Compact and flexible basis functions for quantum Monte Carlo calculations

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Molecular calculations in quantum Monte Carlo frequently employ a mixed basis consisting of contracted and primitive Gaussian functions. While standard basis sets of varying size and accuracy are available in the literature, we demonstrate that reoptimizing the primitive function exponents within quantum Monte Carlo yields more compact basis sets for a given accuracy. Particularly large gains are achieved for highly excited states. For calculations using nondiverging pseudopotentials, we introduce Gauss–Slater basis functions that behave as Gaussians at short distances and Slaters at long distances. These basis functions further improve the energy and fluctuations of the local energy for a given basis size. Gains achieved by exponent optimization and Gauss–Slater basis use are exemplified by calculations for the ground state of carbon, the lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries, carbon dimer, and naphthalene. Basis-size reduction enables quantum Monte Carlo treatment of larger molecules at high accuracy. © *2010 American Institute of Physics*. [doi:10.1063/1.3342062]

I. INTRODUCTION

In traditional quantum chemistry (QC) calculations, molecular orbitals are often expanded in a combination of contracted Gaussian basis functions and primitive Gaussian basis functions. For each occupied orbital, a contracted function is constructed to reproduce the corresponding atomic orbital from an effectively single-electron theory such as Hartree–Fock (HF),[1,2] or the natural orbital from a post-HF method.[3,4]

While a single primitive Gaussian has an incorrect long-range asymptotic behavior, a contracted basis function can reproduce the correct asymptotics over a reasonable range. However, even contracted functions are unable to produce the correct electron-nucleus cusps[5] since they have zero gradient at the origin. Despite these shortcomings, Gaussians are used in QC calculations because they permit analytical evaluation of the two-electron integrals.[6]

In contrast to traditional QC methods, quantum Monte Carlo (QMC) calculations[7] enjoy greater wave function flexibility by using Monte Carlo integration to evaluate matrix elements. In particular, bases need not be restricted to Gaussians. For calculations employing a potential that diverges at the nucleus, Slater basis functions can exactly reproduce the correct electron-nucleus cusp and long-range asymptotic behavior of the orbitals. In fact, for all-electron QMC calculations, highly accurate results have been obtained by employing compact basis sets consisting of Slater functions with optimized exponents.[8,9]

Conversely, the basis sets used for nondivergent pseudopotential calculations in QMC have deviated little from typical QC basis sets. For these pseudopotentials, orbitals have no electron-nucleus cusp. In this case, Gaussian basis functions are more appropriate than Slater functions at small electron-nuclear distances but still have incorrect long-range asymptotics.

Contracted and primitive Gaussian functions are frequently splined on a radial grid for QMC. Splining contracted Gaussians presents a definite computational advantage since evaluating polynomials is much cheaper than evaluating a linear combination of Gaussians. In contrast, splining primitive Gaussians provides minimal benefit at best.

We propose two ideas for improving basis sets for pseudopotential calculations in QMC. First, primitive basis function exponents are optimized for each system. This provides greater accuracy with a compact basis for a wide range of chemical environments and excitation levels. To facilitate optimization, the primitive basis functions remain analytic while the contracted functions are splined.

Second, we propose a novel form of primitive basis function appropriate for calculations involving nondiverging pseudopotentials. These primitives, which we call Gauss–Slater (GS) functions, have the short-range behavior of a Gaussian function and the long-range behavior of a Slater function. The utility of our improvements is demonstrated by calculations for the ground state of carbon, the lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries, carbon dimer, and naphthalene.

This paper is organized as follows. In Sec. II, the form and properties of GS functions are introduced. In Sec. III, results of our calculations are discussed. In Sec. IV, concluding remarks are provided. In Appendices A–D, technical details are discussed.

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II. GS BASIS FUNCTIONS

We define GS functions as

$$\varphi^{\zeta}_{nlm}(r,\theta,\phi) = N^{\zeta}_{n} r^{n-1} e^{-[(\zeta r)^2/(1+\zeta r)]} Z^{m}_{l}(\theta,\phi), \tag{1}$$

where r,θ,ϕ are the standard spherical coordinates, n is the principal quantum number, l is the azimuthal quantum number, m is the magnetic quantum number, N^{ζ}_{n} is the normalization factor, and $Z^{m}_{l}(\theta,\phi)$ is a real spherical harmonic.

Notice that for $r \ll 1$ the GS behaves like a Gaussian:

$$\varphi^{\zeta}_{nlm}(r,\theta,\phi) \cong N^{\zeta}_{n} r^{n-1} e^{-(\zeta r)^2} Z^{m}_{l}(\theta,\phi), \tag{2}$$

and for $r \gg 1$ the GS behaves like a Slater:

$$\varphi^{\zeta}_{nlm}(r,\theta,\phi) \cong N^{\zeta}_{n} r^{n-1} e^{-\zeta r} Z^{m}_{l}(\theta,\phi). \tag{3}$$

The GS drift velocity and local energy are well behaved at long distances, while for Gaussians these quantities diverge.

Unlike Gaussians and Slaters, normalization of GSs has no closed form expression. Nevertheless, normalizing an arbitrary GS is trivial with the following scaling relation (see Appendix A) between N^{ζ}_{n} and N^{1}_{n},

$$N^{\zeta}_{n} = \zeta^{n+1/2} N^{1}_{n}. \tag{4}$$

Since GSs are not analytically integrable, the exponential part must be expanded in Gaussians for use in QC programs that employ analytic integrals for evaluating the matrix elements. This expansion is

$$N^{\zeta}_{n} e^{-[(\zeta r)^2/(1+\zeta r)]} = \sum_{i} c^{\zeta}_{i} \sqrt{\frac{2(2\alpha^{\zeta}_{i})^{n+(1/2)}}{\Gamma\left(n+\frac{1}{2}\right)}} e^{-\alpha^{\zeta}_{i} r^2}, \tag{5}$$

where c^{ζ}_{i} is the ith expansion coefficient, and α^{ζ}_{i} is the ith Gaussian exponent. Additionally, the following scaling relations (see Appendix A) hold for the expansion coefficients and Gaussian exponents:

$$\alpha^{\zeta}_{i} = \zeta^2 \alpha^{1}_{i}, \tag{6}$$

$$c^{\zeta}_{i} = c^{1}_{i}. \tag{7}$$

Once the Gaussian expansions are found for unit exponents, expansions of arbitrary GSs follow immediately from the scaling relations.

III. RESULTS

For all applications discussed in this paper, variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC)[10] calculations are performed with the CHAMP QMC code[11] and employ the pseudopotentials and accompanying basis sets of Burkatzki, Filippi, and Dolg (BFD).[12] We choose these pseudopotentials and basis functions since they were constructed for use in QMC and have proved to be quite accurate.

The wave function is of the standard Slater–Jastrow form. All wave function parameters including Jastrow parameters, configuration state function (CSF) coefficients (where applicable), orbital coefficients, and primitive exponents (where applicable) are optimized via the linear method.[13–15] Optimization is performed for a linear combination of the energy and variance of the local energy with weights 0.95 and 0.05, respectively. Optimizing just the energy yields slightly lower energies and somewhat higher variances.

For each system considered, calculations are performed with three different basis sets: (1) the BFD basis, (2) fixed contracted functions and analytical Gaussian primitives with optimized exponents, and (3) fixed contracted functions and analytical GS primitives with optimized exponents. We refer to these basis sets as BFD, G, and GS, respectively.

These three cases allow us to evaluate the improvements our two methods provide to the current basis sets used in QMC. First, if both the G and GS basis sets significantly outperform the BFD basis, then the utility of reoptimizing the basis exponents within QMC will be established. Second, the utility of the GS basis depends on its performance relative to the G basis.

A. Ground state carbon atom

For the carbon atom ground state, ^3P, we consider a complete active space (CAS) wave function with an active space generated by distributing the four valence electrons among the thirteen orbitals of the $n=2$ and $n=3$ shells. Denoted by CAS(4,13), this wave function consists of 83 CSFs comprised of 422 determinants.

In general, a single Slater determinant will not be a CSF when a certain number of electrons have been excited relative to the ground-state HF Slater determinant. However, a CSF can be produced from an arbitrary Slater determinant by applying projection operators for angular momentum $\hat{L}$ and spin $\hat{S}$. Since states with the same L and S but different L_z and S_z are degenerate, we are free to choose convenient L_z and S_z states. We choose $L_z=0$ to make the wave functions real to within a position independent phase, and we choose $S_z=S$ to yield the minimum number of determinants in the CSF. Since the carbon ground state has $L=1$, $S=1$, the projection operators are of the form

$$\hat{P}_{L} = \prod_{L' \neq 1} [\hat{L} - L'(L'+1)], \tag{8}$$

$$\hat{P}_{S} = \prod_{S' \neq 1} [\hat{S} - S'(S'+1)], \tag{9}$$

where the product over all possible angular momentum and spin values omits the desired $L=1$ and $S=1$ values.

Carbon atom VMC results for each basis set are shown in Table I. Included for comparison, coupled cluster calculations with single and double excitations and perturbative triple excitations [CCSD(T)] values for the BFD basis[12] exhibit much larger dependence on basis size than QMC results.

Both the G and GS basis sets outperform the BFD basis set. The $2z$ G basis exhibits a modest gain of 0.3 mH in energy compared to the corresponding BFD basis. The $2z$ GS basis exhibits larger gains of 1 mH in energy and 28 mH in σ, the root-mean-square (RMS) fluctuations of the local energy. The $3z$ GS basis yields identical results, within statistical error, to the $5z$ BFD basis.

TABLE I. VMC energy and RMS fluctuations of the local energy, σ, in Hartrees for CAS(4,13) ground state of carbon using BFD, G, and GS basis functions. Statistical errors on the last digit are shown in parentheses. For each n, the nz basis consists of n S functions, n P functions, and $n-1$ D functions. CCSD(T) values for the BFD basis are included for comparison (Ref. 11).

Type	Size	Energy (H)	σ (H)
BFD	$2z$	−5.431 61(3)	0.1395(6)
	$3z$	−5.433 06(2)	0.099(3)
	$4z$	−5.433 32(2)	0.0904(2)
	$5z$	−5.433 41(2)	0.0905(4)
G	$2z$	−5.431 96(3)	0.138(2)
	$3z$	−5.433 24(2)	0.0989(5)
GS	$2z$	−5.432 64(2)	0.1114(4)
	$3z$	−5.433 44(2)	0.0898(2)
CCSD(T)	$2z$	−5.409 230	N/A
	$3z$	−5.427 351	N/A
	$4z$	−5.431 486	N/A
	$5z$	−5.432 494	N/A

Carbon atom DMC results for each basis set are shown in Table II. These calculations were performed with a time step of τ=0.01 H^{-1} which leads to negligible time step error for these high quality wave functions. DMC depends less on basis size than VMC, as is immediately apparent from the data. Nevertheless, both the G and GS basis sets outperform the BFD basis set. The $3z$ GS basis yields identical results, within statistical error, to the $5z$ BFD basis, and an energy 0.1 mH lower than the $3z$ BFD basis.

Both VMC and DMC results indicate that reoptimizing primitive basis function exponents provides improvements which can be significant for the GS basis. In large systems, the ability to use a $3z$ basis in place of a $4z$ or $5z$ basis determines whether a calculation can be performed.

B. Excited states of carbon

We consider the lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries. These states have configurations $2s^12p^3$, $2s^22p^13s^1$, $2s^22p^13d^1$, and $2s^22p^13d^1$, respectively. The $^3P^o$, $^1D^o$, and $^3F^o$ states have much higher energy than the ground state and $^5S^o$ excited state.

TABLE II. DMC energy in Hartrees for CAS(4,13) ground state of carbon using BFD, G, and GS basis functions. Statistical errors on the last digit are shown in parentheses. For each n, the nz basis consists of n S functions, n P functions, and $n-1$ D functions. Calculations were performed with a time step of τ=0.01 H^{-1} which leads to a negligible time step error for these high quality wavefunctions.

Type	Size	Energy (H)
BFD	$2z$	−5.433 14(2)
	$3z$	−5.433 95(2)
	$4z$	−5.434 04(1)
	$5z$	−5.434 07(1)
G	$2z$	−5.433 42(2)
	$3z$	−5.434 00(2)
GS	$2z$	−5.433 56(2)
	$3z$	−5.434 07(1)

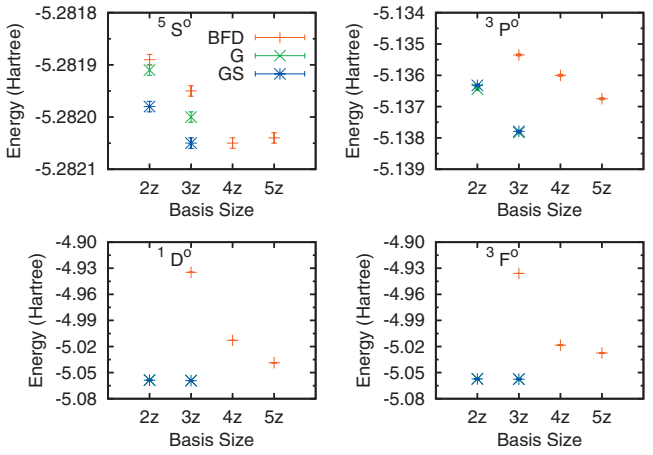

FIG. 1. VMC energies in Hartrees for lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries. For each n, the nz basis consists of n S functions, n P functions, and $n-1$ D functions (where applicable). For $^3P^o$, $^1D^o$, and $^3F^o$ calculations, the BFD basis is augmented with diffuse functions of the aug-cc-pVnZ basis sets (Refs. 4, 16, and 17). For G and GS basis sets, only $2z$ and $3z$ calculations were performed. In many cases, results for G and GS bases are indistinguishable on this scale.

The dominant CSF for each of the three highly excited states occupies orbitals that are unoccupied in the HF ground state. For fair comparison, the BFD basis therefore must be augmented. The diffuse functions of the aug-cc-pVnZ basis sets[4,16,17] are used for this purpose. The BFD nz basis then becomes an $(n+1)z$ basis.

Obtained by application of the projection operators discussed in Sec. III A, the dominant CSF for each of the four excited states has one, one, four, and three Slater determinants, respectively.

VMC results for energies and σ of each system are shown in Figs. 1 and 2. In all cases, the reoptimized exponents provide significant gains in both energy and σ. Results for the three higher-lying states demonstrate that reoptimized exponents are essential for describing states containing orbitals unoccupied in the HF ground state. For these systems, $2z$ results using the G and GS basis sets are substantially better than $5z$ results for the augmented BFD basis set. In the most extreme case of $^3F^o$, the $2z$ GS basis results in 30 mH lower energy and 110 mH lower σ than the $5z$ BFD basis.

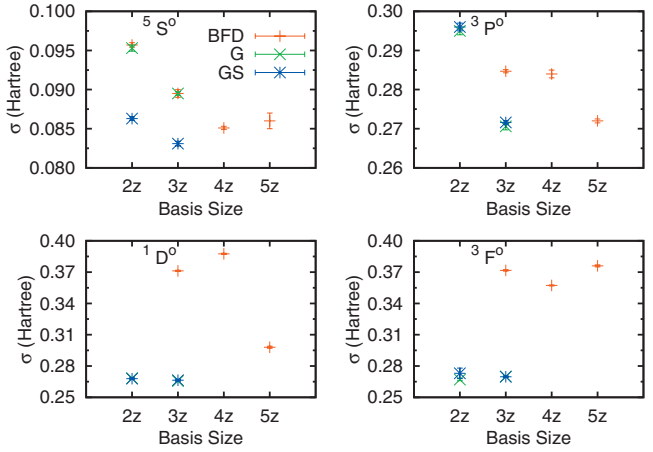

FIG. 2. RMS fluctuations of VMC local energies. See Fig. 1 for notation and details.

TABLE III. VMC energy and σ in Hartrees for single determinant carbon dimer ground state. Statistical errors on the last digit are shown in parentheses. For each n, the nz basis consists of n S functions, n P functions, and $n-1$ D functions, $n-2$ F functions, and $n-3$ G functions.

Type	Size	Energy (H)	σ (H)
BFD	$2z$	−11.026 44(4)	0.4343(9)
	$3z$	−11.030 03(4)	0.4172(4)
	$4z$	−11.030 94(4)	0.4127(7)
	$5z$	−11.030 95(4)	0.4113(6)
G	$2z$	−11.027 07(4)	0.4288(7)
	$3z$	−11.030 30(4)	0.4183(6)
GS	$2z$	−11.029 68(4)	0.4191(6)
	$3z$	−11.030 65(4)	0.4109(6)

The importance of the reoptimized exponents is evident for the excited states of carbon. However, benefits of the GS basis relative to the G basis are never more than several tenths of a mH. On the scale of the plots in Figs. 1 and 2, many G and GS basis results coincide.

C. Carbon dimer

Single determinant calculations were performed for the carbon dimer with initial wave functions generated from the QC code GAMESS.[18] VMC results for each basis set are shown in Table III. The G and GS basis sets outperform the BFD basis set. In particular, the $2z$ G basis attains a 0.6 mH lower energy than the corresponding BFD basis, and the GS basis yields a 3.2 mH lower energy than the BFD basis. The $3z$ GS basis yields an energy within 0.3 mH of and a σ identical to the $5z$ BFD basis results.

DMC results for each basis set are shown in Table IV. These calculations were performed with a time step of $\tau=0.005$ H^{-1} which leads to negligible time step error. The $2z$ G and GS basis sets significantly outperform the corresponding BFD basis set. The $2z$ GS basis yields a result that is essentially converged with respect to basis size. Both VMC and DMC results indicate that reoptimizing primitive basis function exponents provides improvements which can be significant for the GS basis.

TABLE IV. DMC energy in Hartrees for ground state of carbon dimer using BFD, G, and GS basis functions. Statistical errors on the last digit are shown in parentheses. For each n, the nz basis consists of n S functions, n P functions, $n-1$ D functions, $n-2$ F functions, and $n-3$ G functions. Calculations were performed with a time step of $\tau=0.005$ H^{-1} which leads to a negligible time step error.

Type	Size	Energy (H)
BFD	$2z$	−11.055 61(3)
	$3z$	−11.057 19(4)
	$4z$	−11.057 28(4)
	$5z$	−11.057 23(4)
G	$2z$	−11.056 32(3)
	$3z$	−11.057 17(3)
GS	$2z$	−11.057 02(4)
	$3z$	−11.057 19(3)

TABLE V. VMC energy and σ, and DMC energy in Hartrees for single determinant ground state naphthalene, $C_{10}H_8$. Statistical errors on the last digit are shown in parentheses. DMC calculations were performed with a time step of $\tau=0.01$ H^{-1}. For carbon, the $2z$ basis includes 2 S function, 2 P function, 1 D function. For hydrogen, the $2z$ basis includes 2 S functions and 1 P function.

Type	Size	VMC energy (H)	VMC σ (H)	DMC energy (H)
BFD	$2z$	−61.5193(5)	0.980(1)	−61.6479(5)
G	$2z$	−61.5273(4)	0.938(1)	−61.6518(5)
GS	$2z$	−61.5438(4)	0.927(2)	−61.6634(5)

D. Naphthalene

Single determinant calculations were performed for naphthalene, $C_{10}H_8$, with initial wave functions generated from the QC code GAMESS.[18] Calculations were performed only for the $2z$ basis. The intention of this section is not to produce an energy converged with respect to basis size, but to demonstrate that the utility of reoptimizing primitive basis functions, and GS primitives in particular, extends to large systems. VMC and DMC results for each basis set are shown in Table V. The DMC calculations were performed with a time step of $\tau=0.01$ H^{-1}.

At both the VMC and DMC level, wave function quality increases by reoptimizing the primitive Gaussian exponents. The GS basis provides further improvement. In particular, even at the DMC level, the $2z$ G basis attains a 4 mH lower energy than the corresponding BFD basis, and the GS basis yields a 15 mH lower energy than the BFD basis. This is significant since DMC is less sensitive to basis set choice than VMC.

IV. CONCLUSION

The QMC methods have the advantage over standard QC methods of rapid convergence with increasing basis size. Basis-size dependence for pseudopotential calculations in QMC is further reduced by two basis set improvements introduced in this work. Calculations for the ground state of carbon, the lowest lying $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ excited states of carbon, carbon dimer, and naphthalene demonstrate the utility of our contribution.

First, we reoptimized the primitive basis function exponents for each system because the exponents of standard QC and QMC basis sets, such as the BFD basis, represent a compromise. These standard exponents are designed to yield good energies for some range of chemical environments and excitation levels, but they cannot be optimal for all systems. We have shown that reoptimizing primitive basis function exponents for each system yields significant improvements in the energy and fluctuations of the local energy, σ. The most pronounced benefits were observed in higher-lying excited state calculations. In the most extreme case of $^3F^o$ at the variational Monte Carlo (VMC) level, the $2z$ mixed basis was 30 mH lower in energy and 110 mH lower in σ than the $5z$ numerical basis. Although not discussed in this paper, we have found that reoptimization of standard Slater basis exponents used in all-electron calculations also provides considerable improvements in energy and σ.

TABLE VI. Normalization factors for Gauss–Slater basis functions with unit exponent and principal quantum number n.

n	N_n^1
1	1.126 467 421
2	0.576 609 950
3	0.196 581 141
4	0.050 275 655
5	0.010 280 772

Second, we introduced GS basis functions for nondivergent pseudopotential calculations. GS functions behave like Gaussians at short distances and Slaters at long distances. In all systems considered, results obtained using a mixed basis comprised of contracted and primitive basis functions improved when optimized Gaussian primitives were replaced by optimized GS primitives. Importantly, for carbon dimer at the DMC level the $2z$ GS total energies are nearly converged with respect to basis size.

A $3z$ mixed basis with optimized GSs for carbon atom or carbon dimer produces results comparable to the $5z$ BFD basis. Since the number of orbital coefficients to be optimized scales quadratically with basis size, the use of a more compact basis allows larger problems to be attacked in QMC.

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APPENDIX A: SCALING RELATIONS

To derive the scaling relation between N_n^ζ and N_n^1, consider

$$1 = (N_n^\zeta)^2 \int_0^\infty dr\ r^2 r^{2(n-1)} e^{-2[(\zeta r)^2/(1+\zeta r)]}, \tag{A1}$$

$$= \frac{1}{\zeta^{2n+1}} (N_n^\zeta)^2 \int_0^\infty du\ u^{2n} e^{-2[u^2/(1+u)]}, \tag{A2}$$

$$= \frac{1}{\zeta^{2n+1}} \left(\frac{N_n^\zeta}{N_n^1} \right)^2. \tag{A3}$$

Hence, the scaling relation for the normalization factor is

$$N_n^\zeta = \zeta^{n+1/2} N_n^1. \tag{A4}$$

The values of N_n^1 are given in Table VI.

To derive the scaling relations for the parameters α_i^ζ and c_i^ζ in the Gaussian expansion of the GS functions, suppose the best-fit expansion for $\zeta=1$ is

$$N_n^1 e^{-r^2/(1+r)} = \sum_i c_i^1 \sqrt{\frac{2(2\alpha_i^1)^{n+(1/2)}}{\Gamma\left(n+\frac{1}{2}\right)}} e^{-\alpha_i^1 r^2}. \tag{A5}$$

Using Eq. (A4) and performing the substitution $r \to \zeta r$ results in

$$N_n^\zeta e^{-[(\zeta r)^2/(1+\zeta r)]} = \zeta^{n+1/2} \sum_i c_i^1 \sqrt{\frac{2(2\alpha_i^1)^{n+(1/2)}}{\Gamma\left(n+\frac{1}{2}\right)}} e^{-\alpha_i^1 \zeta^2 r^2}, \tag{A6}$$

$$= \sum_i c_i^1 \sqrt{\frac{2(2\alpha_i^1 \zeta^2)^{n+(1/2)}}{\Gamma\left(n+\frac{1}{2}\right)}} e^{-\alpha_i^1 \zeta^2 r^2}, \tag{A7}$$

$$= \sum_i c_i^\zeta \sqrt{\frac{2(2\alpha_i^\zeta)^{n+(1/2)}}{\Gamma\left(n+\frac{1}{2}\right)}} e^{-\alpha_i^\zeta r^2}, \tag{A8}$$

where

$$\alpha_i^\zeta = \zeta^2 \alpha_i^1, \tag{A9}$$

$$c_i^\zeta = c_i^1. \tag{A10}$$

APPENDIX B: SPATIAL DERIVATIVES

A general un-normalized radial basis function has the form

$$R_n^\zeta(r) = r^{n-1} e^{g^\zeta(r)}, \tag{B1}$$

where $g^\zeta(r)$ is an arbitrary function. The gradient is

$$\nabla R_n^\zeta(r) = \frac{\partial R_n^\zeta(r)}{\partial r} \hat{\boldsymbol{r}}, \tag{B2}$$

where

$$\frac{\partial R_n^\zeta(r)}{\partial r} = R_n^\zeta(r) \left[\frac{(n-1)}{r} + \frac{\partial g^\zeta(r)}{\partial r} \right]. \tag{B3}$$

The Laplacian is

$$\nabla^2 R_n^\zeta(r) = \frac{\partial^2 R_n^\zeta(r)}{\partial r^2} + \frac{2}{r} \frac{\partial R_n^\zeta(r)}{\partial r}, \tag{B4}$$

where

$$\frac{\partial^2 R_n^\zeta(r)}{\partial r^2} = R_n^\zeta(r) \left[\frac{\partial^2 g^\zeta(r)}{\partial r^2} - \frac{(n-1)}{r^2} \right] + \frac{1}{R_n^\zeta(r)} \left(\frac{\partial R_n^\zeta(r)}{\partial r} \right)^2. \tag{B5}$$

For GS functions,

$$g^\zeta(r) = -\frac{(\zeta r)^2}{1+\zeta r} \tag{B6}$$

$$\frac{\partial g^\zeta(r)}{\partial r} = -\frac{r\zeta^2(2+\zeta r)}{(1+\zeta r)^2} \tag{B7}$$

$$\frac{\partial^2 g^\zeta(r)}{\partial r^2} = -\frac{2\zeta^2}{(1+\zeta r)^3}. \tag{B8}$$

For Gaussian functions,

$$g^{\zeta}(r) = -\zeta r^2 \tag{B9}$$

$$\frac{\partial g^{\zeta}(r)}{\partial r} = -2\zeta r \tag{B10}$$

$$\frac{\partial^2 g^{\zeta}(r)}{\partial r^2} = -2\zeta. \tag{B11}$$

For Slater functions,

$$g^{\zeta}(r) = -\zeta r \tag{B12}$$

$$\frac{\partial g^{\zeta}(r)}{\partial r} = -\zeta \tag{B13}$$

$$\frac{\partial^2 g^{\zeta}(r)}{\partial r^2} = 0. \tag{B14}$$

APPENDIX C: PARAMETER DERIVATIVES

Wave function optimization via the linear method requires both the derivatives of the wave function with respect to the exponent parameters ζ, and the Hamiltonian acting on those derivatives. From Eq. (A4), the derivative of the normalization with respect to the exponent is

$$\frac{\partial N_n^{\zeta}}{\partial \zeta} = \frac{(n+1/2)}{\zeta} N_n^{\zeta}. \tag{C1}$$

Now consider a general un-normalized radial basis function of the form

$$R_n^{\zeta}(r) = r^{n-1} e^{g^{\zeta}(r)}, \tag{C2}$$

where $g^{\zeta}(r)$ is an arbitrary function. The derivative of the radial part of the wave function with respect to the exponent is

$$\frac{\partial R_n^{\zeta}(r)}{\partial \zeta} = f^{\zeta}(r) R_n^{\zeta}(r), \tag{C3}$$

where

$$f^{\zeta}(r) \equiv \frac{\partial g^{\zeta}(r)}{\partial \zeta}. \tag{C4}$$

The gradient is

$$\nabla\left[\frac{\partial R_n^{\zeta}(r)}{\partial \zeta}\right] = \frac{\partial f^{\zeta}(r)}{\partial r} R_n^{\zeta}(r)\hat{\mathbf{r}} + f^{\zeta}(r)[\nabla R_n^{\zeta}(r)]. \tag{C5}$$

The Laplacian is

$$\nabla^2\left[\frac{\partial R_n^{\zeta}(r)}{\partial \zeta}\right] = \frac{2}{r}\frac{\partial f^{\zeta}(r)}{\partial r}\left[R_n^{\zeta}(r) + r\frac{\partial R_n^{\zeta}(r)}{\partial r}\right] + \frac{\partial^2 f^{\zeta}(r)}{\partial r^2} R_n^{\zeta}(r) + f^{\zeta}(r)\nabla^2 R_n^{\zeta}(r). \tag{C6}$$

For GS functions,

$$f^{\zeta}(r) = -\frac{\zeta r^2(2+\zeta r)}{(1+\zeta r)^2} \tag{C7}$$

$$\frac{\partial f^{\zeta}(r)}{\partial r} = -\frac{\zeta r[4+\zeta r(3+\zeta r)]}{(1+\zeta r)^3} \tag{C8}$$

$$\frac{\partial^2 f^{\zeta}(r)}{\partial r^2} = \frac{2\zeta(\zeta r-2)}{(1+\zeta r)^4}. \tag{C9}$$

For Gaussian functions,

$$f^{\zeta}(r) = -r^2 \tag{C10}$$

TABLE VII. Basis exponents for CAS(4,13) ground state of carbon and ground state of carbon dimer using G and GS basis functions. For each n, the nz basis includes $n-1$ S primitives, $n-1$ P primitives, $n-1$ D primitives, and $n-2$ F primitives (where applicable).

Type	Size	L	C exp.	C_2 exp.
G	$2z$	S	0.087	0.145
		P	0.129	0.196
		D	0.470	0.679
	$3z$	S	0.102	0.127
		S	0.676	0.998
		P	0.104	0.121
		P	0.270	0.423
		D	0.314	0.386
		D	0.982	1.099
		F	N/A	0.783
GS	$2z$	S	0.586	0.853
		P	0.984	1.162
		D	1.810	3.774
	$3z$	S	1.000	1.127
		S	1.258	1.570
		P	1.059	0.703
		P	1.750	1.416
		D	1.132	2.225
		D	1.981	3.228
		F	N/A	2.588

TABLE VIII. Basis exponents for the lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries. For each n, the nz basis includes $n-1$ S primitives, $n-1$ P primitives, and $n-1$ D primitives (where applicable)

Type	Size	L	$^5S^o$ exp.	$^3P^o$ exp.	$^1D^o$ exp.	$^3F^o$ exp.
G	$2z$	S	0.110	0.006	0.087	0.112
		P	0.150	0.157	0.109	0.766
		D	N/A	N/A	0.006	0.006
	$3z$	S	0.356	0.010	0.094	0.096
		S	2.145	0.284	0.496	0.689
		P	0.809	4.868	0.079	0.117
		P	2.262	6.707	0.854	0.524
		D	N/A	N/A	0.007	0.007
		D	N/A	N/A	0.407	0.822
GS	$2z$	S	1.960	0.059	0.756	0.570
		P	1.860	3.002	0.763	0.588
		D	N/A	N/A	0.351	0.293
	$3z$	S	1.148	0.371	0.160	0.894
		S	1.451	0.376	0.931	2.045
		P	1.137	0.691	0.043	1.326
		P	1.325	2.087	0.444	3.016
		D	N/A	N/A	0.238	0.295
		D	N/A	N/A	0.953	1.545

TABLE IX. Basis exponents for ground state naphthalene, $C_{10}H_8$, using G and GS basis functions. For carbon, the $2z$ basis includes 1 S primitive, 1 P primitive, 1 D primitive. For hydrogen, the $2z$ basis includes 1 S primitive.

Type	Size	L	$C_{10}H_8$ C exp.	$C_{10}H_8$ H exp.
G	$2z$	S	0.139	0.099
		P	0.191	N/A
		D	0.754	N/A
GS	$2z$	S	0.875	0.798
		P	1.118	N/A
		D	2.109	N/A

$$\frac{\partial f^{\zeta}(r)}{\partial r} = -2r \tag{C11}$$

$$\frac{\partial^2 f^{\zeta}(r)}{\partial r^2} = -2. \tag{C12}$$

For Slater functions,

$$f^{\zeta}(r) = -r \tag{C13}$$

$$\frac{\partial f^{\zeta}(r)}{\partial r} = -1 \tag{C14}$$

$$\frac{\partial^2 f^{\zeta}(r)}{\partial r^2} = 0. \tag{C15}$$

APPENDIX D: EXPONENTS

To promote use of this basis, exponents for each system studied are given in this appendix. Only exponents of the primitives are given, as the contracted functions are presented elsewhere.[12] Exponents for the ground state of carbon using CAS(4,13) CSFs, and, the ground state of carbon dimer using a single CSF are shown in Table VII. Exponents for the lowest lying excited states of carbon with $^5S^o$, $^3P^o$, $^1D^o$, and $^3F^o$ symmetries are shown in Table VIII. Exponents for the ground state of naphthalene are shown in Table IX. In naphthalene, since atoms of the same atomic species are located at inequivalent geometrical locations, one could independently optimize the exponents for each inequivalent atom, but we have not done so because we expect the resulting gain to be small.

We have found that the carbon S and P exponents change relatively little from one molecule to another (though they do differ more for the atom) while there is considerable leeway in the D exponents (they change considerably even from one optimization to another for a given molecule). This is because the energy and σ are not as sensitive to the D basis functions as they do not appear in the ground-state determinant of the carbon atom. Hence it is possible to find an approximately optimal set of exponents for the atoms in a large molecule, by optimizing them for a small molecule with the same atoms.

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