Multi-sliced Gausslet Basis Sets for Electronic Structure

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We introduce highly local basis sets for electronic structure which are very efficient for correlation calculations near the complete basis set limit. Our approach is based on gausslets, recently introduced wavelet-like smooth orthogonal functions. We adapt the gausslets to particular systems using one dimensional coordinate transformations, putting more basis functions near nuclei, while maintaining orthogonality. Three dimensional basis functions are composed out of products of the 1D functions in an efficient way called multislicing. We demonstrate the new bases with both Hartree Fock and density matrix renormalization group (DMRG) calculations on hydrogen chain systems. With both methods, we can go to higher accuracy in the complete basis set limit than is practical for conventional Gaussian basis sets, with errors near 0.1 mH per atom.

Electronic structure calculations on molecules, solids, and biological systems are performed by thousands of groups worldwide and account for a substantial fraction of the world’s scientific computing. Strongly correlated systems, for which density functional approaches are inadequate, make up a small but important fraction of these calculations. An almost universal problem with methods for strong correlation is poor computational scaling in both system size and accuracy. For example, wavefunction methods, such as coupled cluster or configuration interaction, typically scale as $N^6$ or higher for $N_e$ electrons. Since correlation methods must deal with the two-electron interaction directly, scaling of at least $N^4$ when using $N$ basis functions can appear hard to avoid, since the two-electron interaction terms are described by a tensor $V_{ijkl}$ with four indices running over $N$ values.

A natural way to reduce the size of the $V_{ijkl}$ tensor is through local basis functions. In the extreme case of a grid discretization, the interaction is reduced by a factor of $N^2$ to a matrix $V_{ij}$, with $V_{ij} = 1/|\vec{r}_i - \vec{r}_j|$ for $i \neq j$. For the less extreme case of basis sets where the functions have substantial spatial compactness, we say that two basis functions $b_i$ and $b_j$ “overlap” if there is some point $\vec{r}$ where $b_i(\vec{r})b_j(\vec{r})$ is significantly different from zero. Terms in $V_{ijkl}$ are negligible unless basis functions $i$ and $j$ overlap and also $k$ and $l$ overlap. However, in three dimensions, even for substantially localized functions, many basis functions overlap, particularly if the functions have been orthogonalized, and one may not realize a significant increase in the sparseness of $V_{ijkl}$ for systems small enough to study feasibly. This is unfortunate, since basis methods have several advantages over grids, such as the ability to add extra atom-centered core functions to better resolve the nuclear cusps.

Recently one of us introduced a novel basis function approach that has the same favorable scaling of the interaction as a pure grid [1]. This involved two key ingredients: first, the introduction of a wavelet-related set of highly localized, smooth orthogonal basis functions, called gausslets, where each function is defined as a sum over an underlying grid of simple Gaussians. Second, it was shown that one can construct an accurate purely diagonal interaction $V_{ij}$ for a gausslet basis. This diagonal interaction for a special type of basis is not new in itself: a basis of sinc functions also allows this construction [2]. However, the extreme delocalization of sinc functions is a severe disadvantage as a basis; the gausslet development in Ref. 1 shows that one can get the diagonal property with much more localized functions, where it is based on the ability of gausslets to integrate like a delta function. But the usefulness of gausslets was previously only demonstrated for 1D toy systems.

Here we generalize the gausslet approach to three dimensions and practical electronic structure calculations. Given a 1D basis, one can always generate a 3D basis as coordinate products, i.e. $G_{ijk}(x, y, z) = f_i(x)g_j(y)h_k(z)$. This simple approach produces overly large basis sets. Instead, we introduce coordinate transformations which put more functions near nuclei, and a procedure called multislicing which allows the use of 1D coordinate transformations rather than more complicated 3D transformations. Our multisliced gausslet (MSG) approach is a generalization of our earlier sliced basis approach [3]. We demonstrate the resulting method on hydrogen chain systems [4], using both Hartree Fock and the density matrix renormalization group (DMRG) [5–7]. In both cases the diagonal property allows for dramatically increased basis set size and high accuracy. The combination of MSG and DMRG (MSG-DMRG) allows for simultaneously exact correlation and the complete basis limit, going well beyond chemical accuracy in a controlled way. The MSG-DMRG approach also features approximately linear scaling in one of the directions (which we take to be $z$) along which the system is most extended.

In standard orthogonal wavelet theory, basis sets are made of two types of functions, scaling functions, which carry low momentum, and wavelets, which carry a range of higher momenta. Gausslets are scaling-function-like functions, which are constructed out of sums of Gaussians for convenience. A set of gausslets are shown in Fig. 1(a), highlighting a single gausslet in the center of the figure. To make a 1D basis, one puts a gausslet at each point on an evenly spaced grid, scaling them to match the grid spacing. The oscillatory tails make the gausslets precisely
orthonormal, and they can exactly represent polynomials up to some predetermined order (e.g. 10th order).

Modifying the gausslets with coordinate transformations allows spatially varying resolution. Let $x(u)$ and its inverse $u(x)$ define a 1D smooth one-to-one coordinate mapping, which will be used to make the grid narrow and closely spaced near nuclei, and wide and sparse far away. First consider a 1D arrangement, with just one atom at $x = 0$. Define the gausslets on a uniform grid in the $u$ space and then map to $x$-space, inserting a Jacobian factor to preserve orthonormality. If $G_j(u)$ is a gausslet centered at integer $j$, define

$$\tilde{G}_j(x) = G_j(u(x))\sqrt{u'(x)}.$$

(1)

It is easy to see that the $\tilde{G}_j$ are orthonormal if the $G_j$ are. An approximate local density of gausslets (i.e. inverse spacing) is $\rho(x) = u'(x)$. To choose $u(x)$, consider moving from a nucleus with a high density of basis functions to the tail region with a low density. If one changes the density too quickly, the ability of the basis to represent low-momentum functions will be compromised. It is natural to require the fractional change in $\rho$ when moving from one gausslet to the next to be roughly constant. Thus, one wants

$$\frac{d\rho}{du} \propto \rho.$$

(2)

This implies that $\rho$ falls off as $\sim 1/x$. For small $x$, we need to choose a maximum finite resolution, while keeping $\rho$ smooth. For a single atom, we choose

$$\rho = \frac{1}{s\sqrt{x^2 + a^2}}$$

(3)

where the parameter $s$, the scale, sets or adjusts the overall gausslet spacing, and $a$, the core cutoff, sets the range in $x$ over which we stop decreasing the gausslet spacing. The smallest gausslet spacing at the nucleus is about $a \cdot s$. This form for $\rho$ integrates to give

$$u(x) = \sinh^{-1}(x/a)/s$$

(4)

This transformation is shown in Fig. 1(b), with the resulting 1D functions shown in Fig. 1(c).

For multiple atom 1D systems, one can attempt to add a density of this form for each atom, but the long tails build up too high a density in the center. In the Supplementary Material we describe the simple modification of summing the densities that we use for many atoms [8].

If there were no coordinate transformation, we could make 3D basis functions as single products of gausslets $G_i(x)G_j(y)G_k(z)$. This coordinate-product form greatly simplifies evaluation of integrals defining the Hamiltonian. To keep this form, we apply coordinate transformations to each coordinate separately, in a method we call “multislicing”. In multislicing, the coordinate directions are sliced up sequentially, $z$, then $y$, then $x$. A first coordinate transformation $u^2(z)$ determines a set of $z$-values $z_k$ ($k = 1, 2, \ldots$), with $u^2(z_k) = k$, at which are centered distorted 1D gausslets $\tilde{G}_k(z)$. The plane $z = z_k$ and function $\tilde{G}_k(z)$ together define a $z$-slice. Next we slice up each $z$-slice in the $y$ direction, with a coordinate transformation unique to $k$, $u^2_k(y)$, which defines a set of $y$-values $y_{kj}$. A $y$ “slice” (or “subslice”) of a “parent” $z$-slice is the line $z = z_k$, $y = y_{kj}$, with associated 2D function $\tilde{G}_k(z)\tilde{G}_j(y)$. Finally, for each $y$-slice, define a unique coordinate transformation $u^2_{kj}(x)$, determining a set of $x$ values $x_{kji}$, and 3D basis functions $\tilde{G}_k(z)\tilde{G}_j(y)\tilde{G}_j(x)$. The key point in using this successive procedure is to use of the knowledge of where a slice is, relative to the nuclei, to make subsequent transformations with the lowest density of functions. This is illustrated schematically in 2D in Fig. 1(d). Preserving the product form via multislicing means that some basis functions are long and thin; however, at a later stage on can devise methods to contract such functions with their neighbors, reducing unnecessary degrees of freedom. The details of the coordinate transformations in the multisliced case are discussed in the Supplementary Material.

Each basis function has a well defined center $(x_{kji}, y_{kj}, z_k)$, and we can make a simple rule for which

FIG. 1. (a) Array of gausslets, with the gausslet centered at the origin emphasized to show detail. (b) Coordinate transformation function $u(x)$ for a single atom, with $a = s = 0.7$ in Eq. (3), to give gausslets variable resolution. (c) Distorted gausslet basis based on the transformation of (b), which is orthonormal and allows a diagonal approximation. One of the functions is emphasized. (d) Schematic representation of multislicing in 2D. The vertical lines represent slices, with three shown in detail. Each dot is the center of a basis function, and the shaded rectangles illustrate the principal support region of some of the functions, although they have smooth tails well beyond the rectangles. The multicolored shaded rectangles represent long, thin basis functions which one would want to contract at a later stage.
functions to keep: if the basis function is within a distance $b$ of an atom, we keep it. Here $b = 9$ a.u. proved very accurate ($< 0.1$ mH errors compared to larger $b$) except for $R = 1$ for H$_{10}$, where we used $b = 13$.

Figure 2(a) shows energies for a single hydrogen atom for various $a$ and $s$, using both the standard full Hamiltonian and using a Hamiltonian matrix for which a diagonal approximation is made for the single particle potential [1]. Since there are only $N^2$ single particle terms, not $N^4$, using this diagonal approximation barely improves computational efficiency, but one would expect this approximation to mimic the performance of the more important two-particle diagonal approximation. The diagonal approximation is sensitive to the singularity in the potential at the nucleus, but increasing the basis function density near the nucleus by decreasing $a$, for fixed $s$, nearly eliminates the diagonal approximation error. A simple procedure to systematically converge to the ground state for this system would be to fix $a/s$ to be a constant, say 0.5-0.6, and then decrease $s$.

Figure 2(b) shows the energy for a hydrogen molecule, compared to standard basis sets cc-pVxZ, where x=D, T, and Q, and also compared to the exact energy from a treatment in special coordinates [9]. A diagonal approximation for the two particle interaction is used here and in all subsequent MSG bases, since calculations would not be practical with the standard $V_{ijkl}$ form. All results shown are exact (full CI) given the approximate Hamiltonian. The MSG bases systematically converge to the exact results, and the diagonal approximation for the single particle potential closely approximates the full Hamiltonian, particularly for smaller $s$.

Also shown in Fig. 2(b) is a basis with a special delta-function correction for the nuclear cusp. Increasing the resolution near nuclei by using a small $a$ is inefficient, leading to many basis functions. For example, for the hydrogen atom of Fig. 2(a), taking $a = 0.3$, $s = 0.6$ produced 1179 functions, which resulted in an error of 0.13 mH. Our correction consists of adding a single-particle potential at each atom $\alpha$ of the form $\nu_\alpha \delta(r^2 - r_\alpha^2)$.

The parameter $\nu_\alpha$ is set by “turning off” all nuclear electron potentials for atoms other than $\alpha$ (yet keeping the same set of functions to be used for the entire system), and adjusting $\nu_\alpha$ so that the one-electron ground state energy is the exact hydrogen atom energy $-1/2$. The errors associated with choosing $\alpha$ too large are localized near the nuclei; the delta function potential alters the terms in the Hamiltonian only for the basis functions overlapping with a nucleus. Most importantly, $\nu_\alpha \to 0$ as $a \to 0$ or $s \to 0$, so this correction does not change what the basis converges to, only how fast it converges, accelerating the convergence. In Fig. 2 and for the rest of the results, we set $a = s$ and use the delta correction.

We now turn to a more challenging system, a linear chain of hydrogen atoms spaced $R$ apart. Hydrogen chain systems were the subject of a recent benchmark study, comparing more than a dozen methods, where the main goal was to reach the combined limit of exact correlation, complete basis set, and infinite number of atoms [4]. We first consider unrestricted Hartree Fock (UHF) on H$_{10}$, shown in Fig. 3. The plot shows HF energy differences relative to those of a large Gaussian basis, cc-pV5Z. The convergence of the MSG basis is irregular because the centers of the gausslets are not aligned with the nuclei; but it is easy to get very accurate results and judge the accuracy. At small $R$, the Gaussian basis sets have trouble due to linear dependence [4], leading to a small but noticeable discrepancy between the 5Z and MSG results. As shown in the inset, at $R = 1$ the Gaussians converge slowly, and different extrapolations give different results.
As a rough comparison of the calculational effort for these very high accuracy calculations: for \( R = 1 \), \( a = s = 0.5 \), the MSG basis has just over 13,000 basis functions; the number of two-electron integrals is the square of this, or \( 1.7 \times 10^8 \). The 5Z basis has 550 functions, but the number of integrals \( (N^4, \text{ignoring symmetry}) \) is \( 9.2 \times 10^{10} \). The calculation time of our UHF algorithm, which takes advantage of the diagonal nature of the Hamiltonian, scales as \( N^2 N_e \), where \( N_e \) is the number of electrons, with the dominant part coming from a Davidson diagonalization, for \( N_e \) eigenvectors, of the Fock matrix.

For correlated calculations, to decrease the number of basis functions, one can use the HF occupied orbitals to contract the MSG basis to smaller size. This can be done in a way that maintains the diagonal form of the interactions. One can also extrapolate in a cutoff that controls this contraction, to obtain results for the uncontracted basis. The largest systems needed for an extrapolation are still about a factor of 2 or 3 smaller than the uncontracted basis, and the results below follow this procedure, which is described in the Supplementary Material.

We now turn to MSG-DMRG calculations for \( \text{H}_{10} \). Our DMRG implementation uses the matrix product operator compression of our earlier sliced basis DMRG (SB-DMRG) approach [3]. This compression makes the calculation time for fixed accuracy per atom scale linearly in the number of atoms in a hydrogen chain both in SB-DMRG and MSG-DMRG. We are currently limited to about 3000–4000 basis functions. (In contrast, standard DMRG in a Gaussian basis—with no diagonal approximation and no compression—is limited to about 100–200 active basis functions.) We find that the DMRG performs very well. For the very high accuracy results shown below, we generally only needed to keep about 200 states for larger \( R \), and up to 400-500 for \( R = 1 \) (due to its more metallic character). This excellent performance is due to the high locality of the basis, which DMRG and other tensor network methods [10–12] strongly prefer.

We find that the correlation energy converges faster with \( s \) than the HF energy. This is not surprising: the representation of the nuclear cusp is poor with a coarse gausslet basis, which is is primarily a single particle effect. Therefore, to get total energies we use the HF energy with very small \( s \), and add to it the correlation energy obtained with a larger \( s \), where the correlation energy is defined by subtracting the unrestricted HF energy from the total energy for the same basis set.

In Fig. 4, we show a comparison of total energies for several methods [4] and our MSG-DMRG for various \( s = a \). All methods attempt to reach the CBS limit; for all but the MSG-DMRG and DMC methods, this involved an extrapolation in the basis set. The energy differences here are generally well below chemical accuracy. Often such high accuracy is unnecessary, but studying the high accuracy limit is an excellent way to demonstrate the usefulness of MSG-DMRG. The energies are measured relative to one of the diffusion Monte Carlo methods, LR-DMC-AGP (or DMC). In Ref. [4], at this level of accuracy, none of the best available methods agreed, so it was not known which was best, and reference plots were made relative to MRCI+Q for smaller systems and AFQMC for larger ones. DMRG based on standard Gaussian basis sets could not be done beyond the TZ level, so no CBS results were available. Here, we find systematic convergence of MSG-DMRG to energies agreeing with the LR-DMC-AGP method. Agreement was poorer at small \( R \) with a DMC method based on an LDA trial function. There are systematic errors in DMC stemming from the fixed node approximation, which are unusually small in this 1D system, but hard to quantify. Since the nature of errors in DMC and MSG-DMRG are completely different, and since the MSG-DMRG energies converge systematically with a control parameter, we can be rather sure that MSG-DMRG and DMC are both getting the most accurate energies.

The MSG-DMRG errors for fixed \( s = a \) are biggest at small \( R \). This is expected; at small \( R \), it would be more natural to scale \( s \) with \( R \), keeping the number of basis function more nearly constant. The smallest grid spacings are about \( a \cdot s \), or about 0.5 for \( s = 0.7 \). Small \( R \) is challenging to the Gaussian basis set methods because the basis functions become linearly dependent.

In this strongly correlated test system in the CBS limit we have demonstrated that MSG-DMRG can be significantly more accurate than existing approaches based on Gaussian basis sets. The MSG bases can be applied to a much wider range of systems, but more work needs to be done in going to larger-Z atoms. It will also be interesting to explore what the favorable computational scaling of MSG bases allows one to do when one is only interested in more limited (e.g. “chemical”) accuracy.

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Supplemental Material for Multi-sliced Gausslet Basis Sets for Electronic Structure

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I. COORDINATE TRANSFORMATIONS FOR TWO OR MORE ATOMS

In the main text we wrote down a simple the ansatz for the local density of gausslets around a nucleus at the origin in 1D

\[ \rho = \frac{1}{s\sqrt{x^2 + a^2}} \]  

where \( s \) sets the overall gausslet spacing and \( a \) sets the core size. It may be desirable to limit the maximum spacing far from atoms, in which case we can modify this to

\[ \rho = \frac{1}{s\sqrt{x^2 + a^2}} + \frac{1}{d} \]  

where \( d \) is the maximum spacing. The density at a nucleus is thus \((as)^{-1} + 1/d\). First consider a line of atoms in 1D. The \( 1/d \) term, if desired, should always be included only in the final expression for \( \rho \), not summed over. Even with the \( 1/d \) term omitted, if we simply add the basis function densities \( \rho \) for each atom, we find a problem: the slowly decaying \( 1/x \) tails of \( \rho \) lead to too high a density in central regions.

To add densities with less buildup and to set a maximum spacing, we can consider the ansatz

\[ \rho(x) = \left[ \sum_{\alpha} \rho_{\alpha}(x)^2 \right]^{1/2} + \frac{1}{d} \]  

where \( \alpha \) labels nuclei. With this form we need to determine \( u(x) \) via numerical integration. This ansatz for \( \rho \) decreases the buildup, but it still puts a greater density in the center of a chain compared to the edges. To fix this, in addition to using Eq. (3), we make the core size an adjustable parameter for each atom, \( a \rightarrow a_\alpha \). By increasing \( a_\alpha \), we can decrease the function density at nucleus \( \alpha \). We use a simple nonlinear minimization to adjust all the \( a_\alpha \) so that the density at each nucleus is a target desired density, which we take as \((as)^{-1}\), the one atom density without any \( 1/d \) term.

We now consider transformations for a chain of atoms in 3D, where atoms have locations \((0,0,z_\alpha)\). For the \( z \) transformation (there is only one) we use the recipe of the previous paragraph. (We would ignore the \( x \) and \( y \) coordinates of each atom in this case even if the atoms were not in a chain.) Next, consider the \( y \) slicing, where we need to choose the parameters defining \( u_\alpha^y(y) \), which determines the \( y \) slicing for a specific \( z \)-slice labeled by \( k \). In the case of chains, where all nuclei have the same \( x \) and \( y \) coordinates, there is effectively only one atom (at the origin) for the \( x \) and \( y \) slicings, and we use Eq. (2). A slice far from all nuclei does not need the density of functions that a near-nucleus slice does, so it should see a bigger core size, \( \tilde{a} > a \). Let \( d_k \) be the distance from the nearest nucleus to \( z \)-slice \( k \) (a plane), i.e. the minimum of \(|z_\alpha - z_k|\) over \( \alpha \). Then we define \( \tilde{a} \) as

\[ \tilde{a} = \sqrt{d_k^2 + a^2}, \]  

Then \( u_k^y(y) \) is determined via Eq. (1) with \( \tilde{a} \) in place of \( a \). The \( x \) slicing is very similar, where instead of \( d_k \), we use \( d_{kj} \), the distance of the \( y \) slice \((k,j)\), which is a line, to the nearest atom.

For an arbitrary 3D arrangement of atoms, the \( z \) slicing would follow the same recipe. The \( y \) and \( x \) slicing would need to use Eq. (3), with effective core sizes \( \tilde{a}_\alpha \). For nuclei far from a slice, one would not want to include any terms in \( \rho \) to modify the density. Precisely specifying how to do this in an arbitrary arrangement would take some experimentation with different recipes, which we have not done.

For almost all the calculations here we have set \( d = 3 \). This choice was based mostly as a small multiple of the decay length in a hydrogen atom: the wavefunction changes on a length scale of order 1, so it does not make much sense to use any functions much larger than this scale. Changing \( d \) should only affect how fast the results converge in \( s \), not what they converge to. The exception is for \( \text{H}_{10} \) at \( R = 1 \). Here, during the HF calculations, we discovered that this system has more extended tails of the wavefunction. This showed up when we adjusted the parameter \( b \) which sets the radius around each nucleus within which we included basis functions, finding that we needed to increase \( b \) from 9 to 13 for accuracies below 0.1 mH. The presence of long tails suggested that we increase \( d \) also, and we ended up using \( d = 9 \), with tests showing nearly identical HF energies for \( d = 7 \) and \( d = 5 \).

II. CONTRACTIONS OF AN MSG BASIS USING HARTREE FOCK ORBITALS

For correlated calculations, it is sometimes helpful or necessary to decrease the number of basis functions, contracting them to a smaller basis. The key question is: what sorts of contractions can be performed which maintain the diagonal form of the two particle interaction? (It seems to be much easier to start with a diagonal form and maintain it through contractions, as opposed to starting with a smaller conventional non-diagonal basis and produce a good diagonal Hamiltonian.) Consider
partitioning the MSG basis functions into disjoint sets of functions, e.g. \{g_1, g_2, g_4\}, \{g_3, g_5, g_{10}\}, ... If we contract each set into a single function, e.g. specifying contraction coefficients \{c_1, c_2, c_3\}, ... then it is simple to show that the interaction for the contracted basis has a diagonal \(V_{ij}\). Also, if one contracts to \(N_b\) functions within each set, with no contractions straddling sets, the interaction takes a block diagonal form with \(N_b^2 N^2\) total nonzero elements, where \(N\) is the new number of functions. This approach is reminiscent of the discontinuous Galerkin method, which has been used for density functional theory calculations; sliced basis DMRG also produce this blocked interaction.

Given the one body reduced density matrix (RDM), also known as the single particle equal time Green’s function, an optimal choice for the contraction coefficients for a set would come from diagonalizing the small block of the RDM connecting the functions in the set. The eigenvectors with maximum occupancy (i.e. eigenvalue) give the optimal contraction coefficients. Here, we have used the approximation for the RDM coming from the occupied orbitals of UHF, where we spin average the RDM to get purely spatial basis functions. This choice has the property that if the largest set occupancy which we do not keep is negligible, then the basis contains the UHF wavefunction. The energy is at least as good as, and normally much better than UHF.

Generally, we want to form our disjoint sets to respect spatial locality. One simple approach is to group functions by atom, assigning each function to the closest atom. This can give quite small basis sets, with block diagonal interactions. This approach could be very useful for use with quantum computers. Alternatively, we can try to maintain the fully diagonal form with \(N_b = 1\), at the expense of larger \(N\). This is useful in trying to reach the complete basis set (CBS) limit. In Fig. 2(d) (main text) we show several long-thin colored blocks which would be good candidates for contracting into one function. We can use the contractions to improve the efficiency of the MSG basis by combining similar sets of functions, particularly in the outer tails of the system. Here we describe a contraction approach which reduces the \(N\) by a factor of about 2-5, which allows extrapolation in a contraction parameter, allowing us to obtain energies of the original MSG basis, as if there were no contraction.

Let us assume we have done unrestricted Hartree Fock and gotten a set occupied spin orbitals. We use the occupied orbitals \(\phi_{\uparrow p}(i)\), where \(p\) labels orbitals and \(i\) labels MSG basis functions, to form an up reduced density matrix (RDM) as

\[
C_{ij}^\uparrow = \sum_p \phi_{\uparrow p}(i) \phi_{\uparrow p}(j) \tag{5}
\]

and similarly for \(C_{ij}^\downarrow\). Then we use the spin averaged RDM, which is \((C_{ij}^\uparrow + C_{ij}^\downarrow)/2\).

We can form a block of the RDM for any subset of the MSG basis functions, i.e. \((i_1, i_2, ...\). Let \(w_\alpha\) be the eigenvalues of this blocked RDM. Let us also refer to this set of functions itself as a “block”. If the block was the whole basis set, then the corresponding eigenvectors would be the natural orbitals, forming an optimal basis (in some sense) for contraction. The eigenvectors of the block-RDM have similar properties. In particular, if the second eigenvalue (sorted in decreasing value; all are non-negative) is negligible, we can contract to the first eigenvector without making any truncation in the HF wavefunction. This contraction would replace the block by one contracted function. The contraction coefficients would be the leading eigenvector. If we have used the diagonal approximation for the MSG basis for the two electron interaction, this contraction to a single function leaves the interaction fully diagonal. This process can be repeated for more blockings, or done simultaneously, keeping in mind that all blocks are disjoint, i.e. no indices in common.

More practically, we can choose a cutoff \(\epsilon_2\) for the size of the second eigenvalue to control whether this contraction is allowed. We would like to contract to as few functions as possible subject to this cutoff for whether a contraction is allowed. It is most efficient to search through pairs of indices, checking whether the second eigenvalue satisfies the cutoff. If it does, then we can contract those two functions together. This can be continued, contracting pairs of functions which have themselves already been contracted. The actual numerical transformation of the Hamiltonian matrices does not need to be done at each step; it can be delayed to the end. Then it is natural, and more optimal, to simply collect the indices making up each block. We can start by making \(N\) blocks, each containing just one index. Then we join pairs of blocks using the cutoff criteria, but the joining is just to merge the sets of indices. Each diagonalization of a blocked RDM is over all the indices in the block, so that the optimal leading eigenvector is obtained with the full freedom of the joined block. How do we search through the pairs of blocks to find blocks to join, if they satisfy the cutoff? One natural way is to look for nearest neighbor blocks, assuming the initial functions are sorted. Once all near neighbor blocks that can be paired are joined, one can look for pairings of more distantly separated blocks. But the precise recipe for joining blocks does not appear to matter very much.

How should the MSG functions be sorted to start this procedure? In 2D DMRG for square lattice models one typically orders sites in a way that looks like a snake: one proceeds column by column, going up one column then down the next. One could do the same thing in a 3D cubic lattice, in order to keep adjacent sites in the 1D list near each other in 3D. One can also do the same ordering in a 3D multisliced context, which we do. This provides an excellent ordering for DMRG even if we do not do any contractions.

This procedure cannot recover the full natural orbitals. Even one natural orbital would extend over the whole system, so it would require a contraction of all functions. I
The key “trick” in evaluating matrix elements is to replace the Coulomb interaction by a sum of Gaussians, a trick which has been known for a long time. Specifically, one can write

$$1/r = \sum_i c_i e^{-a_i r^2}$$

with properly chosen coefficients $a_i$ and $c_i$. Since the integral evaluation ends up being a minor part of our computations, we have chosen a very accurate 220 term representation that is very accurate (better than $10^{-8}$) over a wide range of $r$ ($10^{-8}$ to $10^0$). Representations with fewer terms are known and would be useful if the matrix element evaluation became too time-consuming.

This trick separates 3D integrals into products of 1D integrals for basis functions which are in the coordinate product form, as MSG functions are. For example,

$$\int_{F} e^{-a_i r^2} f(x) g(y) h(z) = \int_{x} \int_{y} \int_{z} e^{-a_i x^2} f(x) e^{-a_i y^2} g(y) e^{-a_i z^2} h(z).$$

One performs the sum over $i$ as the outermost operation.

For the two electron interaction the trick replaces 6D integrals by 2D integrals. For example,

$$\int_{F,F'} e^{-a_{ij}(\vec{r}-\vec{r}')^2} f_1(x)g_1(y)h_1(z)f_2(x')g_2(y')h_2(z') = \left[ \int dx dx' e^{-a_{ij}(x-x')^2} f_1(x)f_2(x') \right] \ldots$$

The justification for using $\epsilon_1$ is that if the occupancy of this block is very small, there is very low probability for two electrons to doubly occupy the block, so there is little need for a second function to describe the local dynamic correlation. However, while this motivation provides a reason for trying this procedure, the key point is that using $\epsilon_1$ and $\epsilon_2$ together works and is useful. Using this procedure for contractions, we have explored the effects of the cutoffs, applying DMRG so find the ground state energy of the resulting Hamiltonians. We find that the error in the energy from these cutoffs varies linearly with the cutoff, and can be extrapolated. The $\epsilon_2$ cutoff is more important, since it controls the representation of the HF wavefunction, so $\epsilon_2$ should be smaller. A reasonable choice is to lock the two together with a fixed ratio. In Fig. 1 we show results for a typical $H_{10}$ system with $\epsilon_2 = \epsilon_1/100$. For small enough cutoffs, we see linear dependence of the energy on the cutoff, which can allow reasonable extrapolation, as shown.

The extrapolations are somewhat improved by separating out the correlation energy and extrapolating that, rather than the total energy. The correlation energy can be added to the HF energy without any contractions for the MSG basis. This gives the energy for a particular MSG basis, primarily defined by the parameters $a$ and $s$, where we normally take $a = s$. As discussed in the main text, one can then also separate out the correlation energy to improve the convergence with $a = s$. In this case, we take the correlation energy for say $a = s = 0.8$, and add it to the HF energy obtained from much smaller $a = s$. This procedure was used for the $H_{10}$ results in the main text.

III. EVALUATION OF HAMILTONIAN MATRIX ELEMENTS FOR THE MSG BASIS

FIG. 1. Energy of $H_{10}$ with $R = 2$, with $a = s = 0.8$, versus $\epsilon_1$, where $\epsilon_2 = \epsilon_1/100$. The red circles show the energy with that cutoff, from DMRG. The DMRG runs have been extrapolated in the truncation error, with error bars shown. The black squares show a separate treatment of the same energies. Here, the correlation energy is obtained (using the same DMRG runs as for the red squares), and a separate UHF calculation for that cutoff. Then each correlation energy is added to the UHF energy for zero cutoff. The green line shows a linear fit to the black points, ignoring the point with $\epsilon_1 = 0.005$. This separate correlation treatment was used for the analysis in the main text.
where the dots represent similar terms for $y$ and $z$.

There are many such 2D integrals to do, so it is important to do these efficiently. There are a wide variety of approaches one could take for this computational task. Our approach was loosely based on the definition of 1D gausslets as a sum of equal-width Gaussians centered on a uniform grid. This defining array-of-Gaussians representation is an excellent basis in many respects, except that it is not orthogonal. But for evaluating integrals, nonorthogonality of an underlying representation is not important. The widths of the Gaussians is chosen to be the grid spacing, but any fixed width bigger than about this would make an excellent basis able to represent almost any function smooth at the scale of the grid. If there were no coordinate transformations, this representation would immediately translate integrals over the 1D basis functions into sums of analytic integrals of the underlying Gaussians.

Unfortunately, the coordinate transformations distort the representation into a nonuniform sum over distorted Gaussians, for which there are no analytic integrals. So, instead, we create a representation of the basis functions as a sum of undistorted but unequal width, unequally spaced Gaussians. The widths and locations of come from a coordinate transformation.

We first create coordinate transformations that put a higher density of functions near nuclei. Instead of multislicing, we choose exactly three 1D coordinate transformations, for $x$, $y$, and $z$. These coordinate transformations are chosen so that the local spacing between grid points is sufficiently small to represent all details of the 1D basis functions arising in the multislicing. This makes these grids finer than the basis grid where the MSG functions live by at least an order of magnitude. For the case of the $x$ direction, we have a function $x(u)$, with grid points $x_i = x(i)$, and local spacing $dx/du$. We put a Gaussian at each grid point, with a width given by $adx/du$. We choose $\alpha > 1$ to make up for the unequal grid spacings; for a uniform grid, $\alpha = 1$ is fine. We find that $\alpha = 1.25$ is a good choice, and we find that it is possible to represent all our 1D basis functions in terms of this array-of-Gaussians representation with high accuracy. We find the coefficients of the Gaussians for each 1D basis function using a least squares procedure. The unequal spacing means that there are many fewer degrees of freedom than the simplest approach one might take, using a uniform very fine grid to represent all the 1D functions.

Once all functions are defined in terms of Gaussians, all integrals (kinetic, and one and two particle potential integrals) are analytic, and the main work is summing over the various terms. We implemented the Hamiltonian construction in the Julia language, and our code runs fast enough to take much less time than the DMRG calculations and also usually less time than the HF calculations.

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