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Accurate Electron Densities at Nuclei Using Small Ramp-Gaussian Basis Sets

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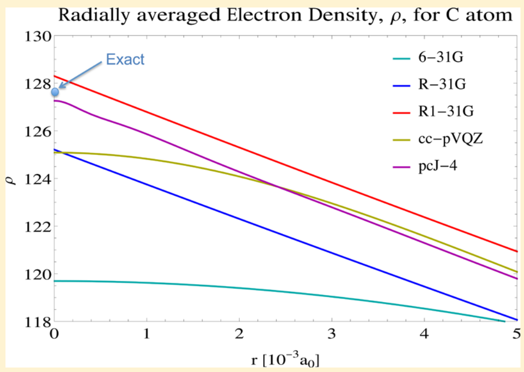
ABSTRACT: Electron densities at nuclei are difficult to calculate accurately with all-Gaussian basis sets because they lack an electron−nuclear cusp. The newly developed mixed ramp-Gaussian basis sets, such as R-31G, possess electron−nuclear cusps due to the presence of ramp functions in the basis. The R-31G basis set is a general-purpose mixed ramp-Gaussian basis set modeled on the 6-31G basis set. The prediction of electron densities at nuclei using R-31G basis sets for Li−F outperforms Dunning, Pople, and Jensen general purpose all-Gaussian basis sets of triple-ζ quality or lower and the cc-pVQZ basis set. It is of similar quality to the specialized pcJ-0 basis set which was developed with partial decontraction of core functions and extra high exponent *s*-Gaussians to predict electron density at the nucleus. These results show significant advantages in the properties of mixed ramp-Gaussian basis sets compared to all-Gaussian basis sets.



1. INTRODUCTION

Standard ab initio quantum chemistry methods use all-Gaussian basis sets, which have no electron−nuclear cusp and thus struggle to accurately predict core-dependent properties. Electron densities at nuclei, ρ_0, are an important example of a core-dependent chemical property that is directly responsible for the Fermi contact term of the indirect spin−spin coupling constant (SSCC) and is also important in the fine structure of the hydrogen spectrum and for relativistic calculations (in the Darwin term). Some studies use the synonym "contact density" for this property.

Unlike traditional all-Gaussian basis sets, the newly developed[1] mixed ramp-Gaussian basis sets do have a cusp due to the presence of a ramp function, which in the simplest case has the unnormalized form $(1 - r)^n$ for $r \leq 1$ and 0 otherwise. These new basis sets are thus expected to give superior results to similar sized all-Gaussian basis sets for ρ_0; this work investigates this hypothesis. Electron density at the nuclei is both an important property in itself and a straightforward, easily explored example of a core-related parameter.

The new R-31G basis set was produced by replacing the 6-fold contracted core basis function in 6-31G with a 2-fold contracted basis function with one ramp and one Gaussian. The R-31G basis set was shown to produce very similar chemistry (e.g., ionization energies, atomization energies, and so on) to the 6-31G basis set for unrestricted Hartree−Fock calculations of molecules in the first-row-only G2 data set. It was recently demonstrated[2] that integrals that arise using ramp basis functions can be evaluated efficiently and that UHF/R-31+G calculation timings are competitive with UHF/6-31+G calculation timings for large linear molecules. For the small systems investigated here, calculation times for UHF/R-31G and UHF/6-31G are similar.

Atomic units are used throughout this paper.

2. BASIS SETS

2.1. All-Gaussian Basis Sets. General-purpose basis sets are designed to give accurate description of chemical energies; for this purpose, inflexible descriptions of the core are generally adequate. Common general-purpose basis sets discussed in this work include the Pople (e.g., 6-31G[3] and 6-311G[4]), Dunning[5] (cc-pVnZ), and Jensen[6,7] (pc-n) basis sets.

However, accurate quantification of ρ_0, and hence the Fermi contact term in the indirect spin−spin coupling constant, requires a more flexible and accurate description of the core.[8−13] The pcJ-n and ccJ-pVnZ basis sets were designed by Jensen[12] to reproduce indirect spin−spin coupling constants accurately. In particular, they contain additional very high exponent core Gaussian primitives and decontraction of the core basis functions. Our tests show that the pcJ-n basis sets are slower than their parent pc-n bases (by about a factor of 2−4), but significantly quicker than the higher quality pcJ-(n+1) basis set.

Our calculations show that pcS-n, ccS-pVnZ, or cc-pCVnZ basis sets do *not* give significantly improved results for ρ_0 compared to their pc-n/cc-pVnZ parent basis sets. This is because the additional primitives are not very high exponent *s* primitives.

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Table 1. Benchmarks for ρ_0 for Atoms and Errors in ρ_0 Using Different Basis Sets

	H	Li	Be	B	C	N	O	F
Benchmark ρ_0								
	0.318	13.83	35.43	71.98	127.56	206.13	311.97	448.71
Large Unpolarised Basis Set $\Delta\rho_0$								
unpol-pcJ-4	−0.000			−0.09	−0.12	−0.25	−0.36	−0.43
Slater Basis Sets $\Delta\rho_0$								
VB1	0.000	0.00	−0.02	−0.07	−0.30	−0.63	−1.24	−1.54
VB2	0.000	0.00	−0.02	−0.01	−0.14	−0.19	−0.45	−0.69
VB3	0.000	0.00	−0.01	−0.00	−0.09	−0.14	−0.32	−0.49
Mixed Ramp-Gaussian Basis Sets $\Delta\rho_0$								
R-31G	−0.020	−0.30	−0.72	−1.39	−2.35	−3.62	−4.91	−6.04
R-31+G	−0.020	−0.28	−0.77	−1.44	−2.38	−3.63	−4.89	−5.99
R1-31G	−0.020	0.35	0.43	0.55	0.74	0.95	1.32	1.93
General-Purpose All-Gaussian Basis Sets $\Delta\rho_0$								
s 6-31G	−0.020	−0.90	−2.02	−4.22	−7.86	−13.04	−19.68	−27.71
6-311G	−0.031	−0.79	−1.99	−3.86	−6.52	−10.48	−15.52	−21.73
pc-0	−0.077	−2.20	−5.66	−11.47	−20.34	−32.87	−49.74	−71.41
cc-pVDZ	−0.050	−0.63	−1.52	−3.07	−5.42	−8.76	−13.36	−19.19
pc-1	−0.035	−1.15	−3.05	−6.26	−11.21	−18.20	−27.72	−39.86
cc-pVTZ	−0.031	−0.32	−1.01	−2.82	−4.90	−7.85	−11.74	−16.75
pc-2	−0.016	−0.39	−1.23	−2.53	−4.42	−7.28	−10.87	−15.55
cc-pVQZ	−0.020	−0.31	−0.7	−1.40	−2.47	−4.09	−6.07	−8.80
pc-3	−0.007	−0.01	−0.18	−0.46	−0.98	−1.76	−2.79	−4.06
Specialised All-Gaussian Basis Sets $\Delta\rho_0$								
pcJ-0	−0.012			−1.30	−2.25	−3.62	−5.55	−7.90
ccJ-pVDZ	−0.004			−0.33	−0.61	−1.01	−1.54	−2.13
pcJ-1	−0.005			−0.79	−1.38	−2.20	−3.29	−4.57
ccJ-pVTZ	−0.030			−0.40	−0.54	−0.89	−1.32	−1.79
pcJ-2	−0.002			−0.36	−0.63	−1.01	−1.48	−1.97
ccJ-pVQZ	−0.002			−0.17	−0.33	−0.56	−0.81	−1.07
pcJ-3	−0.000			0.03	0.03	0.01	0.06	0.19

2.2. Mixed Ramp-Gaussian Basis Sets. The R-31G and R-31+G basis sets are general-purpose basis sets that derive many of their properties from their 6-31G and 6-31+G parent basis sets, and, in particular, our present implementation of R-31G and 6-31G have similar calculation times.[2]

The R-31G basis set was not optimized specifically for electron densities at the nuclei. In fact, the "R" basis function was found by maximizing its overlap with the original 6-fold contracted core basis function in 6-31G. Therefore, it is only the inherent properties of the ramps that will be responsible for superior values of ρ_0 from R-31G, not a consequence of the method of optimization.

We also consider for the first time the R1-31G basis set which is obtained from the R-31G basis by decontracting the 1s core function. This gives additional core flexibility while retaining the same number of primitives.

2.3. Slater Basis Sets. Calculations involving Slater basis sets are difficult but can be done for very small systems. There are results from previous investigations of atoms[14] for ρ_0 with three Slater basis sets, VB1, VB2, and VB3.[15]

The composition of these Slater basis sets[15] for Li and Be is VB1 [5s,1p], VB2 [6s,2p,1d], and VB3 [7s,3p,2d,1f], while, for B−Ne, the composition of these basis sets[15] is VB1 [5s,3p,1d], VB2 [6s,4p,2d,1f], and VB3 [7s,5p,3d,2f,1g]. All basis functions are uncontracted.

The R-31G and R1-31G basis sets are therefore of size similar to that of the VB1 basis, but do not include polarization functions.

3. RESULTS AND DISCUSSION

3.1. Method. We investigate ρ_0 for a set of molecules at the Hartree−Fock level of theory and compare results from different basis sets to benchmark values: the exact result is known for H; for other atomic systems except B we use numerical HF calculations;[16,17] for B HF/VB3 results are used, while for all molecular systems results from HF/pcJ-4 were taken as the benchmark. We report the error $\Delta\rho_0$ for each calculation compared to the benchmark value.

Calculations for all-Gaussian basis sets were performed using Q-Chem.[18] Basis sets not built into the standard Q-Chem installation were sourced from the online basis set exchange library.[19,20]

All calculations involving mixed ramp-Gaussian basis sets were done using the recently developed program RampItUp,[2] a Fortran90 program which calculates integrals in a mixed ramp-Gaussian basis set and performs the HF SCF calculation.

It is important to note that comparison to experiment is currently not the fairest way to assess these new basis sets because all of calculations are at the Hartree−Fock (HF) level. Thus, we have chosen to compare our results to highly accurate HF calculations, either numerical HF results, where available, or HF/pcJ-4 otherwise.

3.2. Atoms. *3.2.1. R-31G, R-31+G, and R1-31G vs Slater Basis Sets.* Since Slater and ramp basis functions both have nonzero electron−nuclear cusps, we not only quantify the electron density at the nucleus, ρ_0, but also quantify the ratio, G, between ρ_0 and its derivative ρ_0' given by

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Table 2. Errors in the HF Cusp Ratio, $G = -\rho_0'/(Z\rho_0)$[a]

	Li	Be	B	C	N	O	F
Mixed Ramp-Gaussian Basis Sets							
R-31G	−0.086	−0.06	−0.05	−0.04	−0.04	−0.03	−0.03
R-31+G	−0.085	−0.06	−0.05	−0.04	−0.04	−0.03	−0.03
R1-31G	−0.061	−0.05	−0.04	−0.03	−0.03	−0.02	−0.02
All-Slater Basis Sets							
VB1	0.010	0.01	0.00	−0.00	−0.01	−0.01	−0.01
VB2	0.011	0.01	0.01	0.00	0.00	0.00	−0.00
VB3	0.011	0.01	0.01	0.00	0.00	0.00	0.00

[a]Results for Slater basis sets from ref 14. The Kato cusp condition gives the exact benchmark result as $G = 2$.

Table 3. Means and Standard Deviations (SD) of ρ_0 Values for Our Test Sets and of $\Delta\rho_0$[a]

	H		C		N		O	
	mean	SD	mean	SD	mean	SD	mean	SD
Benchmark ρ_0								
pcJ-4	0.463	0.022	126.21	0.50	205.09	0.50	310.56	0.39
Large Unpolarised Basis Set $\Delta\rho_0$								
unpol-pcJ-4	−0.001	0.003	0.03	0.04	0.04	0.03	0.07	0.05
Mixed Ramp-Gaussian Basis Sets $\Delta\rho_0$								
R-31G	−0.045	0.011	−2.13	0.12	−3.14	0.12	−4.16	0.09
R1-31G	−0.045	0.011	0.91	0.04	1.37	0.05	1.99	0.07
General-Purpose All-Gaussian Basis Sets $\Delta\rho_0$								
6-31G	−0.045	0.011	−7.61	0.11	−12.56	0.12	−18.90	0.10
6-311G	−0.038	0.014	−6.30	0.04	−10.09	0.04	−14.91	0.04
pc-0	−0.124	0.110	−20.30	0.14	−32.89	0.10	−49.75	0.12
cc-pVDZ	−0.096	0.006	−5.15	0.10	−8.43	0.11	−12.83	0.08
pc-1	−0.086	0.005	−10.98	0.08	−17.91	0.07	−27.21	0.07
cc-pVTZ	−0.051	0.004	−4.76	0.03	−7.60	0.03	−11.41	0.02
pc-2	−0.035	0.002	−4.31	0.06	−7.10	0.02	−10.56	0.05
cc-pVQZ	−0.031	0.002	−2.33	0.01	−3.82	0.01	−5.66	0.01
pc-3	−0.014	0.001	−0.94	0.03	−1.55	0.01	−2.44	0.01
Specialised All-Gaussian Basis Sets $\Delta\rho_0$								
pcJ-0	−0.008	0.012	−2.44	0.12	−3.87	0.10	−5.85	0.14
ccJ-pVDZ	−0.003	0.004	−0.47	0.01	−0.75	0.01	−1.14	0.01
pcJ-1	−0.002	0.004	−1.24	0.01	−1.96	0.01	−2.91	0.01
ccJ-pVTZ	−0.003	0.001	−0.40	0.00	−0.63	0.00	−0.94	0.00
pcJ-2	−0.001	0.000	−0.50	0.00	−0.76	0.00	−1.10	0.00
ccJ-pVQZ	−0.001	0.000	−0.20	0.00	−0.31	0.00	−0.44	0.00
pcJ-3	0.001	0.000	0.15	0.00	0.26	0.00	0.42	0.00

[a]The test sets contains the following molecules: CH, $^3CH_2$, CH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, CN, HCN, CH_3OH, CO, HCO, CO_2, NH, NH_2, NH_3, N_2, NO, O_2, OH, H_2O, and H_2O_2. All geometries are MP2/6-31G(d).

$$G = -\frac{\rho_0'}{Z\rho_0} \tag{1}$$

where Z is the nuclear charge. It can be shown that for the exact wave function, $G = 2$, the so-called Kato-cusp condition.[21] Note that for an all-Gaussian basis set, $G = 0$.

Tables 1 and 2 show that R-31G performs significantly worse (generally more than a factor of 4) than the three Slater basis sets in predicting the cusp properties ρ_0 and G, despite both ramps and Slater functions having nonzero nuclear-electron cusps. R-31+G performs marginally better than R-31G, but this is a small effect and we will thus not consider the R-31+G basis set further in this work. The inferior performance of the R-31G and R-31+G basis sets compared to the all-Slater basis set is somewhat disappointing, though the mixed ramp-Gaussian basis sets will of course still vastly outperform all-Gaussian basis sets in predicting G.

For ρ_0, the errors of R1-31G are about one-third the size of the R-31G errors and are comparable in quality to VB1 for heavy elements, though significantly worse for light elements. R1-31G overestimates ρ_0, whereas almost all other results underestimate this quantity. This occurs because the variational optimization of the wave function preferences occupation of the R basis function to lower the overall energy of the system.

3.2.2. R-31G and R1-31G vs Common All-Gaussian Basis Sets. By basis set definition, R-31G, R1-31G, and 6-31G results for atomic hydrogen are identical. In Table 1 we observe that for hydrogen ρ_0 results from these basis sets are surprisingly good (almost the same as cc-pVQZ).

For non-hydrogen atoms, Table 1 shows that, in absolute terms, R-31G only underestimates ρ_0 by 2%. This is a better prediction than cc-pVQZ and about half the quality of the pc-3 calculation. This is a very promising result; R-31G is a much smaller basis set than the quadruple-ζ all-Gaussian basis sets, yet produces comparable ρ_0 values. This result is attributed to

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the nonzero cusp on the ramp in R-31G which is inherently able to model ρ_0 more accurately than all-Gaussian basis sets. The R1-31G basis set performs even better, with errors in line with pc-3 results.

To put this result in context, the one-electron Darwin energy for an atom is given by $E_{\text{Darwin}} = \pi\alpha^2 Z\rho_0$ E_h = 0.167294 $Z\rho_0$ mE_h, where α is the fine structure constant. For carbon, this equates to 128 mE_h(336 kJ/mol); 6-31G underestimates this energy by 7.9 mE_h (21 kJ/mol), R-31G by 2.4 mE_h (6.2 kJ/mol), and R1−31G by 0.74 mE_h (2.0 kJ/mol).

3.2.3. R-31G and R1-31G vs Specialized Gaussian Basis Sets. In Table 1, for elements B−F, we observe that R-31G prediction of ρ_0 are of approximately the same quality as those for the larger specialized basis set pcJ-0 (slightly worse for B- N and slightly better for O−F). The R-31G results are worse than for this larger specialized basis set.

Increasing the flexibility of the basis set yields clear dividends; with only one extra basis function and no extra primitives, R1-31G predictions are clearly better than pcJ-0 and pcJ-1 results, and comparable to ccJ-pVDZ, ccJ-pVTZ and pcJ-2 results. R1-31G is a much smaller basis set and calculations already are much faster than with larger all-Gaussian basis sets.

3.3. Molecules. Electron density at the nucleus is a core property and affected relatively little by the molecular environment of that nucleus. Therefore, the overall quality of predictions of ρ_0 by different basis sets in molecules will be similar to the quality of results in atoms. This is quantified by the mean error in the electron density at the nuclei across the test set, $\Delta\rho_0$.

In molecules, it is also interesting to see how well a basis set can describe the changes in electron density at the nucleus as the molecular environment varies. This is quantified by the standard deviation (SD) of $\Delta\rho_0$. If the SD of $\Delta\rho_0$ is small, then ρ_0 for the molecule in the basis set can be corrected by a single number (i.e., the error in ρ_0 is systematic). However, if the SD of $\Delta\rho_0$ is large, then a systematic correction factor cannot be used; this indicates that the description of the electron density near the nuclei is not sufficiently flexible to accurately describe the effect of varying the molecular environment on ρ_0.

3.3.1. Hydrogen Nuclei. Though it is possible in molecules for 6-31G, R-31G, and R1-31G to give different results for ρ_0 through an indirect effect of the modified basis set of nearby heavy atoms, the full set of molecular results shows this difference is negligible in practice. As summarized in Table 3, 6-31G, R-31G, and R1-31G give surprisingly good results for the absolute value of ρ_0 (about equivalent to cc-pVTZ). However, they do not represent the change in ρ_0 for different molecular species as well as cc-pVTZ; this is quantified by the SD of $\Delta\rho_0$ (0.011 for X-31G vs 0.004 for cc-pVTZ).

3.3.2. Non-hydrogen Nuclei. The first two rows in Table 3 illustrate the importance of polarization functions for calculating ρ_0; the large unpolarized basis set *unpol*-pcJ-4 is less able to describe the variation of ρ_0 between different molecules than the fully polarized basis set (quantified by the SD of $\Delta\rho_0$). Therefore, the absence of polarization functions in R-31G will immediately reduce its ability to describe the variation of ρ_0 between different molecules (i.e., increase the SD of $\Delta\rho_0$) compared to fully polarized basis sets.

In Table 3, we observe the R-31G predictions of the absolute value of ρ_0 (quantified by the mean of $\Delta\rho_0$) for C, N, O, and F nuclei in molecules, like in atoms, outperforms predictions of all general-purpose triple-ζ basis sets and cc-pVQZ, while being worse than the pc-3 basis set by about a factor of 2. In absolute terms, R-31G generally underestimates ρ_0 by about 1−2%.

Table 3 shows that R-31G outperforms the slightly larger pcJ-0 basis set by about 20% but is not as good as all the higher quality specialized spin−spin coupling basis sets. It is interesting to consider the carbon atom specifically. In atomic carbon, the pcJ-0 result is better than the R-31G result, whereas for molecular systems, the R-31G result is superior. This is a secondary effect of pcJ-0s inferior description of the valence region on the core electrons.

The errors from R-31G and pcJ-0 between different molecules are not as systematic as those for a larger basis set, such as cc-pVQZ, as quantified by the SD of $\Delta\rho_0$. Therefore, the cc-pVQZ errors are more predictable (and thus easier to correct and more likely to cancel when considering relative differences) than the R-31G or pcJ-0 basis set errors. This can be attributed to the small basis sets' lack of flexibility.

R1-31G increases the core basis set flexibility of R-31G, and this shows significant benefit in reducing the SD of $\Delta\rho_0$ by about two-thirds (e.g., from 0.12 to 0.04 for carbon nuclei). The SD of $\Delta\rho_0$ for R1-31G are close to those of the unpolarised basis set limit benchmark; significant further improvements probably require the introduction of polarization functions. It is encouraging that a simple decontraction of the core function, resulting in only one additional basis function and no additional primitives (and thus no extra integrals), yields a basis with most of the flexibility of the unpolarized benchmark basis. By way of illustration, the primitive and contracted basis function composition of R1-31G is (6s4p) → [4s2p], whereas for the unpolarized pcJ-4 basis it is (19s12p) → [11s9p]. Furthermore, the SD of $\Delta\rho_0$ for R1-31G is roughly in line with pc-2 and three times better than pcJ-0 (0.04 vs 0.06 vs 0.12 for carbon nuclei).

The SD of $\Delta\rho_0$ will equate to an error in the properties between the atom and molecule. To provide context, we can convert this SD to an average error in the Darwin energy per carbon atom in molecules compared to the Darwin energy of the carbon atom. For nitrogen, 6-31G and R-31G give errors of 0.12 mE_h (0.32 kJ/mol) and R1-31G gives errors of 0.05 mE_h (0.13 kJ/mol), while cc-pVQZ errors are 0.01 mE_h (0.03 kJ/mol). It is clear, then, why we can ignore this error in the Darwin energy in calculating atomization energies for light elements, while it will be non-negligible for very high precision calculations or for heavier atoms.

Based on these results, we recommend R1-31G as a cheap, high-accuracy method of calculating the Fermi contact term in indirect spin−spin coupling constants and for calculating Darwin relativistic corrections. Addition of polarization functions is expected to improve the performance of this basis set.

4. CONCLUSIONS

For non-hydrogen nuclei, despite its small size, the R-31G basis set produces very good results for HF electron densities at the nucleus because the ramp has a nonzero derivative at the origin. The small, general-purpose mixed ramp-Gaussian basis set R-31G outperforms Dunning, Jensen, and Pople general-purpose all-Gaussian basis sets of up to triple-ζ quality as well as cc-pVQZ. R-31G has about equivalent performance to pcJ-0 (a small specialized basis set). However, it is worse than pc-3 and all specialized basis sets of double-ζ quality and higher. Decontracting the ramp and Gaussian primitive in the core basis function to produce the R1-31G gives even better performance, reducing absolute errors ($\Delta\rho_0$) by about two-thirds.

R-31G has very little core flexibility and is thus significantly worse than cc-pVQZ at reproducing the changes in ρ_0 in different molecules (evidenced by the larger standard deviation of the ρ_0 errors in molecules). The more flexible R1-31G enhances the ability to describe variations in ρ_0 substantially, leading to lower SD of $\Delta\rho_0$; about equivalent to pc-2. To significantly improve the performance of mixed ramp-Gaussian basis sets, polarization basis functions need to be introduced to the basis set; this is an important future area of development and a key motivator for extending the capacities of the RampItUp program to higher angular momentum Gaussians.

These results show an application (electron density at the nucleus) where the superior cusp and inner-electron behavior of the mixed ramp-Gaussian basis sets gives significant advantage over all-Gaussian basis sets. These results provide additional justification for the development of a fully integrated ramp-Gaussian integral package in common quantum chemistry programs. The development of specialized and larger mixed ramp-Gaussian basis sets in the future will be extremely beneficial in further exploring the ability of ramp basis functions to model the electron density at the nuclei and other core-dependent properties.

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Notes

The authors declare no competing financial interest.

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