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Basis functions for electronic structure calculations on spheres

Peter M. W. Gill,^{a)} Pierre-François Loos,^{b)} and Davids Agboola Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

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We introduce a new basis function (the spherical Gaussian) for electronic structure calculations on spheres of any dimension *D*. We find general expressions for the one- and two-electron integrals and propose an efficient computational algorithm incorporating the Cauchy-Schwarz bound. Using numerical calculations for the D = 2 case, we show that spherical Gaussians are more efficient than spherical harmonics when the electrons are strongly localized. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4903984]

I. INTRODUCTION

Consider electronic structure calculations in which the electrons move in *D*-dimensional Cartesian space \mathbb{R}^{D} . If the molecular orbitals (MOs) are delocalized throughout space, the plane waves¹

$$q_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}), \qquad \mathbf{r} \in \mathbb{R}^{D}$$
(1)

form a good basis, because the product of two is a third

$$q_{\mathbf{k}_1}(\mathbf{r})q_{\mathbf{k}_2}(\mathbf{r}) = q_{\mathbf{k}_1 + \mathbf{k}_2}(\mathbf{r}).$$
(2)

If the MOs are localized, the Cartesian Gaussians²

$$g_{\alpha}^{\mathbf{A}}(\mathbf{r}) = \exp(-\alpha |\mathbf{r} - \mathbf{A}|^2), \qquad \mathbf{r} \in \mathbb{R}^D$$
 (3)

are effective, again because the product of two is a third

$$g^{\mathbf{A}}_{\alpha}(\mathbf{r})g^{\mathbf{B}}_{\beta}(\mathbf{r}) = Kg^{\mathbf{P}}_{\alpha+\beta}(\mathbf{r}), \qquad (4)$$

$$K = \exp(-\alpha\beta |\mathbf{A} - \mathbf{B}|^2 / (\alpha + \beta)), \tag{5}$$

$$\mathbf{P} = (\alpha \mathbf{A} + \beta \mathbf{B}) / (\alpha + \beta). \tag{6}$$

Now consider calculations³⁻¹⁰ in which the electrons move on the *D*-dimensional sphere \mathbb{S}^D , i.e., on the surface of a (D+1)-dimensional unit ball. If the average interelectronic separation r_s is small, the MOs are delocalized over the sphere and the (hyper)spherical harmonics¹¹

$$Q_{k,K}(\mathbf{r}) = Y_{k,K}(\mathbf{r}), \qquad \mathbf{r} \in \mathbb{S}^D$$
(7)

(where K is a composite index) provide a useful basis because they are single-valued and the product of two of these functions is a finite sum of several others,

$$Q_{k_1,K_1}(\mathbf{r})Q_{k_2,K_2}(\mathbf{r}) = \sum_k \sum_K c_{k,K}Q_{k,K}(\mathbf{r}),$$
(8)

where $c_{k,K}$ is a generalized Clebsch-Gordan coefficient. However, if r_s is large and the MOs are localized, what are good basis functions?

In this paper, we propose that spherical Gaussian functions (SGFs) are a natural basis set for localized MOs

on a sphere. In Sec. II, we define SGFs and show that the product of two is a third. In Sec. III, we resolve the Coulomb operator on a sphere and use this to derive expressions for integrals over SGFs on the unit sphere. Section IV discusses implementation details of our integral formulae and Sec. V presents some numerical results for Wigner molecules on a 2-sphere. Atomic units are used throughout.

II. SPHERICAL GAUSSIAN FUNCTIONS

The normalized SGF is

$$G_{\alpha}^{\mathbf{A}}(\mathbf{r}) = \frac{\exp(\alpha \mathbf{A} \cdot \mathbf{r})}{\sqrt{2\pi (\pi/\alpha)^{\lambda} I_{\lambda}(2\alpha)}}, \qquad \mathbf{r} \in \mathbb{S}^{D}$$
(9)

where $\mathbf{A} \in \mathbb{S}^{D}$ is a fixed center, $\alpha \ge 0$ is a fixed exponent, I_{λ} is a modified Bessel function¹² and

$$\lambda = (D - 1)/2.$$
(10)

If we define $\mathbf{u} = \mathbf{r} - \mathbf{A}$ then, for a unit sphere, we have $u^2 = 2(1 - \mathbf{A} \cdot \mathbf{r})$ and $G_{\alpha}^{\mathbf{A}}(\mathbf{r}) \propto \exp[\alpha(1 - u^2/2)]$, therefore, decays as a Cartesian Gaussian in *u*. (See Fig. 1). The SGF is single-valued and smooth and decays from a maximum at $\mathbf{r} = \mathbf{A}$ to a minimum at $\mathbf{r} = -\mathbf{A}$. If α is small, the SGF is almost constant over the sphere; if α is large, the SGF is strongly peaked around \mathbf{A} . For this reason, it is a natural basis function for a localized MO on a sphere.

The product of two SGFs is a third SGF, because

$$\exp(\alpha \mathbf{A} \cdot \mathbf{r}) \exp(\beta \mathbf{B} \cdot \mathbf{r}) = \exp(\zeta \mathbf{P} \cdot \mathbf{r}), \quad (11)$$

$$\zeta = \sqrt{\alpha^2 + \beta^2 + 2\alpha\beta\cos\theta}, \qquad (12)$$

$$\mathbf{P} = (\alpha \mathbf{A} + \beta \mathbf{B}) / \zeta, \tag{13}$$

where $\cos\theta = \mathbf{A} \cdot \mathbf{B}$. (See Fig. 1.)

III. INTEGRALS OVER SPHERICAL GAUSSIANS

The hyperspherical harmonic addition theorem¹³ for points on the unit *D*-sphere that subtend an angle ω is

a)Electronic mail: peter.gill@anu.edu.au

^{b)}Author to whom correspondence should be addressed. Electronic mail: pf.loos@anu.edu.au



FIG. 1. An example of the SGF product rule on the unit ring, where $\alpha = 25$, **A** = $(\cos[\pi/3], \sin[\pi/3])$, $\beta = 50$ and **B** = $(\cos \pi, \sin \pi)$ yields $\zeta = 25\sqrt{3}$ and **P** = $(\cos[5\pi/6], \sin[5\pi/6])$.

$$C_n^{\lambda}(\cos \omega) = \frac{2\pi}{n+\lambda} \frac{\pi^{\lambda}}{\Gamma(\lambda)} \sum_K Y_{n,K}^*(\mathbf{r}_1) Y_{n,K}(\mathbf{r}_2), \qquad (14)$$

where C_n^{λ} is a Gegenbauer polynomial and Γ is the Gamma function.¹² The resolution of the Coulomb operator on the *D*-sphere is therefore

$$r_{12}^{-1} = (2 - 2\cos \omega)^{-1/2}$$

$$= \sum_{n=0}^{\infty} \frac{\langle (2 - 2\cos \omega)^{-1/2} | C_n^{\lambda}(\cos \omega) \rangle}{\langle C_n^{\lambda}(\cos \omega) | C_n^{\lambda}(\cos \omega) \rangle} C_n^{\lambda}(\cos \omega)$$

$$= \frac{4^{\lambda} \Gamma(\lambda)^2}{2\pi} \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2})(n + \lambda)}{\Gamma(n + \frac{1}{2} + 2\lambda)} C_n^{\lambda}(\cos \omega)$$

$$= (4\pi)^{\lambda} \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2}) \Gamma(\lambda)}{\Gamma(n + \frac{1}{2} + 2\lambda)} \sum_{K} Y_{n,K}^*(\mathbf{r}_1) Y_{n,K}(\mathbf{r}_2). \quad (15)$$

The product rule (11) yields the overlap integral

$$\left(G_{\alpha}^{\mathbf{A}}|G_{\beta}^{\mathbf{B}}\right) = \frac{I_{\lambda}(\zeta)/\zeta^{\lambda}}{\sqrt{I_{\lambda}(2\alpha)I_{\lambda}(2\beta)/(4\alpha\beta)^{\lambda}}}$$
(16)

and re-normalized kinetic integral (with $\hat{T} \equiv -\nabla^2/2$)

$$\frac{\left(G_{\alpha}^{\mathbf{A}}|\hat{T}|G_{\beta}^{\mathbf{B}}\right)}{\left(G_{\alpha}^{\mathbf{A}}|G_{\beta}^{\mathbf{B}}\right)} = \frac{I_{\lambda+1}(\zeta)}{I_{\lambda}(\zeta)}\frac{(2\lambda+1)\alpha\beta\cos\theta}{2\zeta} - \frac{I_{\lambda+2}(\zeta)}{I_{\lambda}(\zeta)}\frac{(\alpha\beta\sin\theta)^{2}}{2\zeta^{2}}.$$
(17)

Using the Coulomb resolution (15), it can be shown that the re-normalized electron repulsion integral (ERI), in chemist's notation,¹⁴ is

$$\frac{\left(G_{\alpha}^{\mathbf{A}}G_{\beta}^{\mathbf{B}}|G_{\gamma}^{\mathbf{C}}G_{\delta}^{\mathbf{D}}\right)}{\left(G_{\alpha}^{\mathbf{A}}|G_{\beta}^{\mathbf{B}}\right)\left(G_{\gamma}^{\mathbf{C}}|G_{\delta}^{\mathbf{D}}\right)} = \frac{4^{\lambda}\Gamma(\lambda)^{2}}{2\pi}\sum_{n=0}^{\infty}\frac{\Gamma(n+\frac{1}{2})(n+\lambda)}{\Gamma(n+\frac{1}{2}+2\lambda)}$$
$$\times \frac{I_{n+\lambda}(\zeta)}{I_{\lambda}(\zeta)}\frac{I_{n+\lambda}(\eta)}{I_{\lambda}(\eta)}C_{n}^{\lambda}(\cos\chi), \quad (18)$$

where η and **Q** are ket analogs of ζ and **P**, respectively, and $\cos \chi = \mathbf{P} \cdot \mathbf{Q}$. Special cases of these formulae for D = 1 (a ring), D = 2 (a normal sphere), and D = 3 (a glome) are given in Table I. (It should be noted that the ERI for D = 1 is the finite part of an infinite quantity¹⁰).

IV. COMPUTATIONAL EFFICIENCY

In a calculation using N SGFs, computing the nonnegligible ERIs is often the most time-consuming step and, for efficiency, one should use both two-center and four-center cutoffs.¹⁵ The Cauchy-Schwarz bound^{16,17}

$$\left(G_{\alpha}^{\mathbf{A}}G_{\beta}^{\mathbf{B}}|G_{\gamma}^{\mathbf{C}}G_{\delta}^{\mathbf{D}}\right) \le Z_{\alpha\beta}Z_{\gamma\delta} \tag{19}$$

is particularly useful because the required factors

$$Z_{\alpha\beta} = (G^{\mathbf{A}}_{\alpha}G^{\mathbf{B}}_{\beta}|G^{\mathbf{A}}_{\alpha}G^{\mathbf{B}}_{\beta})^{1/2}$$
$$= \frac{\left(G^{\mathbf{A}}_{\alpha}|G^{\mathbf{B}}_{\beta}\right)}{I_{\lambda}(\zeta)/\zeta^{\lambda}}\sqrt{\frac{{}_{1}F_{2}(\lambda+\frac{1}{2},\lambda+1,2\lambda+\frac{1}{2},\zeta^{2})}{2\lambda\Gamma(2\lambda+\frac{1}{2})\sqrt{\pi}}} \qquad (20)$$

(where $_1F_2$ is the generalized hypergeometric function¹²) can be found in closed form. For example, for D = 2,

$$Z_{\alpha\beta} = \frac{\left(G_{\alpha}^{\mathbf{A}}|G_{\beta}^{\mathbf{B}}\right)}{i_0(\zeta)} \sqrt{\frac{\pi}{2}} \frac{\mathbf{L}_0(2\zeta)}{2\zeta},\tag{21}$$

where L_0 is a modified Struve function.¹²

In practice, the sum in (18) must be truncated after M terms but this is not problematic because the series converges rapidly.

TABLE I. Overlap, kinetic, and electron repulsion integrals^a over SGFs on the unit *D*-sphere.

D	$\left(G^{\mathbf{A}}_{lpha} G^{\mathbf{B}}_{eta} ight)$	$\left(G^{\mathbf{A}}_{lpha}\left \hat{T} ight G^{\mathbf{B}}_{eta}$	$\left(\left(G^{\mathbf{A}}_{lpha} G^{\mathbf{B}}_{eta} \right) \right)$	$\left(G^{\mathbf{A}}_{\alpha}G^{\mathbf{B}}_{\beta} G^{\mathbf{C}}_{\gamma}G^{\mathbf{D}}_{\delta}\right)/\left(G^{\mathbf{A}}_{\alpha} G^{\mathbf{B}}_{\beta}\right)/\left(G^{\mathbf{C}}_{\gamma} G^{\mathbf{D}}_{\delta}\right)$
1	$rac{I_0(\zeta)}{\sqrt{I_0(2lpha)I_0(2eta)}}$	$\frac{I_1(\zeta)}{I_0(\zeta)}\frac{\alpha\beta\cos\theta}{2\zeta} - $	$-\frac{I_2(\zeta)}{I_0(\zeta)}\frac{(\alpha\beta\sin\theta)^2}{2\zeta^2}$	$-\frac{4}{\pi}\sum_{n=1}^{\infty}\frac{I_n(\zeta)}{I_0(\zeta)}\frac{I_n(\eta)}{I_0(\eta)}s_nT_n(\cos\chi)$
2	$rac{i_0(\zeta)}{\sqrt{i_0(2lpha)i_0(2eta)}}$	$\frac{i_1(\zeta)}{i_0(\zeta)}\frac{\alpha\beta\cos\theta}{\zeta} -$	$-\frac{i_2(\zeta)}{i_0(\zeta)}\frac{(\alpha\beta\sin\theta)^2}{2\zeta^2}$	$\sum_{n=0}^{\infty} \frac{i_n(\zeta)}{i_0(\zeta)} \frac{i_n(\eta)}{i_0(\eta)} P_n(\cos \chi)$
3	$\frac{I_1(\zeta)/\zeta}{\sqrt{I_1(2\alpha)I_1(2\beta)/(4\alpha\beta)}}$	$\frac{I_2(\zeta)}{I_1(\zeta)}\frac{3\alpha\beta\cos\theta}{2\zeta}$	$-\frac{I_3(\zeta)}{I_1(\zeta)}\frac{(\alpha\beta\sin\theta)^2}{2\zeta^2}$	$\frac{2}{\pi} \sum_{n=1}^{\infty} \frac{I_n(\zeta)}{I_1(\zeta)} \frac{I_n(\eta)}{I_1(\eta)} \frac{nU_{n-1}(\cos\chi)}{n^2 - 1/4}$

 ${}^{a}i_{n}$ is a modified spherical Bessel function, P_{n} is a Legendre polynomial, $\overline{T_{n}}$ and U_{n} are Chebyshev polynomials¹² and $s_{n} = \sum_{p=1}^{n} (2p-1)^{-1}$ is a harmonic number.

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In summary, we recommend the following algorithm: 1: npairs $\leftarrow 0$

2: for i = 1, N do for j = i, N do 3: 4: if $(G_i|G_i)$ > threshold then 5: npairs \leftarrow npairs + 1 Compute $I_{n+\lambda}(\zeta)/I_{\lambda}(\zeta)$ for $0 \le n \le M$ 6: 7: Compute $T_{ij} = (G_i | \hat{T} | G_j)$ 8: Compute $Z_{ij} = \sqrt{(G_i G_j | G_i G_j)}$ 9: end if 10: end for 11: end for 12: **for** *i j* = 1,npairs **do** for kl = ij, npairs do 13: 14: if $Z_{ij}Z_{kl}$ > threshold then Compute $(G_i G_j | G_k G_l)$ 15: 16: end if 17: end for 18: end for

The Gegenbauer polynomials needed in step 15 (see Table I) should be found by forward recursion, e.g.,

$$T_n(z) = 2zT_{n-1}(z) - T_{n-2}(z), \qquad (22)$$

$$P_n(z) = \frac{2n-1}{n} z P_{n-1}(z) - \frac{n-1}{n} P_{n-2}(z), \qquad (23)$$

$$U_n(z) = 2zU_{n-1}(z) - U_{n-2}(z).$$
(24)

V. NUMERICAL RESULTS

In 1904, J. J. Thomson asked¹⁸ what arrangement of n identical charges on a sphere minimizes their electrostatic energy E_0 . This deceptively simple question and its various generalizations have led to much work¹⁹ and, although rigorous mathematical proofs are rare,²⁰ careful numerical investigations²¹ have provided optimal or near-optimal arrangements for many values of n.

Thirty years later, Wigner discovered²² that a low-density electron gas will spontaneously "crystallize": each electron moving with small amplitude around a lattice site in what is now called a "Wigner crystal" (or, in case of a finite number of particles, a Wigner molecule). Such crystals have also been

observed for electrons confined within harmonic wells,^{23–27} cubes,²⁸ squares,²⁹ and spheres.³

The exact energy of a Wigner molecule can be approximated by the sum of its Thomson energy E_0 and the harmonic zero-point energy E_1 of the electrons as they vibrate around the lattice sites.³⁰ These vibrations can be classified according to their irreducible representations $\Gamma_{\rm vib}$ within the point group of the Thomson lattice³¹ (see Table II).

To illustrate the usefulness of SGFs, we have studied *n* same-spin electrons on a 2-sphere with radius *R* and Wigner-Seitz radius $r_s = R\sqrt{2} = 100$, for seven *n* values.

We first consider n = 2, for which the Thomson lattice consists of points at the north and south poles of the sphere. If we place SGFs with exponent α at each pole and minimize the Hartree-Fock (HF) energy¹⁴ with respect to α , we obtain the minimal-basis energy

$$E_{\rm HF}^{\alpha} = 0.008\,270. \tag{25}$$

Adding a second SGF (with exponent β) at each pole and optimizing with respect to both exponents yields the split-valence energy

$$E_{\rm HF}^{\alpha,\beta} = 0.008\,263.\tag{26}$$

This energy, which is obtained using only $N_G = 4$ SGFs, can also be obtained using a spherical harmonic basis, but only by using harmonics with $0 \le \ell \le 5$, of which there are $N_Y = (5 + 1)^2 = 36$. This example reveals how much more efficient SGFs are than spherical harmonics for problems in which the MOs are strongly localized. It can be shown³ that the exact energy is

$$E = 0.007\,993,$$
 (27)

which implies that the reduced (i.e., per electron) correlation energy¹⁴ is $\bar{E}_c = -0.135 \text{ m}E_h$.

We have performed analogous calculations for all values of *n* where the Thomson lattice sites are equivalent. It turns out that there are seven such cases and the results for n = 2, 3,4, 6, 8, 12, 24 are given in Table II.

Although the Wigner-Seitz radius (the average distance between neighboring electrons) is $r_s = 100$ in all cases, we note

TABLE II. Thomson lattices, point groups, vibrational representations $\Gamma_{\rm vib}$, Wigner energies^a E_0 and E_1 , optimal single-zeta exponents α , double-zeta HF energies $E_{\rm HF}$, exact energies E, and reduced correlation energies \bar{E}_c (all in m $E_{\rm h}$) for n same-spin electrons on a 2-sphere with Seitz radius $r_s = 2R/\sqrt{n} = 100$. The final two rows give the number $N_{\rm G}$ of spherical Gaussians and number $N_{\rm Y}$ of spherical harmonics required to achieve $E_{\rm HF}$.

n	2	3	4	6	8	12	24
Lattice	Diameter	Triangle	Tetrahedron	Octahedron	Anti-cube	Icosahedron	Snub cube
Point group	$D_{\infty h}$	D_{3h}	T_d	O_h	D_{4d}	I_h	0
Γ_{vib}	Π_{u}	$A_2^{\prime\prime} + E^{\prime}$	$E + T_2$	$T_{2g} +$	$A_1 + B_1 + B_2 +$	$G_g + H_g +$	$2A_1 + 2A_2 +$
				$T_{1u} + T_{2u}$	$2E_1 + 2E_2 + E_3$	$T_{1u} + G_u + H_u$	$4E + 5T_1 + 6T_2$
E_0	7.071	20.000	36.742	81.529	139.125	283.856	911.811
$E_0 + E_1$	7.912	21.525	39.125	85.573	144.727	292.832	930.387
α	0.050	0.071	0.084	0.107	0.127	0.156	0.227
$E_{ m HF}$	8.263	22.194	39.822	86.438	145.929	294.256	933.275
Ε	7.993	21.589	39.102	_	_	—	_
$-\bar{E}_c$	0.135	0.202	0.180	~0.14	~0.15	~0.12	~0.12
$N_{ m G}$	2	6	8	12	16	24	48
$N_{ m Y}$	36	36	81	196	144	≥225	≥225

 ${}^{a}E_{0}$ is the Coulomb energy of the Thomson lattice; E_{1} is the harmonic zero-point vibrational energy of the lattice.

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that the minimal-basis exponent α grows, i.e., the electrons become more localized, as *n* increases.

For $n \ge 6$, we have not been able to calculate the exact energy E, so we have estimated the reduced correlation energies in these cases using $E \approx E_0 + E_1$. The resulting \overline{E}_c values appear to decrease slowly with n.

Finally, we note that the superior efficiency of SGFs, compared with spherical harmonics, is observed for all *n* values that we have considered. In each case, the number $N_{\rm Y}$ of spherical harmonics required to achieve the HF energy in Table II was an order of magnitude larger than the number $N_{\rm G}$ of SGFs. In fact, for n = 12 and n = 24, not even 196 spherical harmonics (i.e., $0 \le \ell \le 13$) were able to match the energy of the splitvalence SGF basis.

VI. CONCLUDING REMARKS

Cartesian Gaussian basis functions, which are widely used in quantum chemical calculations in \mathbb{R}^D , can be successfully generalized to SGFs for calculations on the sphere \mathbb{S}^D . We have derived formulae for the required overlap, kinetic energy, and electron repulsion integrals and the worst of these involves a rapidly converging infinite series.

In quantum chemical calculations in \mathbb{R}^D , it is common to use both *s*-type Cartesian Gaussians (3) and Gaussians of higher angular momentum (i.e., *p*-type and *d*-type). Integrals over these higher functions can be obtained^{2,15} from the fundamental integrals over *s*-type functions by differentiating with respect to the Cartesian coordinates of the Gaussian center. In a similar way, if desired, one can obtain higher SGFs, and their integrals, by differentiating (9), (16), (17), and (18) with respect to the Cartesian coordinates of **A**, **B**, **C**, and/or **D**.

We are using SGFs in a systematic study of electrons on 2-spheres and 3-spheres and will report our results elsewhere.

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