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.

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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 waves
\begin{equation}
q_k(r) = \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{r}), \quad \mathbf{r} \in \mathbb{R}^D
\end{equation}
form a good basis, because the product of two is a third
\begin{equation}
q_{k_1}(r)q_{k_2}(r) = q_{k_1+k_2}(r)
\end{equation}
If the MOs are localized, the cartesian gaussians
\begin{equation}
g_{\alpha}^A(r) = \exp(-\alpha |\mathbf{r} - \mathbf{A}|^2), \quad \mathbf{r} \in \mathbb{R}^D
\end{equation}
are effective, again because the product of two is a third
\begin{equation}
g_{\alpha}^A(r)g_{\beta}^B(r) = Kg_{\alpha+\beta}^P(r)
\end{equation}
where
\begin{equation}
K = \exp(-\alpha\beta|\mathbf{A} - \mathbf{B}|^2/(\alpha + \beta))
\end{equation}
\begin{equation}
P = (\alpha \mathbf{A} + \beta \mathbf{B})/(\alpha + \beta)
\end{equation}

Now consider calculations 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 harmonics
\begin{equation}
Q_{k,K}(r) = Y_{k,K}(r), \quad \mathbf{r} \in \mathbb{S}^D
\end{equation}
(where $K$ is a composite index) provide a useful basis because it is single-valued and the product of two of these functions is a finite sum of several others
\begin{equation}
Q_{k_1,K_1}(r)Q_{k_2,K_2}(r) = \sum_k \sum_K c_{k,K}Q_{k,K}(r)
\end{equation}
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 Section we define SGFs and show that the product of two is a third. In Section we resolve the Coulomb operator on a sphere and use...
If we define \( u = \mathbf{r} - \mathbf{A} \) then, for a unit sphere, we have \( u^2 = 2(1 - \mathbf{A} \cdot \mathbf{r}) \) and \( G^A_\alpha (\mathbf{r}) \propto \exp [\alpha (1 - u^2/2)] \) 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 \( \alpha \) is small, the SGF is almost constant over the sphere; if \( \alpha \) 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.

\[
G^A_\alpha (\mathbf{r}) = \frac{\exp(\alpha \mathbf{A} \cdot \mathbf{r})}{\sqrt{2\pi (\pi/\alpha)^\lambda I_\lambda(2\alpha)}}, \quad \mathbf{r} \in S^D
\]  

(9)
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 $P = (\cos [5\pi/6], \sin [5\pi/6])$.

The product of two SGFs is a third SGF, because

$$\exp(\alpha A \cdot r) \exp(\beta B \cdot r) = \exp(\zeta P \cdot r)$$  (11)

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

$$P = (\alpha A + \beta B)/\zeta$$  (13)

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

III. INTEGRALS OVER SPHERICAL GAUSSIANS

The hyperspherical harmonic addition theorem for points on the unit $D$-sphere that subtend an angle $\omega$ is

$$C_n^\lambda(\cos \omega) = \frac{2\pi}{n + \lambda \Gamma(\lambda)} \sum_K Y_{n,K}^*(r_1)Y_{n,K}(r_2)$$  (14)
where \( C_n^\lambda \) is a Gegenbauer polynomial and \( \Gamma \) is the Gamma function. The resolution of the Coulomb operator on the \( D \)-sphere is therefore

\[
    r_{12}^{-1} = (2 - 2 \cos \omega)^{-1/2}
    = \sum_{n=0}^{\infty} \frac{\left\langle (2 - 2 \cos \omega)^{-1/2} \right| C_n^\lambda (\cos \omega) \right| C_n^\lambda (\cos \omega)}{\Gamma(n + \frac{1}{2})(n + \frac{1}{2} + 2\lambda)}
    = (4\pi)^{\lambda} \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2}) \Gamma(\lambda)}{\Gamma(n + \frac{1}{2} + 2\lambda)} \sum_K Y_{n,K}^* (r_1) Y_{n,K} (r_2)
\]

The product rule yields the overlap integral

\[
    \langle G_A^\alpha | G_B^\beta \rangle = \frac{I_\lambda(\zeta)/\zeta^\lambda}{\sqrt{I_\lambda(2\alpha)I_\lambda(2\beta)/(4\alpha\beta)^\lambda}}
\]

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

\[
    \frac{\left( G_A^\alpha \right| \hat{T} \left| G_B^\beta \right) \left( G_A^\alpha \right| G_B^\beta \rangle = \frac{I_{\lambda+1}(\zeta) (2\lambda + 1) \alpha \beta \cos \theta}{2\zeta} - \frac{I_{\lambda+2}(\zeta) (\alpha \beta \sin \theta)^2}{2\zeta^2}
\]

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

\[
    \langle G_A^\alpha G_B^\beta \left| G_C^\gamma G_D^\delta \right) \left( G_A^\alpha \right| G_B^\beta \rangle \left( G_C^\gamma \right| G_D^\delta \rangle = \frac{4\lambda \Gamma(\lambda)^2}{2\pi} \sum_{n=0}^{\infty} \frac{\Gamma(n + \frac{1}{2})(n + \lambda) I_{n+\lambda}(\zeta) I_{n+\lambda}(\eta)}{\Gamma(n + \frac{1}{2} + 2\lambda) I_\lambda(\zeta) I_\lambda(\eta)} C_n^\lambda (\cos \chi)
\]

where \( \eta \) and \( Q \) are ket analogs of \( \zeta \) and \( P \), respectively, and \( \cos \chi = P \cdot Q \). 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 quantity.)

### 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. The Cauchy-Schwarz bound

\[
    \langle G_A^\alpha \left| G_B^\beta \left| G_C^\gamma \right| G_D^\delta \rangle \leq Z_{\alpha\beta} Z_{\gamma\delta}
\]
is particularly useful because the required factors
\[ Z_{\alpha \beta} = \left(G_A^G B^G \mid G_A^G B^G \right)^{1/2} \]
\[ = \frac{(G_A^G \mid G_B^G)}{I_\lambda(\zeta)/\zeta^\lambda} \sqrt{\frac{1_F(\lambda + \frac{1}{2}, \lambda + 1, 2\lambda + \frac{1}{2}, \zeta^2)}{2\lambda \Gamma(2\lambda + \frac{1}{2})\sqrt{\pi}}} \]  
(20)

(where \( 1_F \) is the generalized hypergeometric function\[12\]) can be found in closed form. For example, for \( D = 2 \),
\[ Z_{\alpha \beta} = \frac{(G_A^G \mid G_B^G)}{i_0(\zeta)} \sqrt{\frac{\pi}{2} \frac{L_0(2\zeta)}{2\zeta}} \]  
(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.

In summary, we recommend the following algorithm:

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

The Gegenbauer polynomials needed in step 15 (see Table II) should be found by forward
TABLE II. Thomson lattices, point groups, vibrational representations $\Gamma_{vib}$, Wigner energies $E_0$ and $E_1$, optimal single-zeta exponents $\alpha$, double-zeta HF energies $E_{HF}$, exact energies $E$ and reduced correlation energies $\bar{E}_c$ (all in $mE_h$) 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 | $D_{\infty h}$ | $D_{3h}$ | $T_d$ | $O_h$ | $D_{4d}$ | $I_h$ | $O$ |
| $\Gamma_{vib}$ | $\Pi_u$ | $A''_u + E'$ | $E + T_2$ | $T_{2g}^+$ | $A_1 + B_1 + B_2^+$ | $G_g + H_g^+$ | $2A_1 + 2A_2^+$ |
| $T_{1u} + T_{2u}$ | $2E_1 + 2E_2 + E_3$ | $T_{1u} + G_u + H_u$ | $4E + 5T_1 + 6T_2$ |
| $E_0$ | 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 |
| $\alpha$ | 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 | $\sim 0.14$ | $\sim 0.15$ | $\sim 0.12$ | $\sim 0.12$ |
| $N_G$ | 2 | 6 | 8 | 12 | 16 | 24 | 48 |
| $N_Y$ | 36 | 36 | 81 | 196 | 144 | $\geq 225$ | $\geq 225$ |

$^a$ $E_0$ is the Coulomb energy of the Thomson lattice; $E_1$ is the harmonic zero-point vibrational energy of the lattice.

Recursion, e.g.

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

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

$$U_n(z) = 2zU_{n-1}(z) - U_{n-2}(z)$$ \hfill (24)
V. NUMERICAL RESULTS

In 1904, J.J. Thomson asked[19] 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 work[20] and, although rigorous mathematical proofs are rare,[20] careful numerical investigations[21] have provided optimal or near-optimal arrangements for many values of $n$.

Thirty years later, Wigner discovered[22] 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.[30]

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 $\Gamma_{\text{vib}}$ within the point group of the Thomson lattice[31] (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 is points at the north and south poles of the sphere. If we place SGFs with exponent $\alpha$ at each pole and minimize the Hartree-Fock (HF) energy[14] with respect to $\alpha$, we obtain the minimal-basis energy

$$E_{\text{HF}}^{\alpha} = 0.008270$$  \hspace{1cm} (25)

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

$$E_{\text{HF}}^{\alpha,\beta} = 0.008263$$  \hspace{1cm} (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 shown[3] that the exact energy is

$$E = 0.007993$$  \hspace{1cm} (27)
which implies that the reduced (i.e. per electron) correlation energy is $E_c = -0.135 \text{ mE}_h$. 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 that the minimal-basis exponent $\alpha$ 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 $E_c$ 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 spherical gaussian functions (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 and gaussians of higher angular momentum (i.e. $p$-type, $d$-type, etc.). Integrals over these higher functions can be obtained 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 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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