

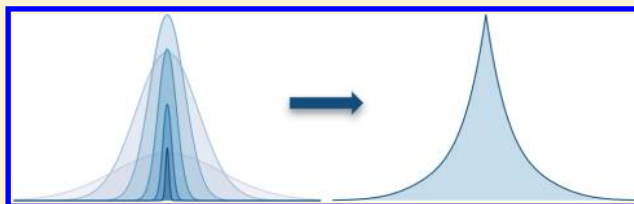
Mixed Ramp–Gaussian Basis Sets

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S Supporting Information

ABSTRACT: We discuss molecular orbital basis sets that contain both Gaussian and polynomial (ramp) functions. We show that, by modeling ramp–Gaussian products as sums of ramps, all of the required one- and two-electron integrals can be computed quickly and accurately. To illustrate our approach, we construct R-31+G, a mixed ramp–Gaussian basis in which the core basis functions of the 6-31+G basis are replaced by ramps. By performing self-consistent Hartree–Fock calculations, we show that the thermochemical predictions of R-31+G and 6-31+G are similar but the former has the potential to be significantly faster.



1. INTRODUCTION

Digital computers are excellent at representing numbers but are incapable of directly representing functions. For this reason, computational scientists who need to construct a function usually represent it as a linear combination of known functions from a basis set, thereby converting the problem of generating the function into the problem of generating numbers (viz. the linear coefficients).

In electronic structure calculations—whether based on the wave function,¹ the electron density (DFT),² or the intracule³—the orbitals play a central role and are invariably expanded in a basis. Over the years, a variety of basis functions have been explored, including Slater functions,^{4,5} wavelets,^{6,7} δ functions,⁸ Gaussians,⁹ and plane-waves, each bringing a different combination of advantages and disadvantages. Slater functions can describe electron–nuclear cusps¹⁰ but require the evaluation of troublesome three- and four-center electron repulsion integrals (ERIs); δ functions obviate the need for ERIs but necessitate very large basis sets; Gaussians and plane-waves are incapable of describing cusps but have become popular choices for calculations on molecular and periodic systems, respectively, primarily because they lead to tractable ERIs.

Since Boys' introduction⁹ of Gaussians in 1950, there has been a vast amount of research on the development and efficient implementation of compact but accurate Gaussian bases for molecular calculations and the work of Huzinaga,¹¹ Pople et al.,^{12,13} Ruedenberg et al.,^{14,15} Almlöf and Taylor,^{16–18} Dunning et al.,^{19–21} and Jensen^{22–24} has been particularly influential.

Although no Gaussian basis can ever properly represent the orbital cusp at a nucleus itself, it can give an adequate account of the orbital in the core regions (i.e., the neighborhoods of nuclei) if it includes Gaussians with sufficiently large exponents and, for this reason, all of the standard bases contain Gaussians of this type. However, the fact that exponents in the range 10^3 – 10^6 are needed confirms that, quite literally, Gaussians are

round pegs trying to fit a square hole. Mathematical analyses by Kutzelnigg and others^{25–29} have shown that the cusp problem is the key factor determining the rate at which Gaussian basis sets converge toward the complete-basis-set limit and the frustrating realization that significant computational effort is expended to treat chemically inert core regions has led many researchers to seek more cost-effective solutions to the cusp problem.

One possibility is to regularize all of the Coulomb operators^{30–37} in the Schrödinger equation so that they no longer produce cusps. However, although a strongly rank-reduced Schrödinger equation³³ can be treated accurately even by modest Gaussian basis sets, overenthusiastic regularization can produce unacceptably large changes in the resulting theoretical model chemistry.

A more robust approach is to construct mixed basis sets that contain a few functions that are deliberately designed to treat the cusps. To this end, Allen,³⁸ Silver,³⁹ Bacskey and Linnett,^{40–43} Lo et al.,⁴⁴ Bugaets and Zhogolev,⁴⁵ and Colle et al.⁴⁶ have considered mixed Slater–Gaussian basis sets, and Pahl and Handy have discussed a planewave–polynomial basis.⁴⁷ However, in each case, difficult mixed ERIs arise which require expensive numerical expansions or quadratures.

In contrast, mixed ramp–Gaussian bases, which have been discussed previously by Bishop,^{48,49} Gimarc,⁵⁰ and Steiner,^{51–58} are more promising. In this manuscript, we argue that such bases not only solve the cusp problem but, if the awkward ramp–Gaussian products are modeled suitably, also lead to straightforward ERIs, many of which can be computed efficiently using multipoles. We discuss basis functions in section 2, mixed basis sets in section 3, basis function products in section 4, one- and two-electron integrals in section 5, a selection of numerical results for small atoms and molecules in

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section 6, and some pertinent conclusions in section 7. Except where noted otherwise, atomic units are used throughout.

2. BASIS FUNCTIONS

Each of the basis functions that we will consider is the product of a radial factor and a normalized spherical harmonic $Y_{lm}(\theta, \varphi)$, where r , θ , and φ are the usual spherical polar coordinates around the center of the function. The angular momentum of a basis function is defined by its quantum numbers l and m and those with $l = 0, 1, 2, \dots$ will sometimes be called s -, p -, d -, ... functions.

2.1. Gaussians. A Gaussian of exponent α is

$$\mathcal{G}_{alm}(\mathbf{r}) = \sqrt{\frac{(l+1)!}{(2l+2)!}} \frac{(8\alpha)^{l+3/2}}{\sqrt{\pi}} \exp(-\alpha r^2) r^l Y_{lm}(\theta, \varphi) \quad (1)$$

with the normalization

$$\langle \mathcal{G}_{alm} | \mathcal{G}_{alm} \rangle = 1 \quad (2)$$

An s -Gaussian centered at A will be denoted by s_A^α and a generic Gaussian by \mathcal{G} . A fixed linear combination of Gaussians with the same l and m values is termed a contracted Gaussian function.

2.2. Ramps. A ramp with degree n and radius r_0 is given by

$$\mathcal{R}_{nlm}(\mathbf{r}) = \sqrt{\frac{(2n+2l+3)!}{(2n)!(2l+2)!}} \frac{1}{r_0^{2l+3}} (1 - r/r_0)^n r^l Y_{lm}(\theta, \varphi) \quad (3)$$

if $r \leq r_0$ but it vanishes elsewhere. It has the normalization

$$\langle \mathcal{R}_{nlm} | \mathcal{R}_{nlm} \rangle = 1 \quad (4)$$

An s -ramp centered at A will be denoted by s_n^A and a generic ramp by \mathcal{R} .

S_n ramps have a cusp (i.e., a discontinuous first derivative) at $r = 0$ (see Figure 1), which allows them to capture the behavior

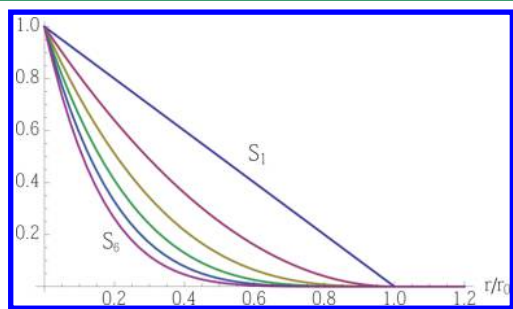


Figure 1. S_n ramps ($n = 1, 2, \dots, 6$), vertically rescaled for clarity.

of molecular orbitals close to nuclei.¹⁰ A ramp of degree n also has a discontinuous n th derivative at $r = r_0$, but this is of no practical importance if n is large. Noninteger ramp degrees are possible, but we will not consider them here.

2.3. Density Ramps. A density ramp with degree n and radius r_0 is given by

$$\mathbb{R}_{nlm}(\mathbf{r}) = \frac{(n+2l+3)!}{n!(2l+2)!} \frac{1}{r_0^{2l+3}} (1 - r/r_0)^n r^l Y_{lm}(\theta, \varphi) \quad (5)$$

if $r \leq r_0$ but it vanishes elsewhere. It is the same as the orbital ramp (3) except that it has the “unit multipole” normalization

$$\langle \mathbb{R}_{nlm} | r^l Y_{lm} \rangle = 1 \quad (6)$$

An s -type density ramp centered at A will be denoted by \mathbb{S}_n^A and a generic density ramp by \mathbb{R} .

The Coulomb and anti-Coulomb⁵⁹ potentials within a ramp are polynomials and, for example,

$$\begin{aligned} \int \mathbb{S}_n(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d\mathbf{r}' \\ = \sqrt{4\pi} \left[\frac{1 - (1-r)^{n+2}}{r} - \frac{n+1}{2} (1-r)^{n+2} \right] \end{aligned} \quad (7)$$

$$\begin{aligned} \int \mathbb{S}_n(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d\mathbf{r}' \\ = \sqrt{4\pi} \left[r + \frac{4}{(n+4)(n+5)} \left(\frac{1 - (1-r)^{n+4}}{r} - \frac{n+1}{4} (1-r)^{n+4} \right) \right] \end{aligned} \quad (8)$$

These will be useful in later sections of this paper.

2.4. Zero Diatomic Differential Overlap. After its introduction in the 1960s, the Neglect of Diatomic Differential Overlap (NDDO) approximation quickly established itself as a powerful method for avoiding difficult two-electron integrals and for increasing the speed of molecular orbital calculations.⁶⁰ Fortunately, we can easily ensure that all pairs of ramps in a molecule are strictly nonoverlapping by choosing their radii r_0 to be less than half of the distance between the closest ramp centers in the molecule. This strategy immediately leads to significant gains in computational efficiency. Noting that the shortest known equilibrium bond length between heavy atoms⁶¹ occurs in O_2^+ , where $r(\text{O}-\text{O}) \approx 2.05$ bohr, we decided to assume that heavy nuclei are always at least 2 bohr apart and then to follow Steiner⁵⁵ by choosing $r_0 = 1$ for all of our ramp functions. This constraint could be relaxed in future work.

2.5. Hydrogen-like Ions. The ground-state energy of a hydrogen-like ion (i.e., H, He⁺, Li²⁺, ...) with nuclear charge Z and orbital angular momentum l is

$$E = -\frac{Z^2}{2(l+1)^2} \quad (9)$$

and the energy afforded by a ramp $\mathcal{R}_{nlm}(\mathbf{r})$ with $r_0 = 1$ and degree n is

$$E(n) = \frac{2n+2l+3}{2} \left[\frac{n(n+l+1)}{2n-1} - \frac{Z}{l+1} \right] \quad (10)$$

It can be shown that, for large Z , the optimal degree and resulting energy are

$$n^{\text{opt}} = \frac{Z}{l+1} - \left(l + \frac{3}{2} \right) + O(Z^{-2}) \quad (11)$$

$$E^{\text{opt}} = -\frac{Z^2}{2(l+1)^2} + \frac{2l+3}{8} + O(Z^{-1}) \quad (12)$$

Thus, even when its radius is fixed at $r_0 = 1$, a single ramp with degree $n \approx Z/(l+1)$ provides a good approximation to the hydrogenic orbitals for large Z .

3. MIXED RAMP–GAUSSIAN BASIS SETS

Mixed ramp–Gaussian basis sets can be designed from first-principles, but in this preliminary study, we decided to introduce ramps to an existing basis, while seeking to retain its model chemistry. Because of its cusp and its simplicity, an s -ramp is superior to a highly contracted Gaussian for modeling the immediate neighborhood of a nucleus, but it is less potent at intermediate distances and is entirely useless for $r > 1$. For this reason, it may be useful to augment the ramp with one or more Gaussians that extend beyond its support. In our modified basis, we retain the valence functions but replace each core function ϕ by the 2-fold contracted function

$$\hat{\phi} = c_1 S_n + c_2 s_\alpha \quad (13)$$

where the parameters c_1 , n , c_2 , and α are determined by fitting. Typically, ϕ is highly contracted, so its replacement by $\hat{\phi}$ results in fewer primitives and potentially significant computational savings. We introduce an s -ramp for a first-row atom and, in a similar way, we could introduce an s -ramp and three p -ramps for a second-row atom, and so on.

To illustrate our approach, we will describe the rampification of the famous 6-31+G basis of Hehre, Ditchfield, and Pople¹³ to form the mixed basis R-31+G for the first-row atoms (i.e., Li to Ne). The core function ϕ in 6-31+G is a 6-fold-contracted s -function. The c_1 , n , c_2 and α parameters (Table 1) were found by considering the charge-conserving least-squares Lagrangian

$$\mathcal{L} = \langle \phi^2 - \hat{\phi}^2 | \phi^2 - \hat{\phi}^2 \rangle + \lambda [\langle \hat{\phi} | \hat{\phi} \rangle - 1] \quad (14)$$

Table 1. Parameters for the Ramp Basis Function Equation 13 in the R-31+G Basis for First-Row Atoms

Atom	Ramp params.		Gaussian params.		Residual \mathcal{L}
	c_1	n	c_2	α	
Li	0.2958990	4	0.8049342	1.404	0.00023
Be	0.3838603	5	0.7153614	2.279	0.00013
B	0.4548135	6	0.6387753	3.327	0.00011
C	0.5120939	7	0.5749880	4.545	0.00011
N	0.5587448	8	0.5219102	5.939	0.00013
O	0.5974355	9	0.4773544	7.505	0.00016
F	0.6298802	10	0.4395960	9.252	0.00020
Ne	0.6573841	11	0.4074466	11.168	0.00024

In all cases, the optimal ramp degree n is $Z + 1$ and the exponent α lies between the two smallest of the six exponents in ϕ , indicating that the ramp and Gaussian model the inner and outer parts of ϕ , respectively. In the absence of other effects, the quartic nature of eq 14 causes \mathcal{L} to decrease as ϕ becomes more diffuse. However, the ramp radius $r_0 = 1$ is uncomfortably tight for the Group 1 and 2 atoms and their residuals are therefore higher than might otherwise have been expected.

Table 2 shows how the moments $\langle r \rangle$ and $\langle r^{-1} \rangle$ differ between the “6” and “R” basis functions in the two-electron atomic ions. The “6” function is always more diffuse than the “R” function and, particularly in the light atoms, it extends significantly beyond $r = 1$ and makes heavy demands on the single Gaussian in eq 13, which must try to capture this behavior by itself.

Rampification produces small changes in calculated properties, and we define the “rampdev”

Table 2. $\langle \phi | r | \phi \rangle$ and $\langle \phi | r^{-1} | \phi \rangle$ in the He-like Ions

Ion	$\langle r \rangle_6$	$\langle r \rangle_R - \langle r \rangle_6$	$\langle r^{-1} \rangle_6$	$\langle r^{-1} \rangle_R - \langle r^{-1} \rangle_6$
Li ⁺	0.5702	−0.0199	2.6903	0.0178
Be ²⁺	0.4123	−0.0077	3.6923	0.0109
B ³⁺	0.3230	−0.0039	4.6936	0.0084
C ⁴⁺	0.2657	−0.0024	5.6921	0.0076
N ⁵⁺	0.2258	−0.0017	6.6892	0.0075
O ⁶⁺	0.1963	−0.0013	7.6852	0.0077
F ⁷⁺	0.1737	−0.0011	8.6810	0.0080
Ne ⁸⁺	0.1558	−0.0009	9.6748	0.0084

$$\Delta = P(R-31+G) - P(6-31+G) \quad (15)$$

of a property P as the difference between its values computed with the rampified and original basis sets. If the rampdevs are consistently small (e.g., below 1 mE_h), we can infer that the rampified and original basis sets afford similar theoretical model chemistries.

4. BASIS-FUNCTION PRODUCTS

Mixed ramp–Gaussian bases yield three types of basis-function products: Gaussian–Gaussian (GG), ramp–ramp (RR), and ramp–Gaussian (RG). Proceeding with these would lead to six families of two-electron integral—(GG|GG), (GG|RR), (GG|RG), (RR|RR), (RR|RG), and (RG|RG)—some of which are computationally troublesome. Therefore, to make the problem tractable, we express all RG and RR products as sums of density ramps. This removes all three- and four-center integrals and is a key advantage of ramp–Gaussian bases over Slater–Gaussian bases.

4.1. GG Products. Gaussian–Gaussian products yield Gaussians of higher exponent,¹ for example,

$$s_\alpha^A s_\beta^B = \left[\frac{2\alpha\beta}{(\alpha + \beta)\pi} \right]^{3/4} \exp \left[-\frac{\alpha\beta}{\alpha + \beta} |\mathbf{A} - \mathbf{B}|^2 \right] s_{\alpha+\beta}^P \quad (16)$$

where $\mathbf{P} = (\alpha\mathbf{A} + \beta\mathbf{B})/(\alpha + \beta)$.

4.2. RR Products. Ramp–ramp products vanish if they are on different centers. Otherwise, their product is a combination of density ramps of higher degree, for example,

$$S_m^A S_n^A = \sqrt{\frac{(2m+3)!(2n+3)!}{4\pi(2m)!(2n)!}} \frac{(m+n)!}{(m+n+3)!} S_{m+n}^A \quad (17)$$

4.3. RG Products. The ramp–Gaussian product $\mathcal{R}^A \mathcal{G}^B$ vanishes except on the domain of the ramp. It is possible, therefore, to use least-squares fitting to model such products by sums of density ramps at \mathbf{A} , that is,

$$\mathcal{R}^A \mathcal{G}^B \approx \sum_{k=1}^K c_{n_k l_k m_k} \mathcal{R}_{n_k l_k m_k}^A = \sum_{k=1}^K c_k \mathcal{R}_k^A \quad (18)$$

We fit the *potentials*, rather than the RG products themselves, using the least-squares functional⁵⁹

$$Z = \left\langle \mathcal{R}^A \mathcal{G}^B - \sum_{k=1}^K c_k \mathcal{R}_k^A \right|_{r_{12}} \left| \mathcal{R}^A \mathcal{G}^B - \sum_{k=1}^K c_k \mathcal{R}_k^A \right\rangle \quad (19)$$

and the charge-conservation constraint

$$\langle \mathcal{R}^A | \mathcal{G}^B \rangle = \sum_{k=1}^K c_k \langle \mathcal{R}_k^A \rangle \quad (20)$$

The c_k can be found by solving of a set of $K + 1$ linear equations involving the integrals

$$A_{jk} = \langle R_j^A | r_{12} | R_k^A \rangle \quad (21)$$

$$b_k = \langle R_k^A | r_{12} | R^A \mathcal{G}^B \rangle \quad (22)$$

Using the anti-Coulomb potential of a ramp, it is easy to find the A_{jk} integrals, for example,

$$\begin{aligned} \langle S_j^A | r_{12} | S_k^A \rangle = 2\pi & \left(\frac{6}{j+4} + \frac{6}{k+4} - \frac{jk-6}{j+k+5} \right. \\ & \left. + \frac{2jk-18}{j+k+6} - \frac{jk-6}{j+k+7} \right) \end{aligned} \quad (23)$$

and the b_k integrals can be reduced to overlap integrals such as those discussed in section 5.

4.4. Example: Modeling Concentric Ss Products.

Concentric $S_n s_\alpha$ products tend to be larger than nonconcentric ones, and it is wise to model them accurately. In calculations with the R-31+G basis, the S_n ramp on each heavy atom is paired with its associated s_α primitive (see eq 13), the three s primitives in the inner valence function, the single primitive in the outer valence function, and the single primitive in the diffuse function.

To illustrate our RG modeling scheme, we consider the product of the S_4 ramp and the diffuse s_α Gaussian ($\alpha = 0.0074$) in the R-31+G basis for the Li atom. If we choose to expand this product as a linear combination of the three density ramps S_4 , S_5 and S_6 , we obtain the matrix equation

$$\begin{pmatrix} \frac{83\pi}{39} & \frac{121\pi}{60} & \frac{657\pi}{340} & \sqrt{4\pi} \\ \frac{121\pi}{60} & \frac{484\pi}{255} & \frac{461\pi}{255} & \sqrt{4\pi} \\ \frac{657\pi}{340} & \frac{461\pi}{255} & \frac{2766\pi}{1615} & \sqrt{4\pi} \\ \sqrt{4\pi} & \sqrt{4\pi} & \sqrt{4\pi} & 0 \end{pmatrix} \begin{pmatrix} c_4 \\ c_5 \\ c_6 \\ \lambda \end{pmatrix} = \begin{pmatrix} 0.025438286123998 \\ 0.024104501118453 \\ 0.023096251562111 \\ 0.013490147389740 \end{pmatrix} \quad (24)$$

As Figure 2 shows, the resulting three-ramp model is within 6×10^{-9} of the $S_4 s_\alpha$ product at all points.

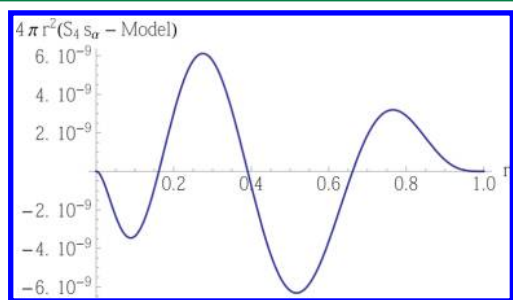


Figure 2. Error in a three-ramp model for a $S_4 s_\alpha$ product in the Li atom.

The density ramps S_{n_k} that we have chosen to model all of the $S_n s_\alpha$ products that arise in the R-31+G basis of the first-row atoms are listed in Tables 10 and 11 of the Supporting Information.

5. INTEGRAL EVALUATION

In this section, we outline methods to compute the one- and two-electron integrals that arise in a ramp–Gaussian basis set. We do not discuss the all-Gaussian integrals, for these have been thoroughly studied previously^{62–64} and we have checked our implementation against integrals from Q-Chem.⁶⁵ We consider the one- and two-electron integrals that arise for s -ramps and s -Gaussians, using the notation $R_{XY} = |\mathbf{X} - \mathbf{Y}|$.

5.1. Ramp–Ramp Integrals $\langle R | \hat{O}_1 | R \rangle$ and $\langle R | r_{12}^{-1} | R \rangle$. If the ramps are concentric, the one-electron integrals are

$$\langle S_m^A | S_n^A \rangle = \sqrt{\frac{(2m+3)!}{(2m)!} \frac{(2n+3)!}{(2n)!} \frac{(m+n)!}{(m+n+3)!}} \quad (25)$$

$$\left\langle S_m^A \left| -\frac{\nabla^2}{2} \right| S_n^A \right\rangle = \langle S_m^A | S_n^A \rangle \frac{mn(m+n+2)(m+n+3)}{2(m+n)(m+n-1)} \quad (26)$$

$$\left\langle S_m^A \left| \frac{1}{|\mathbf{r} - \mathbf{C}|} \right| S_n^A \right\rangle = \begin{cases} \langle S_m^A | S_n^A \rangle (m+n+3)/2 & \mathbf{A} = \mathbf{C} \\ \langle S_m^A | S_n^A \rangle / R_{AC} & \mathbf{A} \neq \mathbf{C} \end{cases} \quad (27)$$

and, from eq 7, the Coulomb integral is

$$\begin{aligned} \left\langle S_m^A \left| \frac{1}{r_{12}} \right| S_n^A \right\rangle = 4\pi & \left[1 + \frac{(m+1)(n+1)}{2(m+n+3)} \right. \\ & \left. + \frac{(m+1)(m+2)(n+1)(n+2)}{2(m+n+3)(m+n+4)(m+n+5)} \right] \end{aligned} \quad (28)$$

If the ramps do not overlap, all one-electron integrals vanish and the Coulomb integral is simply

$$\langle S_m^A | r_{12}^{-1} | S_n^B \rangle = \frac{4\pi}{R_{AB}} \quad (29)$$

5.2. Ramp–Gaussian Integrals $\langle R | \hat{O}_1 | \mathcal{G} \rangle$ and $\langle R | r_{12}^{-1} | \mathcal{G} \rangle$. All of the required integrals can be expressed in terms of the auxiliary integrals

$$w_n = \frac{\sqrt{\beta/\pi}}{R_{AB}} \int_0^1 (1-r)^n [e^{-\beta(r-R_{AB})^2} - e^{-\beta(r+R_{AB})^2}] dr \quad (30)$$

and the practical computation of these quantities is discussed in the Appendix.

If the ramp and Gaussian overlap significantly, the one-electron integrals are

$$\langle S_n^A | s_\beta^B \rangle = K(w_n - w_{n+1}) \quad (31)$$

$$\left\langle S_n^A \left| -\frac{\nabla^2}{2} \right| s_\beta^B \right\rangle = K \left[\frac{n(n+1)}{2} w_{n-1} - \frac{n(n-1)}{2} w_{n-2} \right] \quad (32)$$

$$\left\langle S_n^A \left| \frac{1}{|\mathbf{r} - \mathbf{C}|} \right| s_\beta^B \right\rangle = \begin{cases} K w_n & \mathbf{A} = \mathbf{C} \\ M_{lm}^{Ss} T_C^{lm} & \mathbf{A} \neq \mathbf{C} \end{cases} \quad (33)$$

where

$$K = \sqrt{\frac{(2n+3)!}{(2n)! 8\pi}} \left(\frac{2\pi}{\beta} \right)^{3/4} \quad (34)$$

Table 3. HF Energies, Ionic Radii, and MO Coefficients for He-like Ions

	HF energy		Ionic radius		6-31+G MO coeffs				R-31+G MO coeffs			
	6-31+G	Δ	6-31+G	Δ	6	3	1	+	R	3	1	+
Li ⁺	−7.23549	0.05970	0.5728	−0.0039	0.999	0.016	−0.009	0.001	0.998	0.132	−0.091	0.016
Be ²⁺	−13.60974	0.03547	0.4148	+0.0014	0.998	0.014	−0.006	0.001	0.995	0.087	−0.054	0.013
B ³⁺	−21.98379	0.02475	0.3251	+0.0017	0.998	0.014	−0.005	0.001	0.993	0.064	−0.036	0.009
C ⁴⁺	−32.35763	0.02103	0.2674	+0.0011	0.998	0.013	−0.005	0.001	0.994	0.048	−0.024	0.007
N ⁵⁺	−44.73121	0.01978	0.2257	+0.0008	0.998	0.011	−0.004	0.001	0.994	0.039	−0.019	0.006
O ⁶⁺	−59.10445	0.02009	0.1974	+0.0007	0.998	0.010	−0.003	0.001	0.994	0.034	−0.016	0.006
F ⁷⁺	−75.47742	0.02066	0.1747	+0.0006	0.998	0.009	−0.002	0.001	0.995	0.031	−0.013	0.004
Ne ⁸⁺	−93.85004	0.02184	0.1565	+0.0005	0.998	0.007	−0.001	0.000	0.995	0.028	−0.011	0.004

and M_{lm}^{ss} contains the multipole moments of the $S_n^A s_\beta^B$ product and T_C^{lm} contains the interactions of those multipoles with a unit charge at C. (This is discussed further in the following subsection.) The Coulomb integral is

$$\left\langle S_n^A \left| \frac{1}{r_{12}} \right| s_\beta^B \right\rangle = \sqrt{4\pi} (2\pi/\beta)^{3/4} \left[\frac{\text{erf}(\sqrt{\beta} R_{AB})}{R_{AB}} + \frac{n+1}{2} w_{n+3} - \frac{n+3}{2} w_{n+2} \right] \quad (35)$$

If the ramp and Gaussian overlap negligibly, all of the one-electron integrals are negligible and the Coulomb integral reduces to

$$\langle S_n^A | r_{12}^{-1} | s_\beta^B \rangle = \frac{\sqrt{4\pi} (2\pi/\beta)^{3/4}}{R_{AB}} \quad (36)$$

5.3. Computational Considerations. Our approach to mixed ramp–Gaussian basis sets has two significant computational advantages for the evaluation of two-electron integrals $G_{cd}^{ab} \equiv (abcd)$. The first pertains to cases where the ab and cd densities overlap, the second to the nonoverlapping case.

Replacing highly contracted Gaussians by ramps lowers the mean degree of contraction K of the basis set, and because the ramp–ramp integrals (section 5.1) and ramp–Gaussian integrals (section 5.2) can be computed roughly as quickly as traditional Gaussian–Gaussian integrals, this reduction leads to dramatic savings in the innermost loops of integral algorithms, whose costs scale with K^4 . This has a direct beneficial effect on the computational effort required in the overlapping case.⁶⁶

In large systems, most two-electron integrals are of the nonoverlapping type and are therefore most efficiently computed via multipole–multipole interactions. For example, as described above, all $R^A R^A$ and $R^A G$ products are expressed in terms of ramps on A, and likewise, all $R^C R^C$ and $R^C G$ products are expressed in terms of ramps on C. The integrals associated with these two nonoverlapping sets can therefore be computed via the classical expression⁶⁷

$$G_{cd}^{ab} = M_{lm}^{ab} T_{\lambda\mu}^{lm} N_{cd}^{\lambda\mu} \quad (37)$$

where M_{lm}^{ab} is the (lm) -multipole moment of the ab product around A, $N_{cd}^{\lambda\mu}$ is the $(\lambda\mu)$ -multipole moment of the cd product around C, and $T_{\lambda\mu}^{lm}$ is the interaction between a unit (lm) -multipole at A and a unit $(\lambda\mu)$ -multipole at C. This approach is efficient because the multipole moment matrices M_{ab}^{lm} and $N_{cd}^{\lambda\mu}$ are calculated at the shell-pair level and the interaction matrices $T_{\lambda\mu}^{lm}$ are calculated at the nucleus-pair level. The only shell-

quartet operation is the second matrix–matrix multiplication in eq 37 but this can be performed extremely efficiently using a Level-3 BLAS routine. *This is the key computational advantage of ramps over contracted Gaussian functions.*

6. RESULTS

The one- and two-electron integrals arising in a mixed basis of s -ramps and s - and p -Gaussians have been implemented in a stand-alone Fortran 90 program, and we have used this to perform unrestricted Hartree–Fock (UHF) calculations on molecules containing the atoms H to Ne.

Our goal was to determine the extent to which the inclusion of ramps perturbs the theoretical model chemistry of the original basis set. To this end, we compared the results of HF calculations for helium-like ions, atoms, and small molecules using the 6-31+G and R-31+G bases.

6.1. Helium-like Ions. Table 3 shows the HF energies of the He-like ions. Because these systems have only one occupied orbital and no valence electrons, they reveal the effects of rampification directly. In all cases, the HF/R-31+G energies are higher than the HF/6-31+G energies and the differences, which range from 60 mE_h for Li to around 20 mE_h for the heavier ions, are large: the key question is whether or not they will largely cancel in calculations of chemical energetics.

Why are the HF/R-31+G energies higher than the HF/6-31+G energies? To answer this, we have examined the ionic radii $\langle r \rangle$ and the molecular orbital (MO) coefficients, which are also shown in Table 3. In general, the R-31+G ions are larger than the 6-31+G ions, with significantly larger amounts of the valence and diffuse basis functions contributing to the orbital. The inclusion of these functions helps to describe the outer core region and to correct for the deficiencies of the “R” function in this part of space. The slight dilation of the ion that results from rampification of the basis has predictable effects on the components of the total energies, leading to reductions in the magnitude of the nuclear-attraction, kinetic and two-electron energy components, and an overall destabilization of the ion. These components in the O⁶⁺ ion are shown in the middle columns of Table 4.

6.2. Atoms. Table 4 also compares the HF energy components in the O⁶⁺ ion with those in the O atom. Although the component rampdevs change significantly between the two-electron ion and the neutral atom, it is clear that the qualitative picture is unchanged, and consequently, the rampdev in the total energy of the ion (20 mE_h) is similar to that in the atom (18 mE_h). We conclude from this that almost all of the total energy rampdev originates in the core electrons and this, in turn, suggests that atomic and molecular chemistry will not be significantly affected by rampification.

Table 4. Components of the HF Energy in O⁶⁺ Ion and O Atom

	O ⁶⁺ ion		O atom	
	6-31+G	Δ	6-31+G	Δ
Nuclear attraction	−122.62577	+0.53138	−177.81659	+0.57390
Kinetic	+58.75954	−0.48828	+74.66889	−0.53046
Total one-electron	−63.86623	+0.04310	−103.14770	+0.04344
Coulomb	+9.52356	−0.04603	+36.55634	−0.05153
α exchange	−2.38089	+0.01151	−4.79992	+0.01276
β exchange	−2.38089	+0.01151	−3.39218	+0.01291
Total two-electron	+4.76178	−0.02302	+28.36424	−0.02586
Total	−59.10445	+0.02009	−74.78346	+0.01758

Table 5 gives the HF/6-31+G energies of the ground states of first-row atoms. The R-31+G energies are systematically higher than the 6-31+G energies and the differences are strikingly similar to those in the two-electron ions (Table 3), again confirming that most of the energetic effects of rampification are confined to the core electrons. The table also lists the ionization potentials and electron affinities of the atoms. The rampdevs for these chemical properties are much smaller than those for the total energies, indicating that the core–valence interactions in an atom and its ion are similar and the total energy rampdevs of the neutral and ionized species therefore largely cancel. The largest rampdevs are found for the ionization potentials of Li and Be.

6.3. Molecules. Table 6 shows UHF/6-31+G energies and atomization energies for a set of molecules consisting of all molecules in the G2–1 test set with first-row atoms only.⁶⁸ The total energy rampdevs are almost equal to the sum of the rampdevs of the constituent atoms, reflecting the small core effects on bonding. As usual, the errors are largest in molecules containing Li and Be.

The atomization rampdevs are small and negative for most of the first-row hydrides (i.e., LiH to HF) but significantly larger and invariably positive for the molecules that have bonded heavy atoms (i.e., Li₂ to F₂). Further analysis of these data reveals that almost all of the rampdev stems from interactions between ramps and the valence electrons on adjacent heavy atoms. This explains, for example, why the largest rampdevs arise for LiF (where the relatively inaccurate Li ramp is close to the F atom) and for the triatomic CO₂ (where there are four adjacent ramp–valence interactions). In general, atomization rampdevs tend to be positive, proportional to the number of adjacent ramp–heavy–valence pairs in the molecule, and largest when short bonds are involved.

Table 6. Molecular UHF Total Energies and Atomisation Energies

Molecule	Total energy		Atomization energy	
	6-31+G	Δ	6-31+G	Δ
LiH	−7.97969	+0.05985	0.04998	+0.00010
BeH	−15.14458	+0.03492	0.07675	−0.00038
CH	−38.25571	+0.01946	0.07655	+0.00001
CH ₂ (¹ A ₁)	−38.85758	+0.01943	0.18019	+0.00004
CH ₂ (³ B ₁)	−38.91384	+0.01970	0.23644	−0.00023
CH ₃	−39.54869	+0.01959	0.37306	−0.00012
CH ₄	−40.18105	+0.01917	0.50719	+0.00030
NH	−54.94577	+0.01798	0.06124	−0.00002
NH ₂	−55.53588	+0.01798	0.15312	−0.00002
NH ₃	−56.16611	+0.01793	0.28512	+0.00003
OH	−75.36814	+0.01765	0.08645	−0.00007
H ₂ O	−75.99068	+0.01771	0.21076	−0.00013
HF	−99.99535	+0.01714	0.12960	−0.00008
Li ₂	−14.86715	+0.11847	0.00420	+0.00143
LiF	−106.93738	+0.07487	0.13839	+0.00214
C ₂ H ₂	−76.79667	+0.03819	0.43836	+0.00075
C ₂ H ₄	−78.00806	+0.03866	0.65328	+0.00029
C ₂ H ₆	−79.19814	+0.03806	0.84689	+0.00088
CN	−92.16142	+0.03634	0.09420	+0.00109
HCN	−92.82964	+0.03624	0.26419	+0.00119
CO	−112.67051	+0.03581	0.20613	+0.00124
HCO	−113.18946	+0.03617	0.22684	+0.00088
H ₂ CO	−113.81153	+0.03628	0.35068	+0.00077
CH ₃ OH	−114.99158	+0.03627	0.53426	+0.00078
N ₂	−108.86670	+0.03505	0.09411	+0.00087
N ₂ H ₄	−111.12416	+0.03562	0.35864	+0.00029
NO	−129.17838	+0.03455	0.00863	+0.00099
O ₂	−149.54964	+0.03458	−0.01727	+0.00058
H ₂ O ₂	−150.71399	+0.03471	0.15060	+0.00045
F ₂	−198.65489	+0.03349	−0.08015	+0.00064
CO ₂	−187.51806	+0.05233	0.27022	+0.00230

Ionization potentials (Table 7), electron affinities (Table 8), and proton affinities (Table 9) were also calculated for several of the molecules. Because adding or removing electrons has no effect on the number of adjacent ramp–valence interactions, the rampdevs for these three tables are generally small compared with the atomization rampdevs

7. CONCLUSIONS

We have argued that replacing highly contracted Gaussian core functions by ramp functions is computationally beneficial and chemically benign. The use of ramps is beneficial in three ways: (1) The average degree of contraction of the basis set is

Table 5. Atomic UHF Energies, Ionization Potentials, and Electron Affinities

Atom	UHF energy		Ionization potential		Electron affinity	
	6-31+G	Δ	6-31+G	Δ	6-31+G	Δ
Li (² S)	−7.43147	+0.05995	0.19599	−0.00025	−0.00578	+0.00004
Be (¹ S)	−14.56960	+0.03454	0.29418	+0.00056	−0.02624	−0.00007
B (² P)	−24.52373	+0.02352	0.28967	+0.00019	−0.01099	+0.00000
C (³ P)	−37.68092	+0.01947	0.39741	+0.00007	+0.01992	−0.00001
N (⁴ S)	−54.38629	+0.01796	0.51625	+0.00005	−0.07174	−0.00001
O (³ P)	−74.78346	+0.01758	0.43972	+0.00000	−0.01959	−0.00002
F (² P)	−99.36752	+0.01706	0.57939	−0.00000	+0.04985	−0.00004
Ne (¹ S)	−128.48355	+0.01727	0.73281	+0.00000	−0.28954	+0.00032

Table 7. Molecular Ionization Potentials

Molecule	Cation state	6-31+G	Δ
CH ₄	² B ₁	0.44696	+0.00042
H ₂ O	² B ₁	0.40469	+0.00005
HF	² Π	0.14772	−0.00022
C ₂ H ₂	² Π _u	0.36654	+0.00027
C ₂ H ₄	² B ₁	0.32708	+0.00023
CO	² Σ ⁺	0.47847	+0.00032
N ₂	² Σ ⁺	0.57775	+0.00021
N ₂	² Π _u	0.59361	+0.00036
O ₂	² Π _g	0.50780	−0.00001

Table 8. Molecular Electron Affinities

Molecule	Anion state	6-31+G	Δ
CH	³ Σ [−]	+0.01884	−0.00004
CH ₂	² B ₁	−0.04742	+0.00023
CH ₃	¹ A ₁	−0.06461	+0.00027
CN	¹ Σ ⁺	+0.10728	+0.00014
NH	² Π	−0.05466	+0.00001
NH ₂	¹ A ₁	−0.03876	+0.00002
NO	³ Σ [−]	+0.01891	−0.00020
OH	¹ Σ ⁺	−0.14235	+0.00018
O ₂	² Π _g	+0.00423	+0.00000

Table 9. Molecular Proton Affinities

Molecule	6-31+G	Δ
C ₂ H ₂	0.23270	−0.00013
NH ₃	0.35014	+0.00010
H ₂ O	0.27606	−0.00012

significantly decreased; (2) large numbers of three- and four-center two-electron integrals are removed; (3) many of the other two-electron integrals reduce to multipole–multipole interactions that are computable by matrix multiplication.

We have taken a standard Pople basis set (6-31+G) and shown how to construct its “ramped” analog (R-31+G). Our methodology is general and can easily be applied to any segmented Gaussian basis set. (It is less effective for generally contracted bases but Jensen has recently shown⁶⁹ how to segment a generally contracted basis set without loss of accuracy.) We have shown that 6-31+G and R-31+G afford similar theoretical model chemistries for small atoms and molecules, at least at the HF level. Atomic ionization potentials and electron affinities change by an average of 4.3 and 1.8 meV, respectively, and the changes in molecular atomization energies (1.6 kJ/mol), ionization energies (5.6 meV), electron affinity (3.3 meV), and proton affinities (3.2 meV) are also small.

This preliminary study has explored the application of *s*-ramps to first-row atoms (Li–Ne), but we expect that even greater advantages will accrue when *s* and *p* ramps are applied to second-row atoms (Na–Ar), where large numbers of high-exponent Gaussian primitives can be eliminated. This and constructing entirely new ramp-containing bases are important areas of future research.

In addition to their computational expediency, ramps may also be useful because of their cusps. For example, the accurate calculation of nuclear magnetic resonance (NMR) properties require a faithful representation of the nuclear neighborhoods in molecules and, for this reason, Slater functions have been

advocated⁷⁰ despite the difficult two-electron integrals that they necessitate. Mixed ramp–Gaussian basis sets are less problematic in this respect, and we will explore their application to NMR calculations in future work.

■ APPENDIX: CALCULATION OF THE W_N INTEGRALS

All of the integrals in section 5.2 are expressed in terms of the auxiliary integrals

$$w_n = \frac{\sqrt{\beta/\pi}}{R} \int_0^1 (1-r)^n [e^{-\beta(r-R)^2} - e^{-\beta(r+R)^2}] dr \quad (38)$$

For brevity, we define $x = \sqrt{\beta}(R-1)$, $y = \sqrt{\beta}R$, and $z = \sqrt{\beta}(R+1)$.

Taylor expansion of the Gaussians, followed by termwise integration, yields

$$w_n = \frac{2\beta^{3/2}}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{H_{2k+1}(y)e^{-y^2}}{y} \frac{n!\beta^k}{(n+2k+2)!} \quad (39)$$

where H_k is a Hermite polynomial.⁷¹ If the ramp and Gaussian are concentric (i.e., $R = 0$), we find

$$w_n = \frac{4\beta^{3/2}}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{n!(2k+1)!}{(n+2k+2)!} \frac{(-\beta)^k}{k!} \quad (40)$$

Equations 39 and 40 are computationally useful when β/n is small.

Binomial expansion of the ramp, followed by termwise integration, yields various formulas. If $R = 0$, then

$$w_n = \frac{2\beta^{1/2}}{\sqrt{\pi}} \sum_{k=0}^n \frac{(-1)^k n!}{(n-k)!k!} \frac{\gamma(k/2+1, \beta)}{\beta^{k/2}} \quad (41)$$

If $0 < R \leq 1$ then

$$w_n = \frac{\beta^{-n/2}}{2R\sqrt{\pi}} \sum_{k=0}^n \frac{(-1)^k n!}{(n-k)!k!} \{x^{n-k} [g(x) + (-1)^k g(y)] + z^{n-k} [g(y) - g(z)]\} \quad (42)$$

If $R \geq 1$, then

$$w_n = \frac{\beta^{-n/2}}{2R\sqrt{\pi}} \sum_{k=0}^n \frac{(-1)^k n!}{(n-k)!k!} \{(-1)^k x^{n-k} [g(y) - g(x)] + z^{n-k} [g(y) - g(z)]\} \quad (43)$$

where $g(u) \equiv \gamma((k+1)/2, u^2)$ and γ is the incomplete gamma function.⁷¹ Equations 41–43 are computationally useful when β/n is large.

■ ASSOCIATED CONTENT

Supporting Information

Ramp degrees (Tables 10 and 11) used to model the concentric $S_n S_\beta$ products that arise in the R-31+G basis. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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