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The completeness properties of Gaussian-type orbitals in quantum chemistry

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In this work, I extend results on the convergence of Gaussian basis sets, previously shown for ground state hydrogenic wavefunctions, to orbitals of arbitrary angular momentum. I give rigorous proofs of their asymptotic behaviour, and demonstrate that for methods with regular potential operators - in particular, Hartree-Fock and Kohn-Sham density functional theory - that the assumption of completeness is correct under fairly lenient conditions. The final result under the correct norm is that the convergence in energy follows $\exp(-k\sqrt{M})$ where M is the number of Gaussians and k is a positive constant, generalizing previous results due to Kutzelnigg. This then yields prescriptions for accelerated convergence using even-tempered Gaussians, which could be used as initial guesses in future basis set optimizations.

Keywords — quantum chemistry, basis sets, completeness, gaussians, orbitals, analysis.

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I. INTRODUCTION

Non-relativistic quantum chemistry focuses on the solution of the Schrödinger equation to obtain the wavefunction for the system. From this, expectation values for observables - in particular, the energy - can be calculated. Construction of a wavefunction using computers requires discretization of a continuous problem, and this is normally achieved by expansion of the wavefunction in terms of molecular orbitals. These orbitals are themselves then expanded as linear combinations of one-electron functions, termed a basis set. Most commonly, these functions take the form of Gaussians in the radial part, with spherical harmonics describing the angular part[1,2].

Much work has previously focused on the completeness of the description of an N-electron wavefunction in terms of Slater determinants[3,4], but the more specific problem of the discrete representation of the one-electron functions has been less well explored. In fact, it is *de facto* assumed that simply by adding more Gaussians, convergence of the energy will be achieved towards the so-called "complete basis set" (CBS) limit[5–8] - that is, the lowest energy achievable within whatever ansatz is used - and basis set extrapolation schemes take advantage of this[9–12].

The first real consideration of this was by Klahn and Bingel in the late '70s, who demonstrated some sufficient criteria for completeness[13]. It was not until several years later with work by Hill[14], and then Kutzelnigg[15–17], that the asymptotic details of convergence, rather than hypothetical completeness, were considered in any detail. The latter work has variously shown three convergence patterns, the most favourable of which he demonstrated most recently for ground-state hydrogenic wavefunctions, with an innovative use of Gaussian transforms[17]. Finally, Bachmayr and coworkers[18] in 2014 gave a rigorous proof, and asymptotic analysis of, the completeness of even-tempered Gaussian bases. Here, I will show using simpler methods that the approach of Kutzelnigg can be extended much more generally to all mean-field wavefunctions constructed using Gaussian-type orbitals. Moreover, I will demonstrate it for convergence in the correct energy norm, giving detailed comparison with other weaker measures of error, remarkably ending up at the same result despite considerable differences in the error distributions. This indirectly is a representation of how the electronic cusp dominates the error, as should be expected from work on explicitly-correlated methods[19–21].

Within the formalism of second quantization, both the observables and the wavefunction are written in terms of operators, with the formal (anti)symmetry requirements following from the underlying Lie algebra of these operators. I briefly introduce this formalism, before expounding upon the representation of the wavefunction in a finite basis. This discretization of a continuous operator has an associated error, which vanishes in the limit of a complete basis, and is thus termed the basis set incompleteness error (BSIE). The conditions under which a particular choice of basis becomes complete and how this affects the convergence of energy calculations forms the main focus of this article.

II. WAVEFUNCTIONS

Conventionally, a given system in quantum chemistry is represented using a basis of M orthonormal one-electron spin orbitals $\{\phi_P\}$ in some Hilbert space, H, depending on the nuclear and spin coordinates, $\mathbf{x}_i$ of an electron i.[41] For a system of N-electrons, N such orbitals are combined into a Slater determinant:

$$|\phi_{P_1}\phi_{P_2}\cdots\phi_{P_N}| = \hat{A}\left[\phi_{P_1}(\mathbf{x}_1)\phi_{P_2}(\mathbf{x_2})\cdots\phi_{P_N}(\mathbf{x_N})\right] \tag{1}$$

where the operator $\hat{A} = N^{-1/2}\sum_{\hat{\pi}\in S_N}\hat{\pi}$ is an antisymmetriser, permuting electron coordinates according to the symmetric group S_N. The total N-electron wavefunction can then in principle be represented exactly by linear combinations of Slater determinants in the limit that the spin orbital basis tends to completion. In practice this is restricted to finite M, rather than taken to infinity. These Slater determinants span a space comprising the N-fold tensor product of Hilbert spaces, and the set of all such N-dimensional spaces form a Fock space. In the formalism of second quantization, points in Fock space are represented in terms of creation and annihilation operators, $a_p^\dagger$ and a_p, acting on the vacuum.

Any operator representing a physical observable must be number conserving, and thus be represented with equal numbers of creation and annihilation operators. In particular, an m-electron operator will involve the destruction and creation of particles in m orbitals.[42] The non-relativistic, molecular electronic Hamiltonian in second quantization notation (and atomic units) is written as a sum of one- and two-electron operators:

$$\hat{H} = \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \frac{1}{2}\sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q \tag{2}$$

where the matrix elements are defined to be

$$h_{PQ} = \int d^4\mathbf{x}_1 \ \phi_P^*(\mathbf{x}_1)\hat{h}_1\phi_Q(\mathbf{x}_1) \tag{3}$$

$$g_{PQRS} = \int d^4\mathbf{x}_1 \ d^4\mathbf{x}_2 \ \phi_P^*(\mathbf{x}_1)\phi_R^*(\mathbf{x}_2)\hat{V}_{12}\phi_P(\mathbf{x}_1)\phi_S(\mathbf{x}_2) \tag{4}$$

In general, the spectrum of the molecular Hamiltonian will comprise continuous and point spectra, corresponding to free and bound states, where we are primarily interested in the latter. If we consider the expectation value over a particular state vector, $|n\rangle$, we see that the one-electron term gives $h_{PQ} \langle n|a_P^\dagger a_Q|n\rangle$, such that the left- and right-vectors differ in their occupations of orbitals P and Q. The orthonormality of the spin orbitals then implies that this is zero unless $P = Q$. Similarly, for the two-electron terms, we must either have $P = Q, R = S$, or $P = S, R = Q$, with the latter carrying a negative sign due to the exchange of S and Q. The total energy of this state is thus given by:

$$E_n = \langle n|\hat{H}|n\rangle = \sum_P h_{PP} + \frac{1}{2}\sum_{PR}\left[g_{PPRR} - g_{PRRP}\right] \tag{5}$$

A. Rayleigh-Ritz and Galerkin methods

The central problem of quantum chemistry is thus to find the eigenstates and eigenvalues of the above Hamiltonian. In practice, the dimensionality of the problem requires the use of computers, which in turn necessitates discretizing the equations. For simplicity and clarity, we consider the one-electron, spin-integrated case,[43] posed as follows: find $\lambda \in \mathbb{R}$ and $u \in H^1(\mathbb{R}^3)$ with $\|u\|_{L^2(\mathbb{R}^3)} = 1$, such that

$$a(u, v) = \lambda \langle u|v\rangle \ \ \forall \ v \in H^1(\mathbb{R}^3) \tag{6}$$

where we have defined the bilinear form

$$\begin{aligned} a : H^1(\mathbb{R}^3) \times H^1(\mathbb{R}^3) &\to \mathbb{R} \\ (u, v) &\mapsto \langle u|\hat{H}|v\rangle \end{aligned} \tag{7}$$

We write $\|\cdot\|_X$ to denote the norm induced on a given space, X, the details of which will be defined later. Note that we look at the first Sobolev space H^1, rather than the Lebesgue space L^2. This is due to the presence of the differential operator in the Hamiltonian; at first it may seem that the second Sobolev space is the relevant one, but the operator is self-adjoint such that $\langle u|\nabla \cdot \nabla|v\rangle = \langle \nabla u|\nabla v\rangle$.[44] The physical relevance of these spaces is that they reflect the differentiability of the wavefunction. The first space thus describes the smoothness of the wavefunction, while the second its curvature - intuitively, restrictions on these are used as boundary conditions when solving the Schrödinger equation.

We then introduce a finite set of M basis functions, $\{\varphi_m\}$, which collectively span some subspace $B_M \subset H^1(\mathbb{R}^3)$. We then make a guess to the true eigenfunction using the linearity of the space:

$$u_M(\mathbf{r}) = \sum_m c_m \varphi_m(\mathbf{r}) \tag{8}$$

Since a is self-adjoint and bilinear, the Rayleigh-Ritz Theorem[22,23] implies what is commonly termed the variational principle:

$$\lambda \langle u_M|u_M\rangle \leq a(u_M, u_M) \tag{9}$$

That is, the eigenvalue determined from the guess gives an upper-bound on the true eigenvalue. We can thus vary the coefficients, c_m, to determine the lowest possible eigenvalue, giving the best possible estimate to the true energy of the system (the Rayleigh-Ritz method). This dimension reduction is used both in Hartree-Fock[24,25], where a mean field potential is used and the wavefunction restricted to a single state in Fock space, and in configuration interaction methods[26], where multiple states are included in a linear combination. These are thus specific examples of a more general class of Galerkin methods. The bilinearity of equation 7 then guarantees that the problem is well-posed, and allows for the application of Cea's lemma[27]:

Lemma 1 (Cea's lemma) *Let u and $\bar{u}_M$ be the true and Galerkin solutions to the problem in equation 6. Then for some constant $K > 0$, we have*

$$\|u - \bar{u}_M\|_{H^1(\mathbb{R}^3)} \leq K \inf_{u_M \in B_M} \|u - u_M\|_{H^1(\mathbb{R}^3)} \tag{10}$$

where B_M is the subspace spanned by a set of M Gaussian functions.

That is, the Galerkin solution is the best approximation from B_M to u up to a constant. More to the point, this means it is sufficient to study the structure of B_M to determine the quality of the wavefunction thus obtained.

B. Atomic basis functions

For the case of a single electron in the central field of a nucleus, i.e. a hydrogenic atom, the above system is exactly soluble. The wavefunction in spherical coordinates separates into radial and angular parts, $\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$, where the Y_{lm} are the spherical harmonics, and n, l, m are the principal, azimuthal, and magnetic quantum numbers, respectively. The normalized radial functions corresponding to the point spectrum (bound states) for a hydrogenic system with nuclear charge Z are given by:

$$R_{nl}(r) = \left(\frac{2Z}{n}\right)^{3/2+l} \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} r^l \exp(-Zr/n) L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) \tag{11}$$

where $L_n^a(x)$ are the associated Laguerre polynomials.[28] These do not form a complete basis for the one-particle Hilbert space unless Z is allowed to vary. In contrast, Slater- and Gaussian-type orbitals (STOs and GTOs), given in equations 12 and 13 respectively, do form complete sets - explained shortly in Definition III.1 for fixed exponents[13].

$$\varphi_{nlm}^{S}(\mathbf{r}) = \frac{(2\zeta)^{l+3/2}}{\sqrt{(2l+2)!}} r^l \exp(-\zeta r) Y_{lm}(\theta, \phi) \tag{12}$$

$$\varphi_{nlm}^{G}(\mathbf{r}) = \frac{2^{l+3/4}(\sqrt{\zeta})^{l+3/2}}{\pi^{1/4}\sqrt{(2l+1)!!}} r^l \exp(-\zeta r^2) Y_{lm}(\theta, \phi) \tag{13}$$

It is more practical, however, to allow the exponent to vary and restrict the quantum numbers to relevant shells. Typically, basis set extrapolations also add higher angular momentum functions at each stage, particularly for correlation consistent sets where such functions are vital in the subsequent, correlated parts of the calculation.

Clearly, the STOs are more similar to the true hydrogenic functions than the GTOs, and thus are expected be a better description of atomic orbitals in general. The latter in particular give a poor description in both very near to, and very far from, the nucleus, as they lack a cusp at the origin and decay as $\exp(-r^2)$. This is demonstrated in Figure 1. However, the matrix elements in equations 3 and 4 can be evaluated analytically over GTOs, due to the Gaussian product theorem[29]. This means that the integrals are far more efficient to compute, to the point where it is feasible to use considerably more functions such that the inadequacies are irrelevant.

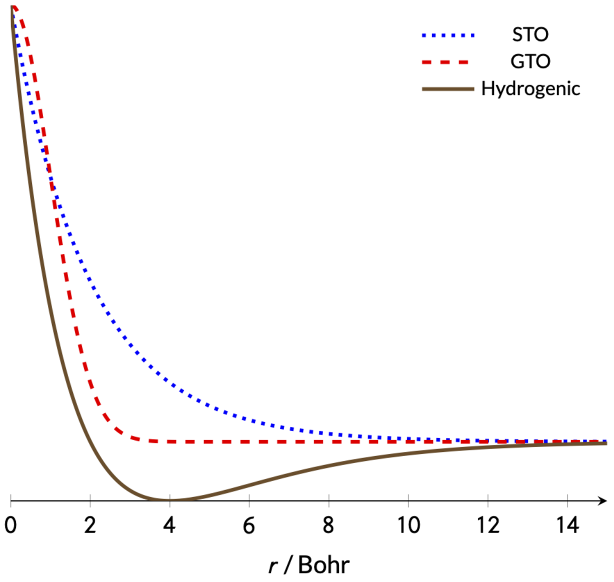

FIG. 1. The radial part of the 2s orbital of a hydrogenic atom, and the equivalent (nodeless) Slater- and Gaussian-type orbitals. Note in particular how the GTO lacks a cusp at the origin and decays too rapidly. Note that the orbitals are not normalised, so as to make it easier to see the differences between them.

III. CONVERGENCE PROPERTIES OF GAUSSIAN BASIS SETS

The accuracy of the results from application of the Galerkin method will depend strongly on the quality of the basis used. Given that some form of self-consistent field (SCF) calculation, namely Hartree-Fock (HF) or Kohn-Sham (KS), is the starting point of almost all quantum chemistry methods, this implies that an understanding of the properties of the particular choice of basis is essential. In particular, it is often assumed that by systematically adding additional functions, convergence to the exact result can be achieved - that is, an assumption of completeness of the basis with respect to the energy norm. The conditions under which this is true, however, are neither well-known nor widely studied in the chemistry community. This section takes the analysis of Kutzelnigg[17] as a starting point, and significantly extends it by considering the approximation of arbitrary angular momentum STOs by finite linear combinations of GTOs, using more robust metrics than the L^{∞}-norm.

A. Completeness results

Completeness of a basis with respect to the norm induced on a Hilbert space, H, is defined as follows:

Definition III.1 *The basis $\{\varphi_m\}$ is complete with respect to the norm $\|\cdot\|_X$ if, for any $\epsilon > 0$ and $f \in H$, there exists an integer $N > 0$ and coefficients $\{c_n\}$ such that*

$$\left\| f - \sum_{n=1}^{N} c_n \varphi_n \right\|_X < \epsilon$$

Essentially, this means that it is possible to get arbitrarily close to any point in the Hilbert space. The definition of distance is almost arbitrary, and as such this property depends critically on the particular choice of metric.[45] The usual choices are the L^p-norms:

Definition III.2 *The L^p-norm for some $f \in H$ and $1 \leq p < \infty$, with $H \subseteq L^p(S)$, is given by*

$$\|f\|_p = \left(\int_S f^p \right)^{1/p}$$

The L^∞-norm is then

$$\|f\|_\infty = \sup_{s \in S} |f(s)|$$

If the underlying σ-algebra, S, is equipped with finite measure, these norms are equivalent; in particular, $\|f\|_p \geq \|f\|_q$ for $p < q$.[22] The Lebesgue measure over $\mathbb{R}^n$ is not finite[30], however, such that these inequalities do not hold, but they do illustrate that completeness in the L^1-norm is generally the strongest result. The exception is the case $\|f\|_\infty \leq \|f\|_p$, which is always true for $1 \leq p < \infty$[23].

Klahn and Bingel[13] have given sufficient (but not necessary) conditions for completeness of the Slater- and Gaussian-type bases in the L^2-norm:

Lemma 2 *Let $\{\zeta_n\}_{n=1}^{\infty}$ be a sequence of positive numbers. Then systems of functions comprising the radial parts of equations 12 or 13 are complete in $L^2(\mathbb{R}^+)$ if the sequence has:*

1. *a limit point $\zeta \in (0, \infty)$, or*
2. *a monotonically increasing subsequence $\{\zeta_{n_i}\}$ whose elements tend to infinity, such that $\sum_{n_i} \frac{1}{\zeta_{n_i}} \to \infty$.*

For example, sequences of the form $\{n\}$ or $\{n^{-1}\}$ lead to complete sets, but it is not possible to determine whether this is true for $\{n^2\}$ or $\{n^{-2}\}$, although the lemma suggests they may not be. Moreover, this condition implies over-completeness of the basis, as an arbitrary, countable subset of the functions can be removed without affecting the criteria given above. The completeness of the spherical harmonics then implies that it is sufficient to consider just the radial parts as above[31].

Having determined that it is possible to form a complete basis, it is natural to ask how the errors behave as the finite basis tends towards completeness. As Kutzelnigg stated recently "If convergence is guaranteed, this does not imply convergence is fast enough to be of any practical use"[17]. Previous studies have demonstrated three types of asymptotic behaviour for the incompleteness error, ϵ_M (where M is the dimension of the basis): $\epsilon_M \sim M^{-p}$; $\epsilon_M \sim \exp(-pM)$; and $\epsilon_M \sim \exp(-p\sqrt{M})$, all for some $p > 0$[16,17]. For example, the inverse power law is observed for Hermite functions, while in the usual Gaussian basis, it is possible to achieve either kind of exponential convergence. Clearly, the second of these is more efficient.

As noted earlier, however, completeness in the L^2-norm is not sufficient for energy convergence. Instead, we consider the so-called energy norm. The molecular Hamiltonian is semi-bounded below, such that there exists a positive constant c, such that the operator $c + \hat{H}$ is positive definite. Shifting the datum in this way does not change the domain of the operator, such that the closure of that domain is still the first Sobolev space, H^1. The energy norm is then defined as follows:

Definition III.3 *Given $f \in H^1(\mathbb{R}^+)$ and the first-order differential operator $\hat{D}$ on H^1, the energy norm is given by*

$$\|f\|_{H^1} = \langle f|c + \hat{D}|f\rangle^{1/2}$$

Mikhlin[32] and Kato[33] have separately shown that completeness in the H^2-norm, where $\hat{D}$ is replaced with the kinetic energy operator $\hat{T}$ in the above, is sufficient to guarantee convergence of the energy in the Rayleigh-Ritz method. As $H^2 \subset H^1 \subset L^2$, it follows that this is a stronger requirement than completeness in the energy norm. Klahn and Bingel[13] additionally extended the work of Mikhlin to provide a necessary and sufficient criterion for convergence in the H^1-norm, albeit not one that has proven to be practically useful. These results have previously been excellently summarised by Cancés and coworkers[34]. The culmination of this was a proof of completeness of Hermite and even-tempered GTOs with respect to the H^1-norm by Bachmayr et al.[18]. The latter made use of sinc approximation theory to arrive at their proof, necessitated by the use of less stringent assumptions on the wavefunction. In the following, I present a simpler, novel proof of this result, assuming that the orbitals in question are regular - for practical purposes, this assumption is known to be valid[35].

Consider the Galerkin problem as described in equation 6, in the particular case of HF or KS SCF.[46] We denote the true and Galerkin orbitals by $\{\phi_i\}$ and $\{\phi_{i,M}\}$, respectively, to distinguish them from general points $u_m \in B_M$, where B_M is the subspace of L^2 spanned by a set of M GTOs. We first need the following preliminary result:

Lemma 3 *For the closed-shell SCF problem with $N_{el.}$ electron using an M-dimensional Gaussian basis spanning $B_M \subset L^2$, there exists a constant $K > 0$ such that*

$$\sum_{i=1}^{N_{el.}/2} \|\phi_i - \phi_{i,M}\|_{H^1} \leq K \sup_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1} \tag{14}$$

Proof By Cea's Lemma (equation 10) for each i there exists a constant K_i such that

$$\|\phi_i - \phi_{i,M}\|_{H^1} \leq K_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1}$$

By definition, the supremum over a set is an upper bound for that set, such that by defining $K = \sum_i K_i$, we have

$$\sum_i K_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1} \leq K \sup_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1}$$

The result then follows. ▮

This allows us to prove the main result of this section:

Theorem 4 *Let $E[\{\phi\}]$ denote the Hartree-Fock energy functional over some set of orbitals, $\{\phi\}$, satisfying Lemma 3. Then there exists a constant $K > 0$ such that*

$$\epsilon_N = |E[\{\phi_i\}] - E[\{\phi_{i,N}\}]| \leq K \sup_i \inf_{u_m \in B_M} \|\phi_i - u_m\|^2_{H^1} \tag{15}$$

Proof Consider the following inner product, $\langle u | c + \hat{h} + \hat{V}_{\text{eff.}} | v \rangle$, where $\hat{h}$ is the one-electron operator defined in equation 2, and $\hat{V}_{\text{eff.}}$ is some effective one-electron approximation to the two-electron operator in the same equation. The relevant analogue of equation 5 then gives the following:

$$\sum_i \langle \phi_i | c + \hat{h} + \hat{V}_{\text{eff.}} | \phi_i \rangle = \frac{1}{2} N_{\text{el.}} c + \sum_i (h_{ii} + V_{ii}) = E[\{\phi_i\}] + k$$

where $k = N_{\text{el.}} c/2$ does not depend on the choice of orbitals. This together with the bilinearity of the inner product means that

$$\begin{aligned}
&\sum_i \langle \phi_i - \phi_{i,N} | c + \hat{h} + \hat{V}_{\text{eff.}} | \phi_i - \phi_{i,N} \rangle \\
&\quad = 2k + E[\{\phi_i\}] + E[\{\phi_{i,N}\}] - \sum_i \left[\langle \phi_i | c + \hat{h} + \hat{V}_{\text{eff.}} | \phi_{i,N} \rangle + \text{h. c.} \right] \\
&\quad \geq 2k + E[\{\phi_i\}] + E[\{\phi_{i,N}\}] - \sum_i \left[\langle \phi_i | c + \hat{h} + \hat{V}_{\text{eff.}} | \phi_i \rangle + \text{h. c.} \right] \\
&\quad \geq |E[\{\phi_i\}] - E[\{\phi_{i,N}\}]| = \epsilon_N
\end{aligned}$$

where we note that the constant k terms are positive, and h. c. denotes the Hermitian conjugate of the preceding term. The third and fourth lines follow from the fact that the true orbitals necessarily provide a lower bound on the energy functional. We then use the fact that the domain of the effective Hamiltonian here is the same as that of the kinetic energy operator, simplying the underlying Sobolev spaces are identical. This is clearly true for the $c+\hat{h}$ terms, as these take the same form as the kinetic energy operator. The proof that this is true for the potential operator is non-trivial, however, and relies on its regularity[33]. Given this equivalence, the above becomes

$$\epsilon_N \leq \sum_i \|\phi_i - \phi_{i,N}\|_{H^1}^2$$

Then, given norms are necessarily non-negative, we have that $\sum_i \|f\|^2 \leq [\sum_i \|f\|]^2$, such that applying Lemma 3, there exists a positive constant $K^{1/2}$ such that

$$\begin{aligned}
\sum_i \|\phi_i - \phi_{i,N}\|_{H^1}^2 &\leq \left[K^{1/2} \sup_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1} \right]^2 \\
&= K \sup_i \inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1}^2
\end{aligned}$$

This completes the proof. ∎

In essence, this demonstrates three important things:

1. the error in the energy decays as the square of the error in the wavefunction;
2. convergence of the wavefunction in the energy norm is sufficient to ensure absolute convergence of the energy;
3. it is sufficient to consider only the best approximation of a one-electron orbital by a Gaussian.

Note that there is no dependence in the above on the particular choice of potential, so long as it is regular, and the analysis could be extended to consider other observables than the energy given an appropriate functional. This emphasizes that the wavefunction is the vital quantity, and all observables follow from the wavefunction. Methods in quantum chemistry, including typical basis function optimizations, often focus on only the energy, and in doing so are ignoring the root cause of incompleteness errors.

B. Gaussian transforms of Slater-type orbitals

The Slater-type orbitals of equation 12 are nodeless equivalents of the hydrogenic orbitals in equation 11. This suggests that it is reasonable to take the general form of an atomic orbital to be that of an STO. As demonstrated above, it suffices just to consider the radial part, then using the result in Theorem 4, we can obtain the asymptotic behaviour of the error in the energy. To do this, it is desirable to have an exact representation of the STOs in a Gaussian basis, such that the truncation to a finite basis can be introduced systematically.

Kutzelnigg used the Gaussian transform[17], essentially a special type of Laplace transform, to achieve this for the ground-state 1s orbital of a hydrogenic atom. This was first introduced to quantum chemistry by Shavitt *et al.* as a tool for the evaluation of integrals over Slater-type orbitals[36]. It takes the following form:

$$\exp(-r) = \frac{1}{2\sqrt{\pi}} \int_0^\infty t^{-3/2} \exp\left(-\frac{1}{4t}\right) \exp(-tr^2)dt = \int_0^\infty f(t,r)dt$$

This integral can then be approximated by a finite Riemann sum of the form

$$\exp(-r) \approx \sum_{m=1}^{M} w_m c(t_m) \exp(-t_m r^2)$$

where the w_m and t_m are weights and abscissae that depend on the Riemann partitioning of the integral, and $c(x) = x^{-3/2}\exp[-1/(4x)]$. This demonstrates a clear analogy with expanding an orbital in a finite Gaussian basis, and could lead to prescriptions on how to best

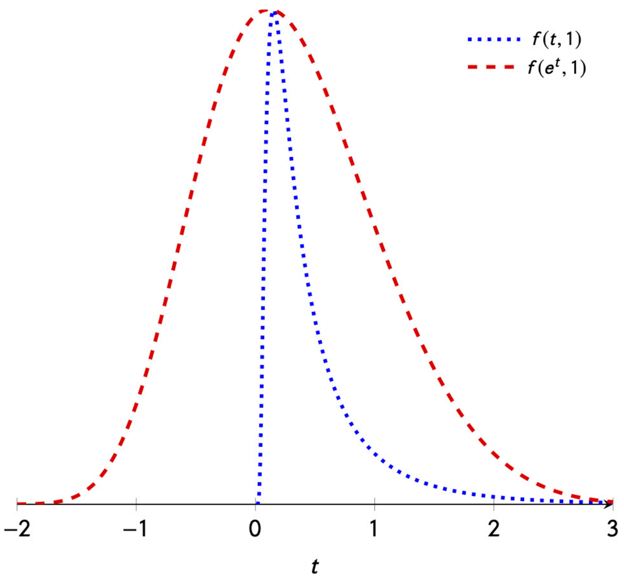

FIG. 2. Plots of the untransformed and transformed integrands, $f(t,r)$, for the Gaussian transform of e^{-r}, in the case $r=1$. Note how the transformed integrand is more symmetric about the origin, and closer to bell-shaped as a result.

form near-complete bases systematically. Kutzelnigg's particular choice of discretization was using the trapezium rule, corresponding to equally-spaced abscissae with unit weight, on the basis that this is known to work surprisingly well for bell-shaped integrands[37]. However, Figure 2 demonstrates that the integrand in its current form is skewed, such that the transformation $s = \exp(t)$ needs to be applied first, which symmetrizes the integral, as can be seen in the Figure.

The transformed integral is then split into three distinct portions by applying lower and upper cutoffs, s_l and s_u, to the range of integration. Defining $g(s,r) = f(\exp(s),r)\exp(-s)$, this is then:

$$\exp(-r) = \int_{-\infty}^{s_l} g(s,r)ds + \int_{s_l}^{s_u} g(s,r)ds + \int_{s_u}^{\infty} g(s,r)ds$$

There are thus three sources of error in the discretization: the lower and upper truncation errors associated with neglecting the first and third integrals above, denoted $\varepsilon_l(r)$ and $\varepsilon_u(r)$, respectively; and that associated with using a finite sum for the middle integral, denoted $\varepsilon_m(r)$. The former terms correspond to the poor long-range behaviour of GTOs, where any such expansion will essentially have a finite extent, whereas the STO will decay far less rapidly. The largest source of error for the latter term, on the other hand, will be the poor description of the nuclear cusp. Kutzelnigg focused in his exposition on the latter -

specifically $r = 0$ - in what he called the 'local approximation'[17]; I will demonstrate this is equivalent to considering the L^∞-norm of the error. He then went on to consider numerically the associated error in the energy expectation value in this framework. The previous sections have demonstrated, however, that this is the weakest norm in which to consider the errors, and is not sufficient to ensure convergence, either in wavefunction or energy.

Moreover, as only the 1s orbital with fixed exponent was considered, it is not clear whether the conclusions hold for orbitals of arbitrary principal quantum number and exponent - that is, that the errors asymptotically go as $\exp(-k\sqrt{M})$ for some positive constant k. Clearly, one could apply all results for $\exp(-r)$ to $r^l \exp(-r)$, assuming that the GTOs are also replaced by ones of the form $r^l \exp(-\alpha r^2)$. Indeed, this means that abritrary angular momenta can be considered. It is not, however, customary to expand the nth principal quantum number shell by Gaussians of the form $r^{n+l} \exp(-\alpha r^2)$, which is what would be necessary to expand the ns orbital, rather only the angular momentum is included in the power. Thus, we must generalise the transform to STOs of the form $r^{n-1} \exp(-\alpha r)$.

In the following section, I will extend this analysis by considering the errors for a general Slater-type orbital in the L^∞-, L^1-, and H^1-norms. To do so, we need the Gaussian transform as above but in the general case, which is derived in the appendix:

$$\begin{aligned} r^{n-1} \exp(-\alpha r) &= \int_0^\infty c_n(t) \exp(-tr^2) dt = \int_0^\infty f_n(t, r) dt \\ c_n(t) &= \frac{1}{2^n \sqrt{\pi}} t^{-(n+1)/2} \exp\left(-\frac{\alpha^2}{4t}\right) H_n\left(\frac{\alpha}{2\sqrt{t}}\right) \end{aligned} \tag{16}$$

where $\alpha > 0$ and $H_n(x)$ is the nth physicist's Hermite polynomial. We can define $g_n(s, r)$ in the same way as above by making the transformation $t = \exp(s)$. Then, using the trapezium rule with M points, corresponding to an expansion in M GTOs, the abscissae used in the middle integral are given by

$$s_k = s_l + \left(k - \frac{1}{2}\right) h \tag{17}$$

where $h = (s_u - s_l)/M$ is the chosen interval width, and $k = 1, 2, \ldots, M$. This implies that $s_u = s_l + Mh$, such that for fixed M, there are only two variable parameters: s_l and h.

C. Discretization errors

Firstly, consider the untransformed integrand, $f_n(t, r)$, in equation 16. Its only dependence on r is in the $\exp(-tr^2)$ term at the end, which has its maximum at the origin.

Moreover, consideration of $\partial_r f_n(t,r)$ for fixed t trivially shows the only stationary point is at the origin. As $f_n(t,r)$ necessarily tends to zero as $r \to \infty$, the continuity of the function implies that it always attains its maximum absolute value when $r = 0$. Therefore, we have in general that

$$\sup_{r\in[0,\infty)} f_n(t,r) = |f_n(t,0)| \; \forall \; t \in [0,\infty)$$

This implies from Definition III.2 that

$$\|\varepsilon\|_\infty = |\varepsilon(0)| \tag{18}$$

such that the so-called ‘local approximation’, restricting attention to $r = 0$, simply corresponds to the L^∞-norm. We look at this case first as it is the simplest, before moving on to the stronger L^1-norm and then finally the H^1-norm, allowing us to make conclusions about the energy convergence.

1. The infinity norm

In the case where $r = 0$, the lower truncation error is given by

$$\|\varepsilon_l\|_\infty = \frac{1}{2^n\sqrt{\pi}} \int_0^{t_l} t^{-(n+1)/2} \exp\left(-\frac{\alpha^2}{4t}\right) H_n\left(\frac{\alpha}{2\sqrt{t}}\right) dt$$

Making the substitution $z = \alpha/(2\sqrt{t})$, such that $\alpha^2 dz = -2z^3 dt$, this becomes

$$\|\varepsilon_l\|_\infty = \frac{1}{\alpha^{n-1}\sqrt{\pi}} \int_{z_l}^{\infty} z^{n-2} \exp(-z^2) H_n(z) dz$$

where $z_l = \alpha/(2\sqrt{t_l})$. The Hermite polynomials can be expanded as

$$H_n(x) = \sum_{k=0}^{n} b_k^{(n)} x^k$$

where the coefficients are defined by the recurrences

$$b_k^{(n+1)} = b_{k-1}^{(n)} - n b_k^{(n-1)} \text{ for } k > 0, \text{ and } b_0^{(n+1)} = -n b_0^{(n-1)}$$

with $b_0^{(0)} = 1$, $b_0^{(1)} = 0$, and $b_1^{(1)} = 2$. The integral thus reduces to a linear combination of standard integrals of the form

$$\int_{z_l}^{\infty} z^{k+n-2} \exp(-z^2) dz = \frac{1}{2}\Gamma\left(\frac{k+n-1}{2}, z_l^2\right)$$

where $\Gamma(n, z)$ is the upper incomplete gamma function[28].

Following the same procedure for the upper truncation error gives identical results, but with the integrals being in terms of the lower incomplete gamma function[28], $\gamma(n, z)$. Both errors are summarised below:

$$\left\|\varepsilon_l^{(n)}\right\|_\infty = \frac{1}{2\alpha^{n-1}\sqrt{\pi}}\left|\sum_{k=0}^{n} b_k^{(n)}\Gamma\left(\frac{k+n-1}{2}, \frac{\alpha^2}{4t_l}\right)\right| \tag{19}$$

$$\|\varepsilon_u^{(n)}\|_\infty = \frac{1}{2\alpha^{n-1}\sqrt{\pi}}\left|\sum_{k=0}^{n} b_k^{(n)}\gamma\left(\frac{k+n-1}{2}, \frac{\alpha^2}{4t_u}\right)\right| \tag{20}$$

The behaviour of the lower error as a function of t_l for a few cases of n is shown in Figure 3. Note that in the special case $n = \alpha = 1$, we recover

$$\left\|\epsilon_l^{(1)}\right\|_\infty = 1 - \operatorname{erf}\left(\frac{1}{2\sqrt{t_l}}\right) \text{ and } \|\epsilon_u^{(1)}\|_\infty = \operatorname{erf}\left(\frac{1}{2\sqrt{t_u}}\right)$$

where we have written it in terms of the error function. For convenience, we will fix t_l (and therefore t_u) by requiring that the upper and lower truncation errors be equal. The result above that $s_u = s_l + Mh$ implies that $t_u = t_l \exp(Mh)$, such that defining $x = \alpha^2/(4t_l)$, we have

$$\frac{\alpha^2}{4t_u} = x\exp(-Mh)$$

Therefore, setting equations 19 and 20 to be equal is achieved by requiring that, for each $K = (k+n-1)/2$, $k = 0, 1, \ldots, n$:[47]

$$\Gamma(K, x) = \gamma(K, \beta_h x)$$

where $\beta_h = \exp(-Mh)$. For small t_l, i.e. large x, the leading order term in the series expansions of the incomplete gamma functions gives

$$x^{K-1}\exp(-x) = (\beta_h x)^K \exp(-\beta_h x)$$

However, large x implies large Mh, such that $\beta_h \ll 1$. Thus the above becomes

$$\exp[-(1-\beta_h)x] \approx \exp(-x) \sim \beta_h^K x$$

i.e. $x - \ln x \sim KMh$. The linear term dominates the logarithm, meaning that overall $x \sim KMh$.

The terms in the sum in equation 19 go themselves as $x^{K-1}\exp(-x)$ to leading order in x, meaning that the overall error is dominated by the largest value of K, i.e. $K_{\max} = n - 1/2$.

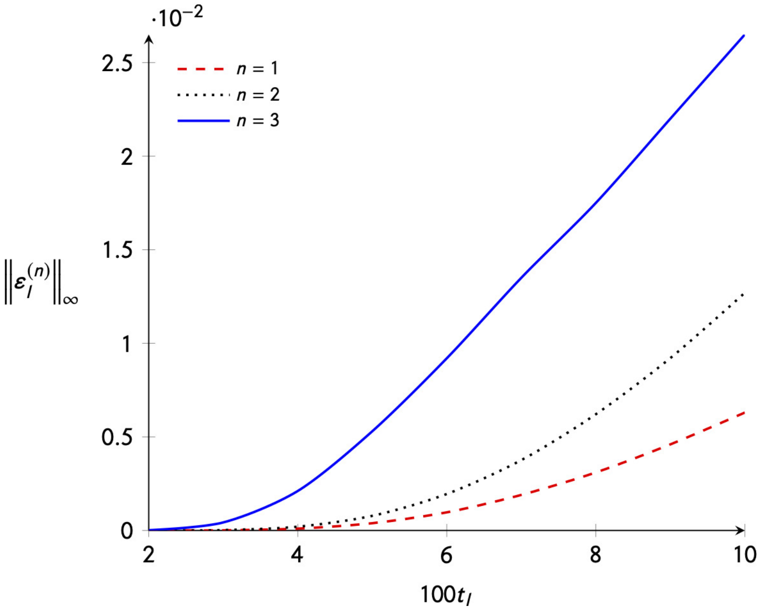

FIG. 3. The L^∞-norm of the lower truncation error as a function of the threshold, t_l, for $n = 1$, 2, and 3, with $\alpha = 1$.

Note that this is positive for all integers $n > 0$. This implies that for sufficiently small t_l, the truncation errors behave as

$$\left\|\varepsilon_l^{(n)}\right\|_\infty \sim (K_{\max}Mh)^{K_{\max}-1}\exp(-K_{\max}Mh) \tag{21}$$

That is, they show exponential convergence with the basis dimension, M. In particular, when $n = 1$, $K = 1/2$, it goes as $\exp(-Mh/2)$, showing that Kutzelnigg's result is a special case of the above. Interestingly, keeping Mh fixed and considering varying $K_{\max}$ - i.e. varying n - we can rewrite this as

$$\left\|\varepsilon_l^{(n)}\right\|_\infty \sim \frac{(Mh)^{K_{\max}-1}}{K_{\max}}\exp(K_{\max}[\ln K_{\max} - Mh])$$

suggesting that the error will generally increase with K. This is borne out in Figure 3.

For the region between the cutoffs, the reason for using the trapezium rule becomes clear - it is possible to write the discretization error in the following form:

$$\varepsilon_m^{(n)}(r,\theta) = 2\int_{s_l}^{s_u} g_n(s,r)\cos\left(\frac{2\pi s}{h} + \theta\right) ds \tag{22}$$

where θ is a phase factor that depends on where the abscissae are placed. There are two options for dealing with this phase: average over it, or select a particular choice. As we are primarily interested in the asymptotics, it seems logical to set $\theta = 0$, which is equivalent to placing the abscissae in the centre of each segment of length h. In the following, $\varepsilon_m(r)$ will be taken to mean $\varepsilon_m(r, 0)$. By the same logic as before, the L^∞-norm is then found by considering $r = 0$:

$$\left\|\varepsilon_m^{(n)}\right\|_\infty = 2\left|\int_{s_l}^{s_u} g(s,0)\cos\left(\frac{2\pi s}{h}\right) ds\right|$$

Using the fact that $\cos(x)$ is the real part of $\exp(ix)$ and extending the integration to the entire real line, this becomes:

$$\left\|\varepsilon_m^{(n)}\right\|_\infty = 2\left|\mathrm{Re}\left\{\int_{-\infty}^{\infty} g(s,0)\exp\left(\frac{2\pi i s}{h}\right) ds\right\}\right| = 2\left|\mathrm{Re}\left\{\mathcal{F}\{g_{r=0}\}\left(\frac{1}{h}\right)\right\}\right|$$

where $\mathcal{F}$ denotes a Fourier transform. It is assumed that the error introduced by extending the integration limits should be negligible; it is not equivalent to including the truncation errors above, due to the cosine in the integrand. Expanding the Hermite polynomials and using the linearity of the Fourier transform then allows us to write

$$\mathcal{F}\{g_{r=0}\}(z) = \sum_{k=0}^{n} b_k^{(n)}\left(\frac{\alpha}{2}\right)^{2k}\mathcal{F}\left\{\exp\left(\tau_{n,k}s - \frac{\alpha^2}{4}\exp(-s)\right)\right\}$$

where $\tau_{n,k} = -(k+n-1)/2$. The remaining transform is simply the Fourier representation of the complex Gamma function[38], such that

$$\begin{aligned}\left\|\varepsilon_m^{(n)}\right\|_\infty &= 2\left|\sum_{k=0}^{n}\omega_{n,k}(\alpha)\mathrm{Re}\left\{\Gamma\left(\tau_{n,k} + \frac{i}{h}\right)\right\}\right| \\ \omega_{n,k}(\alpha) &= b_k^{(n)}\left(\frac{\alpha}{2}\right)^{2k}\exp\left(\tau_{n,k}\ln\frac{\alpha^2}{4}\right)\end{aligned} \tag{23}$$

This is not really a simplification, as the real part of the complex Gamma function is itself defined by an integral. However, it is much easier to evaluate, and standard asymptotic expansions exist for it[28]. The indefinite phase means that the error oscillates, but the behaviour can be extracted by considering the peaks; this phase-averaged error as a function of h is shown for a few cases of n in Figure 4.

For small h, such that $x = 1/h$ is large, Stirling's approximation gives

$$\Gamma(\tau + ix) \sim (\tau + ix)^{(\tau + ix - 1/2)}\exp[-(\tau + ix)]$$

such that the real part goes to leading order as $\exp(-\tau)x^{-x-1/2}\cos(x)$, with the cosine introducing the aforementioned oscillations. Therefore the discretization error, which is

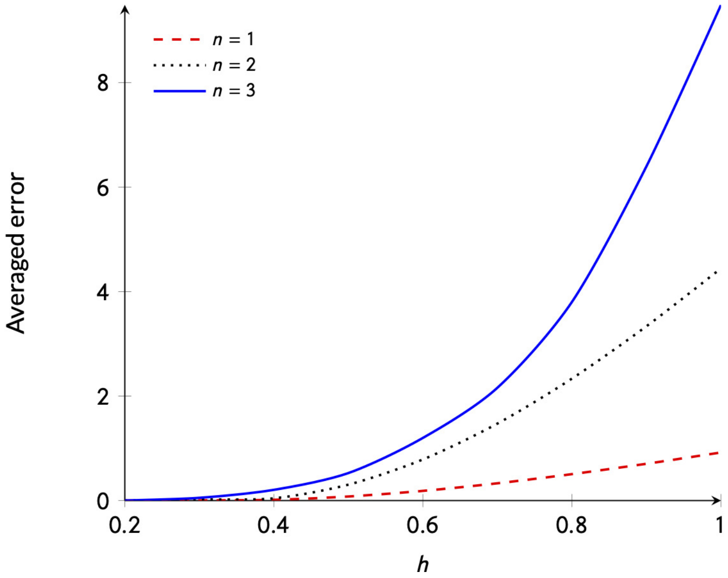

FIG. 4. The phase-averaged L^∞-norm ($\|\epsilon\|_\infty$ averaged over a unit sphere) of the discretization error as a function of the spacing, h, for $n = 1$, 2, and 3, with $\alpha = 1$.

dominated by the largest k term in the sum, asymptotically behaves as

$$\left\|\varepsilon_m^{(n)}\right\|_\infty \sim \exp\left(-n + \frac{1}{2}\right) \exp\left(\frac{\ln h}{h}\right) \sim \exp\left(-n - \frac{1}{h}\right) \tag{24}$$

Combining this with the truncation errors in equation 21, the total error follows

$$\epsilon(h) = \exp(-K_{\max} M h) + \exp\left(-\frac{1}{h}\right)$$

The optimal value of h is found by setting the derivative of this to zero:

$$\epsilon'(h) = -K_{\max} M \exp(-K_{\max} M h) + \frac{1}{h^2} \exp\left(-\frac{1}{h}\right) = 0$$

This is solved exactly when $h = 1/\sqrt{K_{\max} M}$, i.e. when the two sources of error become equal. Thus, the total error in the finite basis expansion is

$$\left\|\varepsilon^{(n)}\right\|_\infty \sim \exp(-\sqrt{K_{\max} M}) \tag{25}$$

Thus, the result of Kutzelnigg has been generalized to all STOs. Note that, as this is in the infinity norm, it represents a lower bound on the error.

2. The absolute-value norm

Assuming that the lower cutoff threshold, t_l, is small enough that the Hermite polynomial does not change sign on the interval $[0, t_l]$,[48] the L^1-norm for the truncation error is given by

$$\left\|\varepsilon_l^{(n)}\right\|_{L^1} = \int_0^\infty dr \int_0^{t_l} dt\ |f_n(t,r)| = \left|\int_0^{t_l} dt \int_0^\infty dr\ f_n(t,r)\right|$$

The only r-dependent part of f_n is in the $\exp(-tr^2)$ term, such that the inner integral above is a standard Gaussian integral, leading to

$$\left\|\varepsilon_l^{(n)}\right\|_{L^1} = \frac{\sqrt{\pi}}{2}\left|\int_0^{t_l} dt\ t^{-1/2} f_n(t,0)\right|$$

This is therefore identical to the integral needed for the L^∞-norm but with an additional factor of $t^{-1/2}$; by the same logic, this also applies for the upper truncation error. As such, we can immediately write down the results for the lower and upper truncation errors using equations 19 and 20:

$$\left\|\varepsilon_l^{(n)}\right\|_{L^1} = \frac{1}{4\alpha^n}\left|\sum_{k=0}^{n} b_k^{(n)} \Gamma\left(\frac{k+n}{2}, \frac{\alpha^2}{4t_l}\right)\right| \tag{26}$$

$$\left\|\varepsilon_u^{(n)}\right\|_{L^1} = \frac{1}{4\alpha^n}\left|\sum_{k=0}^{n} b_k^{(n)} \gamma\left(\frac{k+n}{2}, \frac{\alpha^2}{4t_u}\right)\right| \tag{27}$$

This means that the asymptotics will be identical to equation 21, but with a slightly different prefactor and $K_{\max} = n$. There is a somewhat stronger dependence on the exponent, α, here; in both cases, smaller α (more diffuse orbitals) result in larger errors, but there is an additional factor of $1/\alpha$ in the above compared to in the infinity norm. The only significant change is that the order of the gamma functions has increased by 1/2, which means that in general the L^1-error will be substantially larger than the L^∞-error, as expected. It is reasonable to expect this to be an upper bound on the L^p-normed errors, although there may be edge cases where this is not true.

Following the same procedure, the middle error (equation 22) integrated over r also introduces a factor of $t^{-1/2} = \exp(-s/2)$. This has the simple effect of adding $-1/2$ to each $\tau_{n,k}$, but with equation 23 otherwise remaining the same. This allows us to immediately state the result for the asymptotics of the total error in the L^1-norm:

$$\left\|\varepsilon^{(n)}\right\|_{L^1} \sim \exp(-\sqrt{nM}) \tag{28}$$

This suggests that the asymptotic behaviour in any L^p-norm will follow this square-root exponential convergence with respect to basis size. In particular, this implies that the wavefunction converges in this way in the L^2-norm, which is necessary, but not sufficient, to assure convergence in the energy.

3. *The energy norm*

The lack of sufficiency above leads us to finally consider the energy norm. Using definition III.3, we have that

$$\|\varepsilon\|_{H^1}^2 = c\,\|\varepsilon\|_{L^2}^2 + \langle\varepsilon|\hat{D}\varepsilon\rangle \tag{29}$$

where c is a finite, positive constant necessary to make the operator positive definite. From the above, we have the behaviour of the first term, such that we need only consider the second term. As we are considering $H^1(\mathbb{R}^+)$, the differential operator is simply $\hat{D} = d/dr$, such that

$$\varepsilon_D^2 = \langle\varepsilon|\hat{D}\varepsilon\rangle = \int_0^\infty dr \left(\int_{\mathcal{D}} dt\ f_n(t,r)\right)\left(\int_{\mathcal{D}} dt\ \frac{d}{dr} f_n(t,r)\right)$$

where the domain of integration $\mathcal{D}$ in the inner integrals depends on which particular error is being considered. The derivative is easily found as $f_n'(t,r) = -2tr f_n(t,r)$.

As before, it is easiest to perform the r-integration first. In the case of the lower truncation error, we get

$$\begin{aligned}\left\|\varepsilon_l^{(n)}\right\|_D^2 &= 2\left|\int_0^{t_l} dt_1\ f_n(t_1,0)\int_0^{t_l} dt_2\ t_2 f_n(t_2,0)\int_0^\infty dr\ r\exp(-(t_1+t_2)r^2)\right| \\ &= \left|\int_0^{t_l} dt_1\ f_n(t_1,0)\int_0^{t_l} dt_2\ \frac{t_2 f_n(t_2,0)}{t_1+t_2}\right|\end{aligned}$$

This is essentially a convolution, and thus could in principal be solved using Fourier transforms; the result is messy, however, and not particularly enlightening. Instead, we consider directly the asymptotic region of small t_l, corresponding to small t_1 and t_2 in the integration, where $f_n(t,0)$ is dominated by the $\exp(-\alpha^2/(4t))$ term and $t_2/(t_1+t_2) \sim 1/t_1$ for fixed t_1; the latter term is itself then dominated by the exponential. This means that

$$\left\|\varepsilon_l^{(n)}\right\|_D^2 \sim 2^{-2n}\left[\int_0^{t_l} dt\ \exp\left(-\frac{\alpha^2}{4t_1}\right)\right]^2$$

Making the substitutions $u_i = \alpha^2/(4t_i)$ for $i = 1,2$, this can be written in terms of upper incomplete gamma functions as follows:

$$\left\|\varepsilon_l^{(n)}\right\|_D \sim 2^{-n}\left|\Gamma\left(-1, \frac{\alpha^2}{4t_l}\right)\right| \tag{30}$$

For the upper truncation error, we take the large-t limit, such that $f_n(t,0)$ is dominated by the leading power in the Hermite polynomial, i.e.

$$f_n(t,0) \sim 2\alpha^{-(n+1)}\left(\frac{\alpha^2}{4t}\right)^{n+1/2}$$

In this instance, $t_2/(t_1+t_2) \sim 1$ for fixed t_1, such that overall we have

$$\left\|\varepsilon_u^{(n)}\right\|_D^2 \sim 4\alpha^{-2(n+1)} \left[\int_{t_u}^{\infty} dt \, \left(\frac{\alpha^2}{4t}\right)^{n+1/2}\right]^2$$

such that

$$\left\|\varepsilon_u^{(n)}\right\|_D \sim \frac{\alpha^n}{2^{n-1}(2n-1)} \frac{\sqrt{t_u}}{t_u^n} \tag{31}$$

As was done for the infinity norm, we require the upper and lower errors to be asymptotically equal. Writing $x = \alpha^2/(4t_l)$ such that $\beta_h x = \alpha^2/(4t_u)$, and using the large-$x$ expansion of the gamma function, this gives

$$\exp(-x)x^{-2} = (\beta_h x)^{n-1/2}$$

Remembering that $n - 1/2 = K_{\max}$ from earlier, and taking logarithms, we get

$$x - (K_{\max} - 1)\ln x \sim K_{\max} M h$$

which means $x \sim K_{\max} M h$, exactly the same result as for the L^∞-norm. As the error in equation 30 is a gamma function just as in equation 19, the truncation errors have the same asymptotic behaviour here:

$$\left\|\varepsilon_l^{(n)}\right\|_D \sim \exp(-K_{\max} M h) \tag{32}$$

All that remains is to consider the discretization error. We note that the cosine in equation 22 does not depend on r, and $\partial_r g_n(s,r) = -2r\exp(s) g_n(s,r)$. Applying the same procedure as above, integrating out r gives

$$\left\|\varepsilon_m^{(n)}\right\|_D^2 = \left|\int_{s_l}^{s_u} ds_1 \; g_n(s_1,0)\cos\left(\frac{2\pi s_1}{h}\right) \int_{s_l}^{s_u} ds_2 \; \frac{g_n(s_2,0)\cos(2\pi s_2/h)}{1+\exp(s_1-s_2)}\right|$$

By extending the range of integration, each integral in the above could be treated as the real part of a Fourier transform as was done for the L^∞-norm. The problem is the convolution term, $1/[1+\exp(s_1-s_2)]$, in the inner integral. Using the Convolution Theorem[38] and the result for the transform of $g_n(s,0)$ from earlier (equation 23), but keeping only the $n = k$ term, we can expand the inner integral above follows:

$$\int_{-\infty}^{\infty} ds_2 \; \frac{1}{1+\exp(s_1-s_2)} \int_{-\infty}^{\infty} dz \;\; \exp\left[2\pi i s_2(1/h - z)\right]\Gamma(\tau_{n,n} + iz)$$

We know that for small h the gamma function in this goes as $\exp(-1/h)$, such that the inner integral above becomes a Dirac-delta, where the transforms here are taken in a distributional sense. We are thus left with

$$\exp\left(-\frac{1}{h}\right)\int_{-\infty}^{\infty} ds_2\ \frac{\exp(2\pi i s_2/h)}{1+\exp(s_1-s_2)}\delta(s_2) = \frac{\exp(-1/h)}{1+\exp(s_1)}$$

The remaining integral is again of the form of a Fourier transform of $g_n(s,0)/[1+\exp(s)]$, such that repeating the procedure, we conclude that

$$\left\|\varepsilon_m^{(n)}\right\|_D \sim \exp\left(-\frac{1}{h}\right) \tag{33}$$

Combining equations 32, 33, and 29, we see that exactly the same results hold in the H^1-norm as in the L^∞-norm, despite the respective error distributions being very different over the majority of their domains. That is, the optimal h is again found when $h = 1/\sqrt{K_{\max}M}$, leading to total errors converging as

$$\left\|\varepsilon^{(n)}\right\|_{H^1} \sim \exp(-\sqrt{K_{\max}M}) \tag{34}$$

D. Prescriptions for convergent basis sets

The natural discretization within the trapezium rule is as follows:

$$\phi_n(r) \approx h\sum_{m=1}^{M} c_n(t_m)\exp(-t_m r^2) \tag{35}$$

The above analysis suggests that the optimal choice of h is $1/\sqrt{K_{\max}M}$, with $t_l = \alpha^2/(4h)$, such that

$$\begin{aligned} t_m &= t_l \exp\left(\left[m-\frac{1}{2}\right]h\right) = \gamma_{n,M}\beta_{n,M}^{m-1},\ k = 1,2,\ldots,M \\ \gamma_{n,M} &= \frac{\alpha^2}{4}\sqrt{K_{\max}M}\exp\left(-\frac{1}{2\sqrt{K_{\max}M}}\right) \\ \beta_{n,M} &= \exp\left(\frac{1}{\sqrt{K_{\max}M}}\right) \end{aligned} \tag{36}$$

That is, we have arrived at a so-called even-tempered expansion, with a fixed prefactor, $\gamma_{n,M}$, and exponent, $\beta_{n,M}$, for each basis size. Such an expansion was first suggested as a means to systematically reach the CBS limit by Feller and Ruedenberg[39]. In general, it can be seen that the exponent will steadily tend towards unity as the basis dimension tends to infinity, as the spacing between the abscissae (which are now the exponents) decreases. Larger values of α lead directly to larger prefactors, as should be expected - the diffusivity

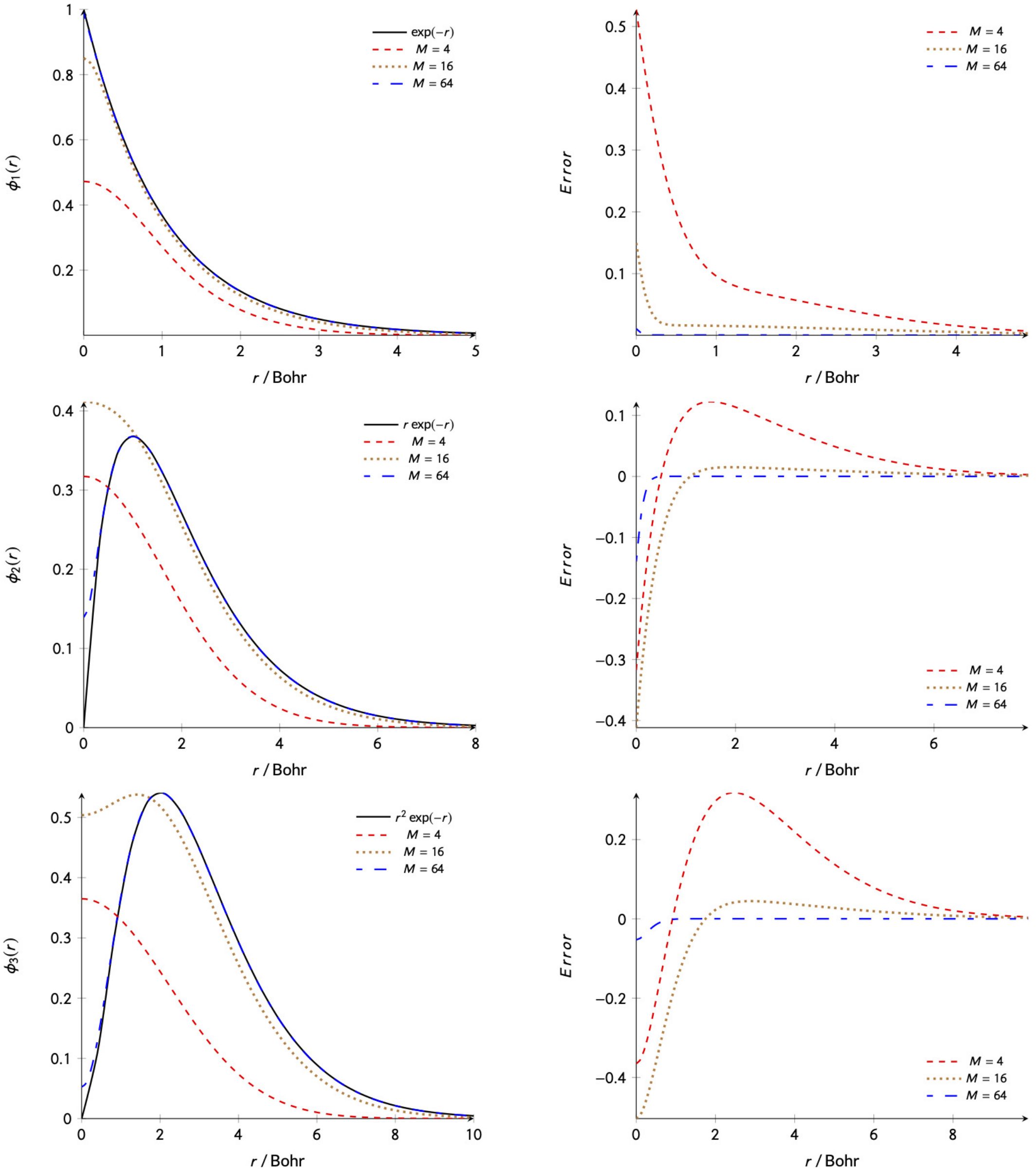

FIG. 5. Approximations to Slater-type orbitals with $n = 1$ (top), $n = 2$ (middle), and $n = 3$ (bottom) for different basis dimensions, M, are shown on the left, and their respective error distributions on the right - note that the $M = 64$ curves on the left often overlap with the exact solution. As $K_{\max} = n - 1/2$, from top to bottom is also increasing this parameter. For all of these, $\alpha = 1$ - increasing/decreasing this would simply decrease/increase the width of the orbitals, such that the parameter can effectively be seen as a scaling. The approximants were formed using the even-tempered scheme suggested by the asymptotic analysis. In all cases, the error at the origin dominates, and rapidly decreases with M.

of the gaussians should reflect the diffusivity of the original STO. Finally, larger n leads to smaller exponents, reflecting the fact that orbitals with higher principal quantum number tend to have larger radii. The performance of these expansions with increasing M for a few values of n is shown in Figure 5, where the convergence can clearly be seen.

Somewhat interestingly, excellent agreement is achieved quite rapidly in the long-range, with the error at the origin always dominating. This is unsurprising, as this constitutes a much larger portion of the domain, such that it is effectively weighted to be more important. Additionally, the cusp at the origin is by definition a reflection of discontinuity in the derivative, a property that the gaussians do not possess. Thus it is expected that improved convergence can only be achieved by improving the description at the origin; this is the basis for the highly successful explicitly correlated methods[20]. Additionally, we note that this poor behaviour at the origin is exactly why consideration of the L^{∞}-norm led to the correct result, despite it not rigorously being sufficient to ensure convergence.

Having demonstrated the behaviour of the wavefunction, it remains to consider the completeness of the designed basis with respect to the energy. From equation 36, we see that for each choice of M, the exponent $\beta = 1 + \delta_M$ for some $\delta_M > 0$, such that δ_M tends to strictly monotonically to zero as M tends to infinity. This means that the sequence $\{\gamma\beta^{m-1}\}$ is both monotonically increasing and unbounded. Moreover, the geometric series gives that the sum to infinity of $\alpha\beta^{-m}$ is α/δ, which tends to infinity as δ tends to zero - equivalent to M tending to infinity. As such, condition two of Lemma 2 is satisfied, meaning the even-tempered basis of GTOs of the type in equation 13 described herein is complete in $H = L^2(\mathbb{R}^3)$. Therefore, given the continuity of tensor product maps, a Slater determinant formed of N orbitals each expanded in the (inifinite) Gaussian basis is complete in the product space $H^{\otimes M}$. Completeness within each component of a direct sum trivially ensures completeness in the summed space, such that any point in Fock space can be satisfactorily described.

Finally, having ensured convergence in the wavefunction, convergence in the energy is also achieved. Choosing $u \in B_M$[49] to be the linear combination described in equation 35, we see that for any particular orbital ϕ_i:

$$\inf_{u_m \in B_M} \|\phi_i - u_m\|_{H^1} \leq \|\phi_i - u\|_{H^1}$$

Therefore, using this and equation 34, we can apply Theorem 4, to get that the error in the

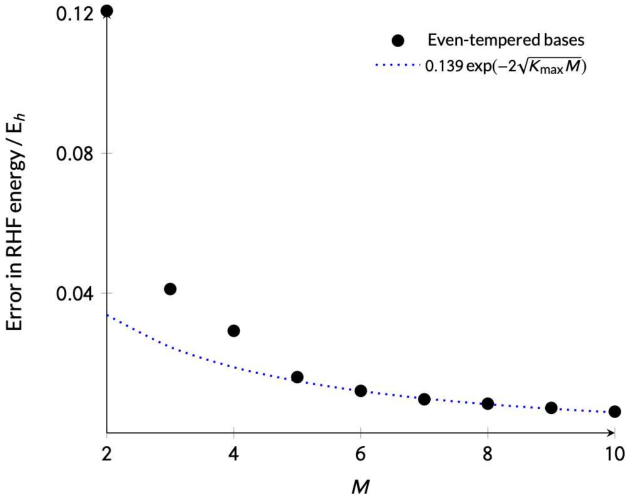

FIG. 6. The error convergence of the RHF energy of the hydrogen molecule using progressively larger even-tempered bases. Excellent agreement is seen with the predicted asymptotic exponential decay. Note that $n = 1$ such that $K_{\max} = 1/2$.

Hartree-Fock energy, ϵ_M, behaves as follows:

$$\epsilon_M \sim C\left[\exp(-\sqrt{K_{\max}M})\right]^2 = C\exp(-2\sqrt{K_{\max}M}) \tag{37}$$

for some $C > 0$. In the particular case of the hydrogen 1s orbital, where $n = \alpha = 1$, we have that $K_{\max} = 1/2$, such that we expect energy convergence of the form $C\exp(-\sqrt{2M})$. Figure 6 shows that this is exactly the observed asymptotic behaviour for the restricted Hartree-Fock (RHF) energy of the hydrogen molecule using the even-tempered basis described above, with a relatively low prefactor of $C = 0.139$.

IV. CONCLUSIONS

The idea that basis sets can be systematically constructed to achieve convergence in the energy has become a central tenet of quantum chemistry. In this paper, I have confirmed that this is a rigorous and reasonable assumption to make. By analytical means, I have shown that it is sufficient to consider convergence of the wavefunction in terms of only the one-electron functions, by treating mean-field methods as Galerkin-type problems. The energy error then converges as the square of the wavefunction error, leading to an asymptotic behaviour following $\exp(-k\sqrt{M})$ where M is the number of Gaussians and k is a positive constant. This is in agreement with previous results[17], but extended to arbitrary molecular orbitals. It also matches closely with the results of Bachmayr et al.[18], although achieved through different means, with subtle differences in the form of the constants. For practical purposes, i.e. in extrapolation procedures, the slightly simpler form given here is perhaps more useful.

The analysis has led to prescriptions for an even-tempered basis that best uses the favourable limiting convergence. However, this is not supposed to be a practicable basis set on its own. Rather, its practical use is in either providing initial guesses for further basis set optimization, or for rapidly generating systematically converging results, to which other basis sets can be compared. Further work could investigate, for example, best polynomial approximations to the even-tempered form. Relaxing the even-tempered restraint would allow for much smaller basis sets to be constructed but without losing the desirable completeness properties.

Finally, it should be noted that the results presented here apply only to convergence in the energy, and for methods with regular potential operators. Properties depending on derivatives of the energy would require further extension to norms in higher-order Sobolev spaces. In principle, this should be simple using the machinery developed here. The regularity requirement is much more difficult, however, as the true two-electron potential is not regular[40]. As such, these results are currently limited effectively to HF and KS-DFT energies. Extension to correlated methods in a rigorous manner remains a diabolically complex problem in mathematical analysis.

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CONFLICT OF INTEREST

There are no conflicts of interest to declare.

APPENDIX

The general Gaussian transform of a Lebesgue-integrable function, $f(t)$, defined for all $t \geq 0$ is given by

$$F(r) = \mathcal{G}\{f\}(r) = \int_0^\infty f(t)\exp(-tr^2)dt \tag{38}$$

This is related to the standard Laplace transform by the mapping

$$\mathcal{L}\{f\}(s) = \mathcal{G}\{f\}(\sqrt{s}\}$$

which is continuous and bijective, given that $r, s \geq 0$. As such, the problem of finding the Gaussian transform representation of a general Slater-type orbital

$$\phi_n(r) = r^{n-1}\exp(-\alpha r)$$

for some real $\alpha > 0$ and integer $n > 0$ reduces to the problem of finding the inverse Laplace transform of $\phi_n(\sqrt{r})$. This can be found using the Bromwich integral (also known as Meilin's inverse formula):

$$f(t) = \mathcal{L}^{-1}\{F\}(t) = \frac{1}{2\pi i}\lim_{\eta\to\infty}\int_{\gamma-i\eta}^{\gamma+i\eta} F(s)\exp(st)ds \tag{39}$$

where γ is a real number chosen such that the contour lies in the right half-plane.

Using $F(s) = \phi_n(\sqrt{s})$, inserting into equation 39, and making the substitution $u = \sqrt{s}$, such that $2udu = ds$, we get

$$f(t) = \frac{2}{2\pi i}\lim_{\eta\to\infty}\int_{\gamma-i\eta}^{\gamma+i\eta} u^n\exp(tu^2 - \alpha u)du$$

Note that this is not truly a substitution, but a transformation of the complex plane - it only behaves as a substitution due to the analyticity of the integrand in the relevant portion of the complex plane. Completing the square in the exponential, and translating the contour such that $z = u - \alpha/(2t)$, this becomes

$$f(t) = \frac{1}{i\pi}\exp\left(-\frac{\alpha^2}{4t}\right)\lim_{\eta\to\infty}\int_{\gamma-i\eta}^{\gamma+i\eta}\left(z + \frac{\alpha}{2t}\right)^n\exp(tz^2)dz$$

Setting $\gamma = 0$, which we can do as there is no singularity in the original integrand along the imaginary axis, and carefully substituting $it^{-1/2}z$ for z, the remaining integral turns into the standard integral representation of the nth physicist's Hermite polynomial, H_n:

$$\begin{aligned}\int_{\gamma-i\eta}^{\gamma+i\eta}\left(z + \frac{\alpha}{2t}\right)^n\exp(tz^2)dz &= it^{-(n+1)/2}\int_{-\infty}^{\infty}\left(iz + \frac{\alpha}{2\sqrt{t}}\right)^n\exp(-z^2) \\ &= \frac{i\sqrt{\pi}}{2^n}t^{-(n+1)/2}H_n\left(\frac{\alpha}{2\sqrt{t}}\right)\end{aligned}$$

Therefore overall we get

$$f(t) = \frac{1}{2^n\sqrt{\pi}} t^{-(n+1)/2} \exp\left(-\frac{\alpha^2}{4t}\right) H_n\left(\frac{\alpha}{2\sqrt{t}}\right)$$

Finally, inserting this into equation 38, we see that the Gaussian transform of a Slater-type orbital is given by

$$\phi_n(r) = \frac{1}{2^n\sqrt{\pi}} \int_0^\infty t^{-(n+1)/2} \exp\left(-\frac{\alpha^2}{4t}\right) H_n\left(\frac{\alpha}{2\sqrt{t}}\right) \exp(-tr^2)dt \tag{40}$$

In particular, for the case $n = \alpha = 1$, whence $H_1(x) = 2x$, this reduces to the transform used by Kutzelnigg:

$$\exp(-r) = \frac{1}{2\sqrt{\pi}} \int_0^\infty t^{-3/2} \exp\left(-\frac{1}{4t}\right) \exp(-tr^2)dt$$

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[41] The Hilbert space is usually taken to be $L^2(\mathcal{X}, d^4x)$, where $\mathcal{X} = \mathbb{R}^3 \times \mathrm{Spin}(1/2)$.

[42] These orbitals need not be distinct.

[43] Generalization to the many-body case is simple, but notationally busy.

[44] In essence, we require that the kinetic energy is well-defined.

[45] A normed linear space, such as a Hilbert space, is a particular subclass of metric space.

[46] This requirement ensures regularity of the potential operator, i.e. that $[\hat{V}, \hat{V}^\dagger] = 0$.

[47] This requirement is sufficient, but not necessary.

[48] This will be true unless n is very large.

[49] Recall that B_M is the space spanned by M Gaussians, in this case the even-tempered ones from this section.