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Basis functions for electronic structure calculations on spheres

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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

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

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

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

If the MOs are localized, the Cartesian Gaussians²

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

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

$$g_{\mathbf{A}}^{\alpha}(\mathbf{r})g_{\mathbf{B}}^{\beta}(\mathbf{r}) = Kg_{\mathbf{A}+\mathbf{B}}^{\alpha+\beta}(\mathbf{r}), \quad (4)$$

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

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

Now consider calculations^{3–10} 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

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

(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,

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

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

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

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

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

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 $G_{\mathbf{A}}^{\alpha}(\mathbf{r}) \propto \exp[\alpha(1 - u^2/2)]$, 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

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

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

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

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

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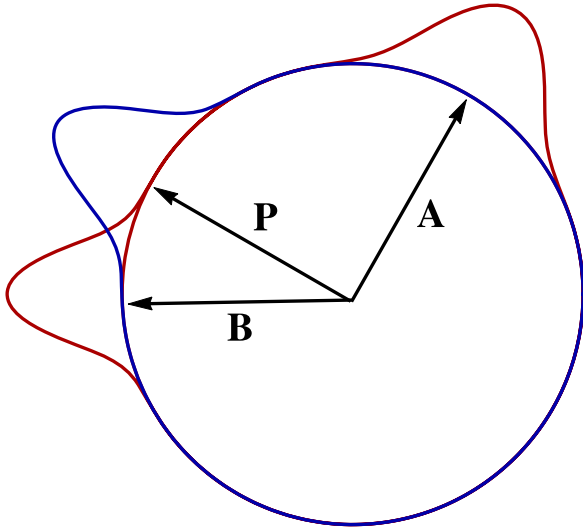


FIG. 1. An example of the SGF product rule on the unit ring, where $\alpha = 25$, $\mathbf{A} = (\cos[\pi/3], \sin[\pi/3])$, $\beta = 50$ and $\mathbf{B} = (\cos \pi, \sin \pi)$ yields $\zeta = 25\sqrt{3}$ and $\mathbf{P} = (\cos[5\pi/6], \sin[5\pi/6])$.

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

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

$$\begin{aligned} r_{12}^{-1} &= (2 - 2\cos \omega)^{-1/2} \\ &= \sum_{n=0}^{\infty} \frac{\langle (2 - 2\cos \omega)^{-1/2} | C_n^\lambda(\cos \omega) \rangle}{\langle C_n^\lambda(\cos \omega) | C_n^\lambda(\cos \omega) \rangle} C_n^\lambda(\cos \omega) \\ &= \frac{4^\lambda \Gamma(\lambda)^2}{2\pi} \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2})(n + \lambda)}{\Gamma(n + \frac{1}{2} + 2\lambda)} C_n^\lambda(\cos \omega) \\ &= (4\pi)^\lambda \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2}) \Gamma(\lambda)}{\Gamma(n + \frac{1}{2} + 2\lambda)} \sum_K Y_{n,K}^*(\mathbf{r}_1) Y_{n,K}(\mathbf{r}_2). \end{aligned} \quad (15)$$

The product rule (11) yields the overlap integral

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

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

$$\begin{aligned} \frac{\langle G_\alpha^{\mathbf{A}} | \hat{T} | G_\beta^{\mathbf{B}} \rangle}{\langle G_\alpha^{\mathbf{A}} | G_\beta^{\mathbf{B}} \rangle} &= \frac{I_{\lambda+1}(\zeta)}{I_\lambda(\zeta)} \frac{(2\lambda + 1)\alpha\beta \cos \theta}{2\zeta} \\ &\quad - \frac{I_{\lambda+2}(\zeta)}{I_\lambda(\zeta)} \frac{(\alpha\beta \sin \theta)^2}{2\zeta^2}. \end{aligned} \quad (17)$$

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

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

where η and \mathbf{Q} are ket analogs of ζ and \mathbf{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 non-negligible 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}

$$\langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} | G_\gamma^{\mathbf{C}} G_\delta^{\mathbf{D}} \rangle \leq Z_{\alpha\beta} Z_{\gamma\delta} \quad (19)$$

is particularly useful because the required factors

$$\begin{aligned} Z_{\alpha\beta} &= \langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} | G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} \rangle^{1/2} \\ &= \frac{\langle G_\alpha^{\mathbf{A}} | G_\beta^{\mathbf{B}} \rangle}{I_\lambda(\zeta) / \zeta^\lambda} \sqrt{\frac{{}_1F_2(\lambda + \frac{1}{2}, \lambda + 1, 2\lambda + \frac{1}{2}, \zeta^2)}{2\lambda \Gamma(2\lambda + \frac{1}{2}) \sqrt{\pi}}} \end{aligned} \quad (20)$$

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

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

where \mathbf{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	$\langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} \rangle$	$\langle G_\alpha^{\mathbf{A}} \hat{T} G_\beta^{\mathbf{B}} \rangle / \langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} \rangle$	$\langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} G_\gamma^{\mathbf{C}} G_\delta^{\mathbf{D}} \rangle / \langle G_\alpha^{\mathbf{A}} G_\beta^{\mathbf{B}} \rangle / \langle G_\gamma^{\mathbf{C}} G_\delta^{\mathbf{D}} \rangle$
1	$\frac{I_0(\zeta)}{\sqrt{I_0(2\alpha)I_0(2\beta)}}$	$\frac{I_1(\zeta)}{I_0(\zeta)} \frac{\alpha\beta \cos \theta}{2\zeta} - \frac{I_2(\zeta)}{I_0(\zeta)} \frac{(\alpha\beta \sin \theta)^2}{2\zeta^2}$	$-\frac{4}{\pi} \sum_{n=1}^{\infty} \frac{I_n(\zeta)}{I_0(\zeta)} \frac{I_n(\eta)}{I_0(\eta)} s_n T_n(\cos \chi)$
2	$\frac{i_0(\zeta)}{\sqrt{i_0(2\alpha)i_0(2\beta)}}$	$\frac{i_1(\zeta)}{i_0(\zeta)} \frac{\alpha\beta \cos \theta}{\zeta} - \frac{i_2(\zeta)}{i_0(\zeta)} \frac{(\alpha\beta \sin \theta)^2}{2\zeta^2}$	$\sum_{n=0}^{\infty} \frac{i_n(\zeta)}{i_0(\zeta)} \frac{i_n(\eta)}{i_0(\eta)} P_n(\cos \chi)$
3	$\frac{I_1(\zeta)/\zeta}{\sqrt{I_1(2\alpha)I_1(2\beta)/(4\alpha\beta)}}$	$\frac{I_2(\zeta)}{I_1(\zeta)} \frac{3\alpha\beta \cos \theta}{2\zeta} - \frac{I_3(\zeta)}{I_1(\zeta)} \frac{(\alpha\beta \sin \theta)^2}{2\zeta^2}$	$\frac{2}{\pi} \sum_{n=1}^{\infty} \frac{I_n(\zeta)}{I_1(\zeta)} \frac{I_n(\eta)}{I_1(\eta)} \frac{n U_{n-1}(\cos \chi)}{n^2 - 1/4}$

^a i_n is a modified spherical Bessel function, P_n is a Legendre polynomial, T_n and U_n are Chebyshev polynomials¹² and $s_n = \sum_{p=1}^n (2p-1)^{-1}$ is a harmonic number.

In summary, we recommend the following algorithm:

```

1: npairs ← 0
2: for i = 1, N do
3:   for j = i, N do
4:     if (Gi|Gj) > threshold then
5:       npairs ← npairs + 1
6:       Compute In+λ(ζ)/Iλ(ζ) for 0 ≤ n ≤ M
7:       Compute Tij = (Gi|T̂|Gj)
8:       Compute Zij = √(GiGj|GiGj)
9:     end if
10:  end for
11: end for
12: for ij = 1, npairs do
13:   for kl = ij, npairs do
14:     if ZijZkl > threshold then
15:       Compute (GiGj|GkGl)
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.,

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

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

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

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 Γ_{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

$$E_{\text{HF}}^\alpha = 0.008\,270. \quad (25)$$

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

$$E_{\text{HF}}^{\alpha,\beta} = 0.008\,263. \quad (26)$$

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 $0 \leq \ell \leq 5$, 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

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

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 Γ_{vib} , Wigner energies^a E_0 and E_1 , optimal single-zeta exponents α , double-zeta HF energies E_{HF} , exact energies E , and reduced correlation energies \bar{E}_c (all in $\text{m}E_h$) 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_G of spherical Gaussians and number N_Y of spherical harmonics required to achieve E_{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	O
Γ_{vib}	Π_u	$A''_2 + E'$	$E + T_2$	$T_{2g} + T_{1u} + T_{2u}$	$A_1 + B_1 + B_2 + 2E_1 + 2E_2 + E_3$	$G_g + H_g + T_{1u} + G_u + H_u$	$2A_1 + 2A_2 + 4E + 5T_1 + 6T_2$
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_{HF}	8.263	22.194	39.822	86.438	145.929	294.256	933.275
E	7.993	21.589	39.102	—	—	—	—
$-\bar{E}_c$	0.135	0.202	0.180	~0.14	~0.15	~0.12	~0.12
N_G	2	6	8	12	16	24	48
N_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.

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

For $n \geq 6$, 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 \bar{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_Y of spherical harmonics required to achieve the HF energy in Table II was an order of magnitude larger than the number N_G of SGFs. In fact, for $n = 12$ and $n = 24$, not even 196 spherical harmonics (i.e., $0 \leq \ell \leq 13$) were able to match the energy of the split-valence 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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