer, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2932−2941.
(33) Krukau, A. V.; Scuseria, G. E.; Perdew, J. P.; Savin, A. *J. Chem. Phys.* **2008**, *129*, 124103.
(34) Henderson, T. M.; Janesko, B. G.; Scuseria, G. E.; Savin, A. *Int. J. Quantum Chem.* **2009**, *109*, 2023−2032.
(35) Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56−61.
(36) Ten-no, S. *J. Chem. Phys.* **2007**, *126*, 014108.
(37) Robinson, J. E.; Bassani, F.; Knox, R. S.; Schrieffer, J. R. *Phys. Rev. Lett.* **1962**, *9*, 215−217.
(38) Mohammed, A.-R. E.; Sahni, V. *Phys. Rev. B* **1984**, *29*, 3687−3690.
(39) Henderson, T. M.; Janesko, B. G.; Scuseria, G. E. *J. Chem. Phys.* **2008**, *128*, 194105.
(40) Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. *J. Chem. Phys.* **2009**, *130*, 054112.

(41) Watson, M. A.; Handy, N. C.; Cohen, A. J. *J. Chem. Phys.* **2003**, *119*, 6475−6481.

(42) Krykunov, M.; Ziegler, T.; Van Lenthe, E. *Int. J. Quantum Chem.* **2009**, *109*, 1676−1683.

(43) Krykunov, M.; Ziegler, T.; Van Lenthe, E. *J. Phys. Chem.* **2009**, *113*, 11495−11500.

(44) Pitzer, R. M. *Comput. Phys. Commun.* **2005**, *170*, 239−264.

(45) Barnett, M. P.; Coulson, C. A. *Phil. Trans. R. Soc. London, Ser. A* **1951**, *243*, 221−249.

(46) Barnett, M. P. The Evaluation of Molecular Integrals by the Zeta-Function Expansion. In *Methods of Computational Physics*; Alder, B., Fernbach, S., Rotenberg, M., Eds.; Academic Press: New York, 1963; Vol. 2, pp 95−153.

(47) Barnett, M. P. *J. Chem. Phys.* **2000**, *113*, 9419−9428.

(48) Rüdenberg, K. *J. Chem. Phys.* **1951**, *19*, 1459−1477.

(49) Wahl, A. C.; Cade, P. E.; Roothan, C. C. J. *J. Chem. Phys.* **1964**, *41*, 2578−2599.

(50) Fernández Rico, J.; Fernández, J. J.; Ema, I.; López, R.; Ramírez, G. *Int. J. Quantum Chem.* **2000**, *78*, 83−93.

(51) Fernández Rico, J.; Fernández, J. J.; López, R.; Ramírez, G. *Int. J. Quantum Chem.* **2000**, *78*, 137−145.

(52) Fernández Rico, J.; Ema, I.; Ramírez, G. *J. Comput. Chem.* **2004**, *25*, 1987−1994.

(53) Guseinov, I. I. *J. Chem. Phys.* **2004**, *120*, 9454−9457.

(54) Byron, F. W., Jr.; Fuller, R. W. *Mathematics of Classical and Quantum Physics*; Addison-Wesley: Reading, MA, 1970; Vol. 2.

(55) Antoziewicz, H. A. Bessel functions of fractional order. In *Handbook of Mathematical Functions*; Abramowitz, M., Stegun, I. A., Eds.; U.S. National Bureau of Standards: Washington, DC, 1964; Vol. 55, pp 435−478.

(56) Davis, P. J. Gamma Functions and Related Functions. In *Handbook of Mathematical Functions*; Abramowitz, M., Stegun, I. A., Eds.; U.S. National Bureau of Standards: Washington, DC, 1964; Vol. 55, pp 253−293.

(57) Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757−10816.

(58) Johnson, E. R.; Becke, A. D. *Can. J. Chem.* **2009**, *87*, 1369−1373.

(59) Baerends, E. J. et al. *ADF2010*; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 2010.

(60) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967.

(61) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51.

(62) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322−328.

(63) te Velde, G.; Baerends, E. J. *Phys. Rev. B* **1991**, *44*, 7888−7903.

(64) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chim. Acta* **1998**, *99*, 391−403.

(65) Ekström, U.; Visscher, L.; Bast, R.; Torvaldsen, A. J.; Ruud, K. *J. Chem. Theory Comput.* **2010**, *6*, 1971−1980.

(66) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(67) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.

(68) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(69) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(70) Ernzerhof, M.; Scuseria, G. *J. Chem. Phys.* **1999**, *110*, 5029−5036.

(71) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(72) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129.

(73) Zhao, Y.; Truhlar, D. G. *Theor. Chim. Acta* **2008**, *120*, 215−241.