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„Extraktion quantifizierbarer Information aus komplexen Systemen”

Numerical analysis of Gaussian approximations in quantum chemistry

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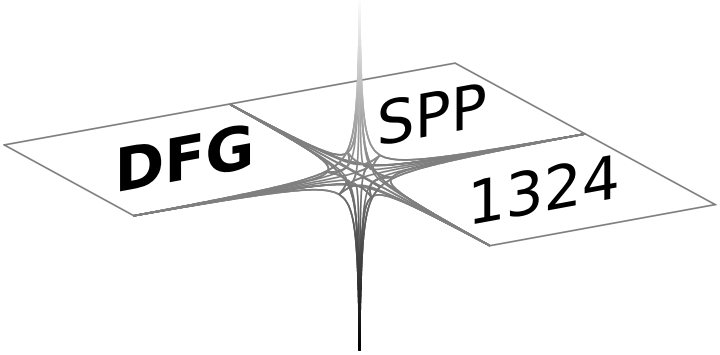
Preprint 128



Edited by

AG Numerik/Optimierung
Fachbereich 12 - Mathematik und Informatik
Philipps-Universität Marburg
Hans-Meerwein-Str.
35032 Marburg

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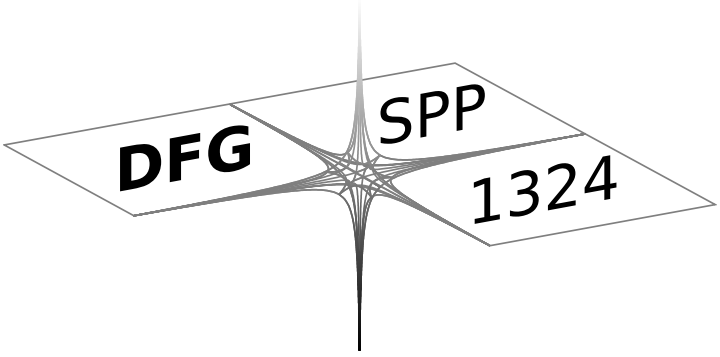

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Numerical analysis of Gaussian approximations in quantum chemistry

Markus Bachmayr[*], Huajie Chen[†], and Reinhold Schneider[‡]

Abstract

Bases of atomic-like functions provide a natural, physically motivated description of electronic states, and Gaussian-type orbitals are the most widely used basis functions in molecular simulations. This paper aims at developing a systematic analysis of numerical approximations based on linear combinations of some Gaussian-type orbitals. We give a priori error estimates for Hermite-type Gaussian bases and for even-tempered Gaussian bases. Some numerical results are presented to support the theory.

1 Introduction

The subject of electronic structure theory is the modelling of many-electron systems in chemistry and physics, which enables the investigation and prediction of properties, such as energies or electron densities, of molecules and materials in condensed phases. Among the different models of electronic structure theory, for large-scale systems Kohn-Sham density functional theory (DFT) [23, 29] achieves so far the best compromise between accuracy and computational cost, and has become the most widely used electronic structure model in chemistry and material science.

Let us consider a molecular system consisting of M nuclei of charges $\{Z_1, \cdots, Z_M\}$ located at the positions $\{\mathbf{R}_1, \cdots, \mathbf{R}_M\}$ and N electrons in the non-relativistic and spin-unpolarized setting. The ground state solutions of the system can be obtained by minimizing the Kohn-Sham energy functional

$$E(\{\phi_i\}) = \frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3} |\nabla\phi_i(x)|^2\,\mathrm{d}x + \int_{\mathbb{R}^3} V_{\mathrm{ext}}(x)\rho(x)\,\mathrm{d}x + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\,\mathrm{d}x\,\mathrm{d}y + \int_{\mathbb{R}^3}\mathcal{E}_{\mathrm{xc}}(\rho(x))\,\mathrm{d}x$$

with respect to wavefunctions $\{\phi_i\}_{i=1}^N$ under the orthogonality constraints

$$\int_{\mathbb{R}^3}\phi_i\phi_j = \delta_{ij}, \quad 1 \le i, j \le N,$$

[*]Institut für Geometrie und Praktische Mathematik, RWTH Aachen, Templergraben 55, 52056 Germany. E-mail: bachmayr@igpm.rwth-aachen.de

[†]Institut für Mathematik, Technische Universität Berlin, Straße des 17. Juni 136, D-10623 Berlin, Germany. E-mail: hjchen@lsec.cc.ac.cn. Financial support from the Alexander von Humboldt Foundation under grant CHN 1138663 STP.

[‡]Institut für Mathematik, Technische Universität Berlin, Straße des 17. Juni 136, D-10623 Berlin, Germany. E-mail: schneidr@math.tu-berlin.de.

where $\rho(x) = \sum_{i=1}^{N} |\phi_i(x)|^2$ is the electron density, $V_{\text{ext}} = -\sum_{k=1}^{M} \frac{Z_k}{|x - \mathbf{R}_k|}$ is the electrostatic potential generated by the nuclei, and $\mathcal{E}_{\text{xc}}(\rho)$ denotes the exchange-correlation energy per unit volume in an electron gas with density ρ. The existence of the minimizer has been established in [2, 32]. The Euler-Lagrange equation corresponding to this minimization problem is the so-called Kohn-Sham equation: Find $\lambda_i \in \mathbb{R}$, $\phi_i \in H^1(\mathbb{R}^3)$, for $i = 1, 2, \cdots, N$, such that

$$\begin{cases} \left(-\frac{1}{2}\Delta + V_{\text{eff}}(\{\phi_i\})\right)\phi_i &= \lambda_i \phi_i \quad \text{in } \mathbb{R}^3, \quad i = 1, 2, \cdots, N, \\ \displaystyle\int_{\mathbb{R}^3} \phi_i \phi_j &= \delta_{ij}, \end{cases} \tag{1.1}$$

where $V_{\text{eff}}(\{\phi_i\})$ is the effective potential corresponding to the last three terms in the energy functional. This nonlinear eigenvalue problem is commonly solved by a self-consistent field iteration (SCF) algorithm [33, 35]. In each iteration, a new Hamiltonian is constructed from a trial electronic state, and a linear eigenvalue problem is then solved to obtain the eigenfunctions for the lowest eigenvalues. In each step, the algorithm requires expansion of the wavefunction into a finite set of basis functions and assembly of the corresponding Galerkin discretization matrix of the Hamiltonian.

The choice of basis functions, which ultimately determines the approximation quality of the wavefunctions, is therefore crucial. There are basically four types of discretization methods that are widely used in electronic structure calculations [35]: the linear combination of atomic orbital methods; the plane wave methods; the real-space methods; and the atomic sphere methods (augmented plane wave methods). Linear combination of atomic orbitals (LCAO) methods are the methods most widely used by chemists, which capture the essence of the atomic-like features of molecules and provide an intuitive description of electronic states. Among them Gaussian-type orbitals (GTO) are used in the overwhelming majority of computations, which were first adopted by Boys [5] and expounded upon in many other texts (e.g. [36, 40]). The great virtue is that all matrix elements can be computed analytically, which greatly simplifies and speeds up the calculations. The GTO methods can be very accurate and efficient, as shown by the highly developed codes used in quantum chemistry (e.g., GAUSSIAN, MolPRO and PSI).

To our knowledge, there are only a few previous works devoted to the numerical analysis of atomic-like orbital bases. Klahn and Morgan studied in [27] the convergence of expansions of the ground state of hydrogen atom in a Hermite Gaussian basis, and showed the error of energy goes as $n^{-3/2}$. By optimization of the exponent, Klopper and Kutzelnigg showed numerically in [28] that the error could go as n^{-2}. Later, Kutzelnigg gave an error estimate for the expansion of $1/r$ and $e^{-\alpha r}$ in the Chebyshev norm and energy expectation value in [30, 31] (see also a contribution in [33]), which implies that the error of even-tempered Gaussian bases goes as $e^{-c\sqrt{n}}$. Braess studied in [6] (see also a joint work with Hackbusch in [7]) the approximation of $1/r$ and $e^{-\alpha r}$ by sums of exponentials in a weighted L^1-norm, as well as the Chebyshev norm, and found an $e^{-c\sqrt{n}}$ behavior of the error. Let us mention that these results are all based on one-dimensional expansion of the radial part of Hydrogen-like 1s wavefunctions, and the error estimates are mainly in L^∞-norm or for the energy expectation value. Gagelman and Yserentant studied very recently in [18] the expansion of the eigenfunctions of Schrödinger operators with smooth confinement potentials in Hermite Gaussian functions, which converge super-algebraically.

The purpose of this paper is to give a systematic numerical analysis of the GTO approximations and derive a priori error estimates of more general wavefunctions in the H^1-norm. It should be noted that our analysis does not only apply to DFT computations, but also

to various wavefunction methods (e.g., Hartree-Fock methods and configuration-interaction methods [21]).

The first important point in our analysis is the regularity of the wavefunctions. It was shown in [17, 24] that the exact electron densities are analytic away from the nuclei and satisfy certain cusp conditions at the nuclear positions. The algebraic convergence rates obtained in [27, 28], which are limited by the cusps of wavefunctions, are far from satisfactory. Similar problems arise in plane wave methods, which yield poor convergence rates in full-potential calculations and huge number of basis functions are needed in the computations. Thanks to the recent studies by Flad et al. in [14], higher regularity in weighted Sobolev space for wavefunctions of Schrödinger type eigenvalue problems can be employed in our analysis, which help to obtain better convergence rates for atomic-like basis functions.

For analysis of even-tempered GTO approximations, another important tool is the integral transform and sinc approximation theory. There are many different choices of GTO bases used in chemistry, most of which cannot be regarded as spectral methods, but rather as discretizations of certain integral representations of the wavefunctions [30]. Therefore, we shall use the Laplace transform to represent the wavefunctions by an integral. The integrands that arise in the transform are of the form required for the application of the sinc approximation theory, which help us to obtain satisfactory convergence rates.

This paper considers only a priori error analysis. The a posteriori error analysis, where even less results are available at present, will be subject of our future work.

The remainder of this paper is arranged as follows: In the coming section, we present the regularity results for wavefunctions of Schrödinger type equations. In Section 3, we give a priori error estimates for numerical approximations using GTO bases, including Hermite Gaussian basis functions and even-tempered Gaussian basis functions. Finally, we show some numerical results and give a concluding remark.

2 Regularity of Wavefunctions

As a model problem, we shall consider the following Schrödinger-type linear eigenvalue problem, which can be viewed as a linearization of (1.1): Find $\lambda \in \mathbb{R}$ and $0 \neq u \in H^1(\mathbb{R}^3)$ such that $\|u\|_{L^2(\mathbb{R}^3)} = 1$ and

$$a(u, v) = \lambda(u, v) \quad \forall\, v \in H^1(\mathbb{R}^3), \tag{2.2}$$

where the bilinear form $a : H^1(\mathbb{R}^3) \times H^1(\mathbb{R}^3) \to \mathbb{R}$ is defined by

$$a(u, v) = \frac{1}{2} \int_{\mathbb{R}^3} \nabla u \cdot \nabla v + \int_{\mathbb{R}^3} V_{\text{eff}}\, u\, v\,, \tag{2.3}$$

and the effective potential V_{eff} is smooth with exception of the singularities at the positions of the nuclei. As the analysis in this paper can be carried out for each nucleus separately, in the remainder of this work we consider a single nucleus located at the origin.

It was shown in [15, 16, 17, 24] that the exact wavefunctions are analytic away from the nuclei and satisfy certain cusp conditions at the nuclei. To study the asymptotic behavior of the wavefunctions, we formally consider the underlying $\mathbb{R}^3$ as a manifold with one conical singularity at the origin [14], which can be realized by introducing charts with polar coordinates. Further details concerning manifolds with conical singularities can be found in [13]. To be more specific, we consider equation (2.2) on the open stretched cone

$$X^\wedge := \mathbb{R}_+ \times S^2.$$

The quotient

$$X^{\triangle} := \overline{\mathbb{R}}_+ \times S^2/(0 \times S^2)$$

corresponds to a manifold with conical point at the origin, which can be identified with $\mathbb{R}^3$. The asymptotic regularity results for wavefunctions used in this paper are based on the results obtained by Flad, Schneider and Schulze [14]. This type of analysis has been introduced to investigate singularities for boundary value problems in conical domains with corners and edges, we refer to [4, 13, 19] for more details. In our case the geometry is fairly simple, while the Coulomb potential fits perfectly in this treatment. The following definitions of weighted Sobolev spaces and asymptotically well behaved functions are from [14].

The open stretched cone $X^{\wedge}$ can be considered as a half space of the infinite cylinder on which we introduce the standard Sobolev space

$$H^s_{\mathrm{cone}}(X^{\wedge}) := \{u \in H^s_{\mathrm{loc}}(\mathbb{R} \times S^2)|_{\mathbb{R}_+ \times S^2} : \ (1-\omega)u \in H^s(\mathbb{R}^3)\} \tag{2.4}$$

for any smooth cut-off function ω, i.e., $\omega = 1$ near 0 and $\omega = 0$ outside some neighborhood of 0. Further, define the sth weighted Sobolev space with index γ of periodic functions on $X^{\wedge}$ by

$$\mathcal{K}^{s,\gamma}(X^{\wedge}) := \left\{u \in \mathcal{D}'(X^{\wedge}) \ : \ |\mathbf{r}|^{|\alpha|-\gamma}\partial^{\alpha}u \in L^2(\mathbb{R}^3) \ \ \forall\ |\alpha| \le s\right\}. \tag{2.5}$$

Note that the difference between Sobolev space and the weighted Sobolev space is only the appearance of the weight function $|\mathbf{r}|^{\alpha-\gamma}$. Neither of the Sobolev spaces in (2.4) nor (2.5) is really appropriate for the infinite open stretched cone $X^{\wedge}$. Instead it is better to consider the combination

$$\mathscr{K}^{s,\gamma}(X^{\wedge}) := \omega\mathcal{K}^{s,\gamma}(X^{\wedge}) + (1-\omega)H^s_{\mathrm{cone}}(X^{\wedge}), \tag{2.6}$$

which provides the appropriate behavior in the limits $|\mathbf{r}| \to 0$ and $|\mathbf{r}| \to \infty$ simultaneously.

Consider the subspace of $\mathcal{K}^{s,\gamma}(X^{\wedge})$ of certain asymptotic type using polar coordinates[1] (r, θ, ϕ). These subspaces consist of functions with asymptotic expansions as $r \to 0$

$$\breve{u}(r,\theta,\phi) \sim \sum_j \sum_{k=0}^{m_j} c_{jk}(\theta,\phi) r^{-p_j} \ln^k r, \tag{2.7}$$

where c_{jk} belong to finite-dimensional subspaces $L_j \subset C^{\infty}(S^2)$ and p_j are taken from a strip of the complex plane, i.e.,

$$p_j \in \left\{z \in \mathbb{C}\colon \frac{3}{2} - \gamma + \vartheta < \mathrm{Re}z < \frac{3}{2} - \gamma\right\}$$

with $-\infty \le \vartheta < 0$. An asymptotic expansion (2.7) is completely characterized by the asymptotic type $P = \{(p_j, m_j, L_j)\}_{j \in \mathbb{Z}_+}$. Together, weight data γ, ϑ, and asymptotic type P define the weighted Sobolev spaces with asymptotics as $r \to 0$,

$$\mathscr{K}^{s,\gamma}_P(X^{\wedge}) := \{u \in \mathscr{K}^{s,\gamma}(X^{\wedge}) : \\ u - \sum_j \sum_{k=0}^{m_j} c_{jk}(\theta,\phi) r^{-p_j} \ln^k r \in \bigcap_{\varepsilon > 0} \mathscr{K}^{s,\gamma-\vartheta-\varepsilon}(X^{\wedge}) \Bigg\}.$$

[1]For a function $u(\mathbf{r})$, we denote by $\breve{u}(r,\theta,\phi)$ the polar coordinate representations, i.e., $u(\mathbf{r}) = \breve{u}(r,\theta,\phi)$. This notation will be used throughout this paper.

Definition 2.1. *A function u is called asymptotically well behaved if*

$$u \in \mathcal{K}_P^{\infty,\gamma}(X^\wedge) \qquad \text{for} \quad \gamma < 3/2 \quad \textit{and} \quad P = \{(-j, 0, L_j)\}_{j\in\mathbb{Z}_+}. \tag{2.8}$$

The finite dimensional spaces $L_j \subset C^\infty(S^2)$ are given by $L_j = \operatorname{span}\{Y_{\ell m}, \ell \le j\}$, where $Y_{\ell m}$ denotes spherical harmonics on S^2.

Throughout this paper, we shall make the assumption that the effective potential is of the form

$$V_{\text{eff}}(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|} + \rho * \frac{4\pi}{|\mathbf{r}|} + v_s(\mathbf{r}) \quad \text{with} \quad v_s \in C^\infty(\mathbb{R}^3), \tag{2.9}$$

where ρ is an asymptotically well behaved function. The following regularity result for eigenfunctions of (2.2) will be used in our analysis. The proof can be found in [14, Theorem 1].

Proposition 2.1. *If u is an eigenfunction of (2.2), then u is asymptotically well behaved.*

Denote by $\mathcal{Y}_{\ell m}$ the solid harmonics

$$\mathcal{Y}_{\ell m}(r, \theta, \phi) = r^\ell Y_{\ell m}(\theta, \phi).$$

Since the solid harmonics $\mathcal{Y}_{\ell m}(r, \theta, \phi)$ have explicit Cartesian expressions (see, e.g. [21]) as

$$\begin{aligned}\mathcal{Y}_{\ell m}(r, \theta, \phi) &= \mathcal{Y}_{\ell m}(r(x, y, z), \theta(x, y, z), \phi(x, y, z)) \\ &= \mathcal{P}_{\ell m}(x, y, z) = N_{\ell m}(x + \operatorname{sgn}(m) iy)^{|m|} \sum_{t=0}^{(\ell-|m|)/2} C_t^{\ell|m|}(x^2 + y^2)^t z^{\ell-2t-|m|}\end{aligned} \tag{2.10}$$

with the constants $N_{\ell m}$ and $C_{\ell m}$, they yield a significant simplification for numerical integrations in computations. Therefore, the solid harmonics are always used as the angular parts of the LCAO bases instead of spherical harmonics $Y_{\ell m}(\theta, \phi)$. The following two propositions will be used in our analysis.

Proposition 2.2. *If u is an eigenfunction of (2.2), then*

$$u \in C^\infty(\overline{\mathbb{R}}_+ \times S^2) \tag{2.11}$$

and it can be expanded using polar coordinates (r, θ, ϕ) as

$$\check{u}(r, \theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} R_{\ell m}(r) \mathcal{Y}_{\ell m}(r, \theta, \phi) \tag{2.12}$$

with $R_{\ell m} \in C^\infty([0, \infty))$.

Proof. The proof of (2.11) is given in [14, Proposition 1], and therefore it only remains to prove (2.12).

Since u is asymptotically well behaved, we have the expansion

$$\check{u}(r, \theta, \phi) = \omega(r) \sum_{j=0}^{k} r^j \alpha_j(\theta, \phi) + \Phi_{k+1}(r, \theta, \phi), \tag{2.13}$$

where $\Phi_{k+1} \in \mathscr{K}^{s,\gamma}(X^\wedge)$ for $\gamma < \dfrac{5}{2} + k$ and $s \in \mathbb{R}$. Note that further details on asymptotic type P are also investigated in [14], which not only demonstrates the absence of logarithmic terms in the expansion (2.7), but also shows that for each j only a finite number of spherical harmonics with $\ell \le -p_j$ can contribute, implying that $\alpha_j(\theta,\phi) \in \operatorname{span}\{Y_{\ell m}(\theta,\phi),\ \ell \le j\}$. This proves that the first part of (2.13) can be represented by $\displaystyle\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} R^a_{\ell m}(r)\mathcal{Y}_{\ell m}(r,\theta,\phi)$ with $R^a_{\ell m}(r) \in C^\infty([0,\infty))$ and $R^a_{\ell m}(r) = 0$ for $r > 1$.

For the second part of (2.13), we define

$$R^b_{\ell m}(r) = \frac{1}{r^\ell}\int_{S^2} \Phi_{k+1}(r,\theta,\phi) Y_{\ell m}(\theta,\phi)\,\mathrm{d}\theta\,\mathrm{d}\phi\,,$$

and have

$$\Phi_{k+1}(r,\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} R^b_{\ell m}(r)\mathcal{Y}_{\ell m}(\theta,\phi)\,.$$

Note that (2.11) implies that $R^b_{\ell m} \in C^\infty((0,\infty))$, and it is only necessary to prove that $R^b_{\ell m}$ is smooth at the origin. Using a direct calculation and the expression of (2.10), we have that if $f(r)$ has a singularity at $r = 0$ such that $f \notin C([0,\infty))$, then $f(r)\mathcal{Y}_{\ell m}(r,\theta,\phi) \notin H^{1+\ell}(\mathbb{R}^3)$. Since for any $\ell \in \mathbb{Z}$ and $s \in \mathbb{R}_+$, there exists sufficiently large k such that $\Phi_{k+1} \in H^{1+\ell+s}(\mathbb{R}^3)$, we can obtain that $R^b_{\ell m}(r) \in C^s([0,\infty))$.

Taking $R_{\ell m}(r) = R^a_{\ell m}(r) + R^b_{\ell m}(r)$, we obtain (2.12) with $R_{\ell m}(r) \in C^\infty([0,\infty))$. This completes the proof. □ □

Proposition 2.3. *If u is an eigenfunction of (2.2), then for any $N \in \mathbb{Z}_+$, there exist smooth functions $\alpha_j(\theta,\phi) \in \operatorname{span}\{Y_{\ell m}(\theta,\phi),\ \ell \le j\} \subset C^\infty(S^2),\ j = 0,1,\cdots,N$, such that*

$$\check{u}(r,\theta,\phi) - \omega(r)\sum_{j=0}^{N} r^j \alpha_j(\theta,\phi) \in H^{5/2+N-\varepsilon}(\mathbb{R}^3). \tag{2.14}$$

Proof. Again we use the asymptotic expansion of u as (2.13). For any $s \in \mathbb{R}$, there exists a sufficiently large k, such that $\Phi_{k+1} \in H^s(\mathbb{R}^3)$. Therefore, for any $N \in \mathbb{Z}_+$, there exists $k > N$ such that $\Phi_{k+1} \in H^{5/2+N-\varepsilon}(\mathbb{R}^3)$. Since a direct calculation and interpolation theory imply that

$$r^k Y_{\ell m}(\theta,\phi) \in H^{k+3/2-\varepsilon}(B(0,1))$$

for $k \ge \ell$ and $B(0,1) \equiv \{x : |x| \le 1\}$, we have

$$\omega(r)\sum_{j=N+1}^{k} r^j \alpha_j(\theta,\phi) \in H^{5/2+N-\varepsilon}(\mathbb{R}^3).$$

This completes the proof. □ □

3 Error Estimates for Gaussian Approximations

In what follows, we shall denote by C a generic positive constant which stands for different values at its different occurrences and is independent of finite dimensional subspaces. We shall use $\lfloor\cdot\rfloor$ and $\lceil\cdot\rceil$ to denote the floor and ceil integer of a real number, respectively.

Let V_δ be the finite dimensional space spanned by a set of GTO basis functions. The Galerkin approximation of the ground state solution of linear Schrödinger-type equation (2.2) is determined by the variational problem: Find $\lambda_\delta \in \mathbb{R}$ and $0 \neq u_\delta \in V_\delta$ such that $\|u_\delta\|_{L^2(\mathbb{R}^3)} = 1$ and

$$a(u_\delta, v) = \lambda_\delta (u_\delta, v) \qquad \forall\ v \in V_\delta. \tag{3.15}$$

Using standard estimates [3, 42], we have that the H^1 error of the finite dimensional approximation is estimated by

$$\|u - u_\delta\|_{H^1(\mathbb{R}^3)} \leq C \inf_{v_\delta \in V_\delta} \|u - v_\delta\|_{H^1(\mathbb{R}^3)}. \tag{3.16}$$

Since a simple calculation leads to

$$|\lambda_\delta - \lambda| = a(u_\delta - u, u_\delta - u) \leq C \|u - u_\delta\|^2_{H^1(\mathbb{R}^3)},$$

we have that the error of eigenvalue approximations goes as the square of the corresponding eigenfunction error.

For the nonlinear Kohn-Sham equation (1.1), we have the discretized problem

$$\begin{cases} (H_{\{\phi_i^\delta\}} \phi_i^\delta, v) &= (\lambda_i^\delta \phi_i^\delta, v) \quad \forall\ v \in V_\delta, \quad i = 1, \cdots, N, \\ \displaystyle\int_{\mathbb{R}^3} \phi_i^\delta \phi_j^\delta &= \delta_{ij} \end{cases}$$

with $H_{\{\phi_i^\delta\}} = -\dfrac{1}{2}\Delta + V_{\text{eff}}(\{\phi_i^\delta\})$. Using similar arguments as in [10] (see also [8]), we can prove the estimate

$$\sum_{i=1}^{N} \|\phi_i - \phi_i^\delta\|_{H^1(\mathbb{R}^3)} \leq C \sup_{1 \leq i \leq N} \inf_{v_\delta \in V_\delta} \|\phi_i - v_\delta\|_{H^1(\mathbb{R}^3)}. \tag{3.17}$$

under certain assumptions (including the coercivity assumption on the tangent space, the regularity assumption of the exchange-correlation term $\mathcal{E}_{\text{xc}}$, and the completeness assumption of the limit of the finite dimensional space). Due to the continuity of the energy functional, for the error in the ground state energy we obtain (cf. [8, 10])

$$|E(\{\phi_i^\delta\}) - E(\{\phi_i\})| \leq C \sum_{i=1}^{N} \|\phi_i - \phi_i^\delta\|^2_{H^1(\mathbb{R}^3)}.$$

Therefore it is only necessary for us to obtain the estimates of the right hand side of (3.16) and (3.17) for specified V_δ.

3.1 Hermite Gaussian Bases

The simplest GTO basis functions may be written in the following form

$$\psi^{\text{GTO}}_{n\ell m}(r, \theta, \varphi) = c_n r^n e^{-\zeta r^2} Y_{\ell m}(\theta, \varphi), \qquad n - \ell = 0, 2, 4, \cdots \tag{3.18}$$

where ζ is a fixed exponent and c_n are normalization constants. If we add polynomials with some odd orders $n - \ell$ to the set of basis functions, this set becomes formally overcomplete, and the error decreases much faster. Unfortunately, the incorporation of odd order polynomials makes the evaluation of integrals as difficult as for Slater type basis functions, and is therefore of less practical interest.

Theorem 3.1. *Let* $V_\delta \equiv V_N = \mathrm{span}\{\psi^{\mathrm{GTO}}_{n\ell m} :\ 0 \le n \le N,\ \ell = n, n-2, \cdots, n-2\left\lfloor \frac{n}{2} \right\rfloor,\ -\ell \le m \le \ell\}$. *If* u *is an eigenfunction of* (2.2), *then*

$$\inf_{v_\delta \in V_N} \|u - v_\delta\|_{H^1(\mathbb{R}^3)} \le C N^{-\frac{3}{4}+\varepsilon}. \tag{3.19}$$

If the basis functions (3.18) *have odd order* $n-\ell$ *included in the basis set for* $n \le K < N$, *say,* $V_\delta \equiv V_N^K = V_N \oplus \mathrm{span}\{\psi^{\mathrm{GTO}}_{n\ell m} :\ 0 \le n \le K,\ \ell = n-1, n-3, \cdots, n-1-2\left\lfloor \frac{n-1}{2} \right\rfloor,\ -\ell \le m \le \ell\}$, *then*

$$\inf_{v_\delta \in V_N^K} \|u - v_\delta\|_{H^1(\mathbb{R}^3)} \le C N^{-\frac{3}{4}-\frac{K}{2}+\varepsilon}. \tag{3.20}$$

Proof. We observe that under the same polynomial orders, the GTOs given in (3.18) span the same space with the harmonic oscillator (HO) functions (see, e.g. [21])

$$\begin{aligned} \psi^{\mathrm{HO}}_{\tilde{n}\ell m}(r,\theta,\varphi) &= R^{\mathrm{HO}}_{\tilde{n}\ell}(r) Y_{\ell m}(\theta,\varphi), \qquad \tilde{n} - \ell = 1, 2, \cdots, \\ R^{\mathrm{HO}}_{\tilde{n}\ell}(r) &= \frac{(2\zeta)^{3/4}}{\pi^{1/4}} \frac{\sqrt{2^{\tilde{n}+1}(\tilde{n}-\ell-1)!}}{\sqrt{(2\tilde{n}-1)!}} (\sqrt{2\zeta} r)^\ell L^{\ell+1/2}_{\tilde{n}-\ell-1}(2\zeta r^2) \exp(-\zeta r^2), \end{aligned} \tag{3.21}$$

where $\tilde{n} = (n+\ell)/2 + 1$ and the polynomials L^α_n are generalized Laguerre polynomials:

$$L^\alpha_n(x) = \frac{x^{-\alpha} e^x}{n!} \frac{d^n}{dx^n}(e^{-x} x^{n+\alpha}).$$

To see this, we note that all Laguerre functions of order n and lower may be written in terms of (3.18) of the same order.

The HO functions are the eigenfunctions of a three-dimensional isotropic harmonic oscillator

$$H = -\frac{1}{2}\Delta + \frac{1}{2}(2\zeta)^2 r^2.$$

with the principal quantum number $2(\tilde{n}-1) - \ell = n$. If we write the Hamiltonian in Cartesian coordinates as

$$H = -\frac{1}{2}\Delta + \frac{1}{2}(2\zeta)^2 (x^2 + y^2 + z^2),$$

which is separable in the three Cartesian directions, then the solution can be expressed as a product of one-dimensional HO functions in Cartesian coordinates

$$\psi^{\mathrm{HO}}_{\tilde{n}\ell m}(r(x,y,z), \theta(x,y,z), \phi(x,y,z)) = \varphi^{\mathrm{HO}}_{ijk}(x,y,z) = \chi^{\mathrm{H}}_i(x) \chi^{\mathrm{H}}_j(y) \chi^{H}_k(z),$$

where χ^{H}_i are Hermite functions of degree i, e.g.,

$$\begin{aligned} \chi^{\mathrm{H}}_i(x) &= \left(\frac{2\zeta}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^i i!}} H_i(\sqrt{2\zeta} x) \exp(-\zeta x^2), \\ H_i(x) &= (-1)^i \exp(x^2) \frac{d^i}{dx^i} \exp(-x^2), \end{aligned}$$

and the quantum number is given by $i + j + k = n$. Define $\tilde{\pi}_N : L^2(\mathbb{R}) \to \mathrm{span}\{\chi^{\mathrm{H}}_k, k \le N\}$ satisfying

$$(v - \tilde{\pi}_N v, v_N) = 0 \quad \forall\ v_N \in \mathrm{span}\{\chi^{\mathrm{H}}_k, k \le N\}.$$

Denote $\tilde{\partial}_x = \partial_x + x$. We define for an integer t,

$$\tilde{H}^t(\mathbb{R}^3) = \{v \in L^2(\mathbb{R}^3) : \tilde{\partial}^\alpha v \in L^2(\mathbb{R}^3),\ 0 \le |\alpha| \le t\}$$

with the associated norm $\|v\|_{\tilde{H}^t(\mathbb{R}^3)} = \left(\sum_{|\alpha|\le t} \|\tilde{\partial}^\alpha v\|^2_{L^2(\mathbb{R}^3)}\right)^{1/2}$. For fractional t, $\tilde{H}^t(\mathbb{R}^3)$ and $\|\cdot\|_{\tilde{H}^t(\mathbb{R}^3)}$ are defined by interpolation theory. It is obtained from a standard spectral analysis [38] that for any v satisfying $\tilde{\partial}^s v \in L^2(\mathbb{R})$ and $s \ge t$, there holds

$$\|\partial^t(v - \tilde{\pi}_N v)\|_{L^2(\mathbb{R})} \le CN^{-(s-t)/2}\|\tilde{\partial}^s v\|_{L^2(\mathbb{R})} \quad t = 0, 1. \tag{3.22}$$

Let us define the projection $\Pi_N : L^2(\mathbb{R}^3) \to \widetilde{V}_N \equiv \mathrm{span}\{\varphi^{\mathrm{HO}}_{ijk}, 0 \le i, j, k \le \frac{N}{3}\}$ as a product of three one-dimensional projections by

$$\Pi_N = \tilde{\pi}_{\lfloor \frac{N}{3} \rfloor, x} \circ \tilde{\pi}_{\lfloor \frac{N}{3} \rfloor, y} \circ \tilde{\pi}_{\lfloor \frac{N}{3} \rfloor, z}.$$

Note that since (2.14) implies in particular that $u \in H^{\frac{5}{2}-\varepsilon}(\mathbb{R}^3)$, which together with the exponential decay property of u (see, e.g. [24, 42]) leads to $u \in \tilde{H}^{5/2-\varepsilon}(\mathbb{R}^3)$. We can thus derive from (3.22) that

$$\|u - \Pi_N u\|_{H^1(\mathbb{R}^3)} \le C\left\lfloor \frac{N}{3} \right\rfloor^{-(\frac{5}{2}-\varepsilon-1)/2} \|u\|_{\tilde{H}^{5/2-\varepsilon}(\mathbb{R}^3)} \le CN^{-\frac{3}{4}+\varepsilon}. \tag{3.23}$$

Since $\widetilde{V}_N \subset \mathrm{span}\{\varphi^{\mathrm{HO}}_{ijk}, 0 \le i+j+k \le N\} = V_N$, we can derive (3.19) from (3.23) directly.

For a given K, by taking $\omega(r)$ in (2.14) that equals $e^{-\alpha r^2}$ in the vicinity of the origin and vanish outside the neighbor of the origin, we can divide u into two parts

$$u(r, \theta, \phi) = e^{-\alpha r^2} \sum_{j=0}^{K} r^j \alpha_j(\theta, \phi) + u_s(r, \theta, \phi),$$

such that $u_s \in H^{5/2+K-\varepsilon}(\mathbb{R}^3)$ according to Proposition 2.3. Therefore, we can obtain from (3.22) that

$$\|u_s - \Pi_N u_s\|_{H^1(\mathbb{R}^3)} \le CN^{-(\frac{3}{2}+K-\varepsilon)/2}\|u_s\|_{\tilde{H}^{5/2+K-\varepsilon}(\mathbb{R}^3)}$$

Take $v_\delta = e^{-\alpha r^2} \sum_{j=0}^{K} r^j \alpha_j(\theta, \phi) + \Pi_N u_s \in V_N^K$, we have

$$\|u - v_\delta\|_{H^1(\mathbb{R}^3)} = \|u_s - \Pi_N u_s\|_{H^1(\mathbb{R}^3)} \le CN^{-(\frac{3}{2}+K-\varepsilon)/2}.$$

This completes the proof. □ □

Remark 3.1. *We mention that it has been shown by Klahn and Morgan in [27] that the error of the ground state energy of the Hydrogen atom goes as $n^{-3/2}$. Furthermore, the one dimensional calculations by Hill in [22] and numerical experiments by Klopper and Kutzelnigg in [28] show that by adding a finite number of functions with odd order polynomials in* (3.18)*, the error of energy is improved by a factor n^{-2} with each additional basis function, which is consistent with our results.*

3.2 Even-Tempered Gaussian Bases

As we see from Theorem 3.1, the approximation by GTO basis functions of the form (3.18) with only even order polynomials converges relatively slowly, while for a basis including the odd powers of r, it converges much faster, since such a basis set can better resolve the singularities of the wavefunctions to be expanded [30]. However, the integration of basis functions including odd powers of r is much more complicated than in the case of only even powers, leading to the same difficulties as for Slater type orbitals in practical computations (see, e.g. [21] for a discussion of GTO integral evaluation). That is why the bases with variable exponents are the most popular choice in practice, in which the radial parts are described exclusively by means of variable exponents, and the only powers of r introduced are those associated with the angular momentum quantum number ℓ of the spherical harmonics. The following set of spherical harmonic GTO basis functions are thus used,

$$\psi^{\mathrm{GTO}}_{\eta_n \ell m}(r,\theta,\varphi) \quad = \quad c_n e^{-\eta_n r^2} r^\ell Y_{\ell m}(\theta,\varphi), \qquad n = 0, 1, \cdots, \tag{3.24}$$

with c_n the normalization constant.

Remark 3.2. *In most of the practical computations, one may construct the basis set from fixed linear combinations of GTOs:*

$$\tilde{\psi}_{a\ell m}(r,\theta,\varphi) = (\sum_{k=1}^{K_a} c_{ak} e^{-\eta_k r^2}) r^\ell Y_{\ell m}(\theta,\varphi), \qquad n = 0, 1, \cdots, \tag{3.25}$$

with c_{ak} the contraction coefficients. Such linear combinations are known as contracted GTOs, and the individual Gaussians from which the contracted GTOs are constructed are referred to as primitive GTOs (see, e.g. [21]). For simplicity, we shall focus on primitive GTOs in this paper.

Some sufficient but not necessary conditions for completeness of the basis set (3.24) have been established in [21, 26]. The criteria are not helpful in practice since they do not guide us towards bases that converge rapidly, but only tell us that it is in principle possible to construct complete basis sets of the simple form (3.24). The optimization of Gaussian exponents is a highly nonlinear problem with multiple solutions. Since an inspection of the exponents reveals that the ratio between the exponents is approximately constant [21], one should be able to obtain the following representation of the exponents

$$\eta_n = \alpha \beta^n \tag{3.26}$$

with the parameters α and β. We shall focus our attention in the following analysis on this specific type of GTOs, which are commonly referred to as even-tempered Gaussian bases.

The main result of this section is the following theorem, which considers the convergence rate of some even-tempered Gaussian approximations for wavefunctions with finite angular momenta and corresponding radial parts that are products of exponentials and polynomials.

Theorem 3.2. *Given an integer L. Let $V_\delta \equiv V_N = \mathrm{span}\{\psi^{\mathrm{GTO}}_{\eta_n \ell m} :\ n \le N,\ 0 \le \ell \le L,\ -\ell \le m \le \ell\}$ with η_n given by the form (3.26). If u has the expression*

$$u(\mathbf{r}) = \check{u}(r,\theta,\phi) = \sum_{0 \le \ell \le L, |m| \le \ell} P_{\ell m, M}(r) e^{-\gamma_\ell r} \mathcal{Y}_{\ell m}(r,\theta,\phi), \tag{3.27}$$

where γ_ℓ are constants and $P_{\ell m,M}$ are the polynomials with degrees no greater than M, then for sufficiently large N, there exist α_N and β_N such that

$$\inf_{v_\delta \in V_\delta} \|u - v_\delta\|_{H^1(\mathbb{R}^3)} \le C_{M,L} e^{-c\sqrt{N}} \tag{3.28}$$

with some constants $C_{M,L}$ and c.

To prove this theorem, we shall apply sinc quadrature approximation results, for details of which we refer to the monograph of Stenger [39]. As a first step, we use these results to prove the following lemma.

Lemma 3.1. *Let $\ell \in \mathbb{N} \cup \{0\}$ and $f(r) \in H^1([0,\infty))$. Assume that $F(s) := \mathcal{L}^{-1}(f(r^{\frac{1}{2}}), s)$ exists, where $\mathcal{L}^{-1}$ is the inverse Laplace transform and there exists $d > 0$ so that $F \circ \exp$ is holomorphic in the strip $\mathscr{D}_d := \{z \in \mathbb{C} : \operatorname{Im} z \in (-d, d)\}$ and satisfies*

$$\int_{-\infty}^{0} e^{(\frac{3}{4}-\frac{\ell}{2})x} |F(e^{x \pm id})| \,\mathrm{d}x + \int_{0}^{\infty} e^{(\frac{5}{4}-\frac{\ell}{2})x} |F(e^{x \pm id})| \,\mathrm{d}x \le C_{d,\ell}$$

with some constant $C_{d,\ell} > 0$. If there exist $\mu_\ell, \hat{x}_\ell, D_\ell > 0$ such that

$$e^{-(\frac{3}{4}-\frac{\ell}{2})x} |F(e^{-x})| + e^{(\frac{5}{4}-\frac{\ell}{2})x} |F(e^{x})| \le D_\ell e^{-\mu_\ell x} \quad \text{for } x \ge \hat{x}_\ell,$$

then for $N \ge \max\{\hat{x}_\ell^2 \mu_\ell/(2\pi d), (\ln^2 2)/(2\pi d \mu_\ell)\}$, there exist α_N, β_N, $c \in \mathbb{R}$ and $f_N \in \operatorname{span}\{e^{-\eta_n r^2}\}_{n=1}^{2N+1}$, with η_n as in (3.26), such that

$$\begin{aligned} &\|r^\ell (f - f_N)\|_{L^2([0,\infty))} + \|r^\ell \partial_r (f - f_N)\|_{L^2([0,\infty))} \\ &\qquad \le 2^{-\ell/2+2} \sqrt{(2\ell+1)!} \left(2C_{d,\ell} + (2\mu_\ell)^{-1} D_\ell\right) e^{-\sqrt{2\pi d \mu_\ell} N}. \end{aligned} \tag{3.29}$$

Proof. We shall first consider the L^2-error estimate in the case $\ell = 0$, i.e., $\|f - f_N\|_{L^2([0,\infty))}$. Let $G(x) = e^x F(e^x)$. By a variable substitution, we obtain

$$f(r) = \int_0^\infty F(s) e^{-sr^2} \,\mathrm{d}s = \int_{-\infty}^{\infty} G(x) e^{-e^x r^2} \,\mathrm{d}x.$$

Let

$$f_h(r) := h \sum_{k=-\infty}^{\infty} G(kh) e^{-e^{kh} r^2}, \qquad f_{Nh}(r) := h \sum_{k=-N}^{N} G(kh) e^{-e^{kh} r^2}$$

and $T(x) := \displaystyle\int_0^\infty e^{-xr^2} \,\mathrm{d}r = \frac{\sqrt{\pi}}{2} x^{-\frac{1}{2}}$. We have

$$\begin{aligned} \|f - f_h\|_{L^2([0,\infty))}^2 &= \int_0^\infty \Big(\int_{-\infty}^{\infty} G(s)\, e^{-e^s r^2} \,\mathrm{d}s - h \sum_{j=-\infty}^{\infty} G(jh)\, e^{-e^{jh} r^2} \Big)^2 \,\mathrm{d}r \\ &= \int_0^\infty \Big(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G(s)\, G(t)\, e^{-(e^s + e^t) r^2} \,\mathrm{d}s \,\mathrm{d}t \\ &\quad + h^2 \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} G(jh)\, G(kh)\, e^{-(e^{jh} + e^{kh}) r^2} \\ &\quad - 2h \sum_{j=-\infty}^{\infty} \int_{-\infty}^{\infty} G(s)\, e^{-e^s r^2} \,\mathrm{d}s\, G(jh) e^{-e^{jh} r^2} \Big) \,\mathrm{d}r, \end{aligned}$$

and by the definition of T,

$$
\begin{aligned}
&= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(s)\,G(t)\,T(e^s+e^t)\,\mathrm{d}s\,\mathrm{d}t \\
&\quad + h^2 \sum_{j=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} G(jh)\,G(kh)\,T(e^{jh}+e^{kh}) \\
&\quad - 2h \sum_{j=-\infty}^{\infty}\int_{-\infty}^{\infty} G(s)\,G(jh)\,T(e^s+e^{jh})\,\mathrm{d}s\,,
\end{aligned}
$$

which can be rewritten as

$$
\begin{aligned}
&= \int_{-\infty}^{\infty} G(s)\Big(\int_{-\infty}^{\infty} G(t)\,T(e^s+e^t)\,\mathrm{d}t - h\sum_{k=-\infty}^{\infty} G(kh)\,T(e^s+e^{kh})\Big)\,\mathrm{d}s \\
&\quad - h\sum_{k=-\infty}^{\infty} G(kh)\Big(\int_{-\infty}^{\infty} G(s)\,T(e^s+e^{kh})\,\mathrm{d}s - h\sum_{j=-\infty}^{\infty} G(jh)\,T(e^{jh}+e^{kh})\Big).
\end{aligned}
$$

Using the result of sinc theory in [39, Theorem 3.2.1] for the last formula, we obtain

$$
\begin{aligned}
\|f-f_h\|^2_{L^2([0,\infty))} = \int_{-\infty}^{\infty} G(s)\frac{i}{2}\int_{-\infty}^{\infty}\Bigg(& G(t-id)\,T(e^s+e^{t-id})\frac{e^{-\pi(d+it)/h}}{\sin[\pi(t-id)/h]} \\
&- G(t+id)\,T(e^s+e^{t+id})\frac{e^{-\pi(d-it)/h}}{\sin[\pi(t+id)/h]}\Bigg)\,\mathrm{d}t\,\mathrm{d}s \\
- h\sum_{k=-\infty}^{\infty} G(kh)\frac{i}{2}\int_{-\infty}^{\infty}\Bigg(& G(t-id)\,T(e^{kh}+e^{t-id})\frac{e^{-\pi(d+it)/h}}{\sin[\pi(t-id)/h]} \\
&- G(t+id)\,T(e^{kh}+e^{t+id})\frac{e^{-\pi(d-it)/h}}{\sin[\pi(t+id)/h]}\Bigg)\,\mathrm{d}t\,, \qquad (3.30)
\end{aligned}
$$

and applying the same result once more yields

$$
\begin{aligned}
= \quad & -\frac{1}{4}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Bigg(\frac{e^{-\pi(d+it)/h}}{\sin[\pi(t-id)/h]}\frac{e^{-\pi(d+is)/h}}{\sin[\pi(s-id)/h]} \\
& G(t-id)\,G(s-id)\,T(e^{t-id}+e^{s-id}) \\
& +\frac{e^{-\pi(d+it)/h}}{\sin[\pi(t-id)/h]}\frac{e^{-\pi(d-is)/h}}{\sin[\pi(s+id)/h]}G(t-id)\,G(s+id)\,T(e^{t-id}+e^{s+id}) \\
& +\frac{e^{-\pi(d-it)/h}}{\sin[\pi(t+id)/h]}\frac{e^{-\pi(d+is)/h}}{\sin[\pi(s-id)/h]}G(t+id)\,G(s-id)\,T(e^{t+id}+e^{s-id}) \\
& +\frac{e^{-\pi(d-it)/h}}{\sin[\pi(t+id)/h]}\frac{e^{-\pi(d-is)/h}}{\sin[\pi(s+id)/h]} \\
& G(t+id)\,G(s+id)\,T(e^{t+id}+e^{s+id})\Bigg)\,\mathrm{d}s\,\mathrm{d}t \\
\leq \quad & \frac{1}{4}\Big(\frac{e^{-\pi d/h}}{\sinh(\pi d/h)}\Big)^2\mathcal{N}(G,T,d)\,, \qquad (3.31)
\end{aligned}
$$

where

$$\begin{aligned}\mathcal{N}(G,T,d) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \big(&|G(t-id)\,G(s-id)\,T(e^{t-id}+e^{s-id})| \\ &+ |G(t-id)\,G(s+id)\,T(e^{t-id}+e^{s+id})| \\ &+ |G(t+id)\,G(s-id)\,T(e^{t+id}+e^{s-id})| \\ &+ |G(t+id)\,G(s+id)\,T(e^{t+id}+e^{s+id})|\big)\,\mathrm{d}s\,\mathrm{d}t\,.\end{aligned}$$

For the latter expression, we obtain the estimate

$$\begin{aligned}&= \frac{\sqrt{\pi}}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Big(\Big|\frac{G(t-id)\,G(s-id)}{(e^{t-id}+e^{s-id})^{1/2}}\Big| + \Big|\frac{G(t-id)\,G(s+id)}{(e^{t-id}+e^{s+id})^{1/2}}\Big| \\ &\quad + \Big|\frac{G(t+id)\,G(s-id)}{(e^{t+id}+e^{s-id})^{1/2}}\Big| + \Big|\frac{G(t+id)\,G(s+id)}{(e^{t+id}+e^{s+id})^{1/2}}\Big|\Big)\,\mathrm{d}s\,\mathrm{d}t \\ &\le \sqrt{2\pi}\bigg(\max\bigg\{\int_{-\infty}^{\infty} e^{-\frac{1}{4}t}e^{t}|F(e^{t-id})|\,\mathrm{d}t, \int_{-\infty}^{\infty} e^{-\frac{1}{4}t}e^{t}|F(e^{t+id})|\,\mathrm{d}t\bigg\}\bigg)^2, \qquad (3.32)\end{aligned}$$

where the right hand side is finite by our assumptions.

We now choose $h := \sqrt{\frac{2\pi d}{\mu_0 N}}$; note that this amounts to taking

$$\alpha = e^{-\sqrt{\frac{2\pi d N}{\mu_0}}}, \quad \beta = e^{\sqrt{\frac{2\pi d}{\mu_0 N}}}$$

as the parameters (3.26) of the even-tempered GTO basis. As a consequence, $N \ge \hat{x}_0^2\mu_0/(2\pi d)$ implies $Nh \ge \hat{x}_0$, and we therefore obtain

$$\begin{aligned}\|f_h - f_{Nh}\|^2_{L^2([0,\infty))} &= h^2\int_{-\infty}^{\infty}\Big(\sum_{|k|>N} G(kh)e^{-e^{kh}r^2}\Big)^2\,\mathrm{d}r \\ &= h^2\sum_{|k|>N}\sum_{|l|>N} G(kh)G(lh)T(e^{kh}+e^{lh}) \\ &\le \frac{h^2\sqrt{\pi}}{2\sqrt{2}}\bigg(\int_{-\infty}^{-N} F(e^{xh})e^{\frac{3}{4}xh}\,\mathrm{d}x + \int_{N}^{\infty} F(e^{xh})e^{\frac{3}{4}xh}\,\mathrm{d}x\bigg)^2 \\ &\le \frac{\mu_0^{-2}\sqrt{\pi}D_0^2}{2\sqrt{2}}e^{-2\mu_0 Nh}. \qquad (3.33)\end{aligned}$$

Since by assumption $N \ge (\ln^2 2)/(2\pi d\mu_0)$, we have $e^{-\pi d/h}/\sinh(\pi d/h) \le 4e^{-\sqrt{2\pi d\mu_0 N}}$ in (3.31). We thus obtain from (3.31) and (3.33) that

$$\begin{aligned}\|f - f_{Nh}\|_{L^2([0,\infty))} &\le \|f - f_h\|_{L^2([0,\infty))} + \|f_h - f_{Nh}\|_{L^2([0,\infty))} \\ &\le \pi^{\frac{1}{4}}\big(2^{\frac{5}{4}}C_d + 2^{-\frac{3}{4}}\mu_0^{-1}D_0\big)e^{-\sqrt{2\pi d\mu_0}\sqrt{N}}\,. \qquad (3.34)\end{aligned}$$

This completes the error estimates for $\|f - f_N\|_{L^2([0,\infty))}$.

For the H^1-seminorm error estimate, i.e. $\|\partial(f - f_N)\|_{L^2([0,\infty))}$, we approximate

$$f'(r) = -2r\int_{-\infty}^{\infty} e^{x}G(x)e^{-e^{x}r^2}\,\mathrm{d}x$$

by

$$f_h'(r) = -2rh \sum_{k=-\infty}^{\infty} e^{kh} G(kh) e^{-e^{kh} r^2},$$

$$f_{Nh}'(r) = -2rh \sum_{k=-N}^{N} e^{kh} G(kh) e^{-e^{kh} r^2}.$$

Applying the same arguments as above to

$$\tilde{G}(x) := -2e^x G(x) \quad \text{and} \quad \tilde{T}(x) := \int_0^\infty r^2 e^{-xr^2} \,\mathrm{d}r = \frac{\sqrt{\pi}}{4} x^{-3/2},$$

we can derive that for the choice $h = \sqrt{\frac{2\pi d}{\mu_0 N}}$ made before, we have

$$\|f' - f_{Nh}'\|_{L^2([0,\infty))} \le \pi^{\frac{1}{4}} \big(2^{\frac{7}{4}} C_d + 2^{-\frac{1}{4}} \mu_0^{-1} D_0\big) e^{-\sqrt{2\pi d \mu_0}\sqrt{N}}$$

with some constant c_2; to this end, note that the same arguments for $\tilde{G}$ and $\tilde{T}$ as (3.32) and (3.33) lead to

$$\mathcal{N}(\tilde{G}, \tilde{T}, d) \le \sqrt{2^3 \pi} \bigg(\max\bigg\{ \int_{-\infty}^{\infty} e^{\frac{5}{4}t} |F(e^{t-id})| \,\mathrm{d}t, \int_{-\infty}^{\infty} e^{\frac{5}{4}t} |F(e^{t+id})| \,\mathrm{d}t \bigg\} \bigg)^2$$

and

$$\begin{aligned} \|f_h' - f_{Nh}'\|_{L^2([0,\infty))}^2 &\le \frac{h^2 \sqrt{\pi}}{\sqrt{2}} \bigg(\int_{-\infty}^{-N} F(e^{xh}) e^{\frac{5}{4}xh} \,\mathrm{d}x + \int_N^{\infty} F(e^{xh}) e^{\frac{5}{4}xh} \,\mathrm{d}x \bigg)^2 \\ &\le \frac{\mu_0^{-2} \sqrt{\pi} D_0^2}{\sqrt{2}} e^{-2\mu_0 N h}. \end{aligned}$$

This completes the proof of (3.29) in the case $\ell = 0$, where we additionally estimate $(2\pi)^{1/4}(1+\sqrt{2}) \le 4$ to simplify the constants.

In the case $\ell > 0$, we can obtain (3.29) by repeating the same arguments as above with

$$T_\ell(x) := \int_0^\infty r^{2\ell} e^{-xr^2} \,\mathrm{d}r = \frac{(2\ell-1)!}{2^{\ell+1}} \sqrt{\frac{\pi}{x^{2\ell+1}}}$$

and

$$\tilde{T}_\ell(x) := \int_0^\infty r^{2+2\ell} e^{-xr^2} \,\mathrm{d}r = \frac{(2\ell+1)!}{2^{\ell+2}} \sqrt{\frac{\pi}{x^{2\ell+3}}},$$

which completes the proof. □ □

The following lemma states that for particular functions that are products of a monomial r^n and an exponential factor $e^{-\gamma r}$ with $\gamma > 0$, the assumptions of Lemma 3.1 are satisfied. Here we use the notation $n!! := n(n-2)(n-4)\cdots(n+1-2\lfloor \frac{n+1}{2} \rfloor)$.

Lemma 3.2. *Let $f_{n,\gamma}(r) := r^n e^{-\gamma r}$ with $n \in \mathbb{N} \cup \{0\}$ and $\gamma > 0$, and let $\ell \in \mathbb{N} \cup \{0\}$. If $F_{n,\gamma}(s) := \mathcal{L}^{-1}(f_{n,\gamma}(r^{\frac{1}{2}}), s)$, then $F_{n,\gamma} \circ \exp$ is holomorphic in the strip $\mathscr{D}_d := \{z \in \mathbb{C} : \operatorname{Im} z \in (-d, d)\}$ for $d \in (0, \frac{\pi}{2})$, and there exists $\hat{C} > 0$ independent of n, ℓ, and d, such that*

$$\begin{aligned} &\int_{-\infty}^0 e^{(\frac{3}{4} - \frac{\ell}{2})x} |F(e^{x \pm id})| \,\mathrm{d}x + \int_0^\infty e^{(\frac{5}{4} - \frac{\ell}{2})x} |F(e^{x \pm id})| \,\mathrm{d}x \\ &\qquad \le \hat{C} n!! \Big(\max\{n, \gamma^n\} (1 + 2\ell + 2n)^{-1} + \gamma^{-\ell - n} \Big(\frac{4}{\cos d} \Big)^{\frac{3}{4} + \frac{\ell}{2} + n} \lceil \ell/2 + n \rceil ! \Big). \end{aligned} \tag{3.35}$$

Moreover, for

$$\mu_\ell := \lfloor \tfrac{n}{2} \rfloor + \tfrac{\ell}{2} + \tfrac{1}{4}\,, \quad \hat{x}_\ell := \max\{2\ln(4\gamma^{-2}(3n+2\ell+2)), 0\}\,,$$

there exists $\hat{D} > 0$ *independent of* n, ℓ, *and* d, *such that*

$$e^{-(\frac{3}{4}-\frac{\ell}{2})x}|F(e^{-x})| + e^{(\frac{5}{4}-\frac{\ell}{2})x}|F(e^{x})| \leq \hat{D}\, n!! \max\{n, \gamma^n\} e^{-\mu_\ell x} \quad \textit{for } x \geq \hat{x}_\ell, \tag{3.36}$$

Proof. For $\gamma = 0$ and $n = 0, 1$, we know

$$\mathcal{L}^{-1}(e^{-\sqrt{r}})(s) = (2\sqrt{\pi})^{-1} s^{-3/2} e^{-\frac{1}{4s}}$$

and

$$\mathcal{L}^{-1}(\sqrt{r}e^{-\sqrt{r}})(s) = -(4\sqrt{\pi})^{-1} s^{-5/2}(2s-1)e^{-\frac{1}{4s}}.$$

Recall that $\mathcal{L}^{-1}(\varphi) = \Phi$ implies $\mathcal{L}^{-1}(r\varphi(r))(s) = \Phi'(s)$ provided that the corresponding integrals exist and $\Phi(0) = 0$ [37]. Applying this property recursively, for $k \in \mathbb{N}_0$ we obtain

$$\mathcal{L}^{-1}(f_{2k,0}(\sqrt{r}))(s) = s^{-\frac{4k+3}{2}} P_{2k}(s)\, e^{-\frac{1}{4s}}$$

$$\text{with} \quad P_0 = (2\sqrt{\pi})^{-1}$$

$$\text{and} \quad P_{2k+2}(s) = -\frac{4k+3}{2} s P_{2k}(s) + s^2 P'_{2k}(s) + \frac{1}{4} P_{2k}(s)$$

for even-order polynomials, as well as

$$\mathcal{L}^{-1}(f_{2k+1,0}(\sqrt{r}))(s) = s^{-\frac{4k+5}{2}} P_{2k+1}(s)\, e^{-\frac{1}{4s}}$$

$$\text{with} \quad P_1(s) = -(4\sqrt{\pi})^{-1}(2s-1)$$

$$\text{and} \quad P_{2k+3}(s) = -\frac{4k+5}{2} s P_{2k+1}(s) + s^2 P'_{2k+1}(s) + \frac{1}{4} P_{2k+1}(s)$$

for odd-order polynomials. For $\gamma > 0$, we thus have

$$\begin{aligned} \mathcal{L}^{-1}(f_{2k,\gamma}(\sqrt{r}))(s) &= \gamma^{-2k} \mathcal{L}^{-1}(f_{2k,0}(\gamma\sqrt{r}))(s) \\ &= \gamma^{2k+1} s^{-\frac{4k+3}{2}} P_{2k}(\gamma^{-2}s) e^{-\frac{\gamma^2}{4s}} \end{aligned}$$

for even-order polynomials and

$$\begin{aligned} \mathcal{L}^{-1}(f_{2k+1,\gamma}(\sqrt{r}))(s) &= \gamma^{-2k-1} \mathcal{L}^{-1}(f_{2k+1,0}(\gamma\sqrt{r}))(s) \\ &= \gamma^{2k+2} s^{-\frac{4k+5}{2}} P_{2k+1}(\gamma^{-2}s) e^{-\frac{\gamma^2}{4s}} \end{aligned}$$

for odd-order polynomials. In summary, we obtain

$$F_{n,\gamma}(s) = \mathcal{L}^{-1}(f_{n,\gamma}(\sqrt{r}))(s) = \gamma^{n+1} s^{-\frac{2n+3}{2}} P_n(\gamma^{-2}s) e^{-\frac{\gamma^2}{4s}} \tag{3.37}$$

and therefore

$$F_{n,\gamma}(e^x) = \gamma^{n+1} e^{-\frac{2n+3}{2}x} P_n(\gamma^{-2}e^x) e^{-\frac{\gamma^2}{4}e^{-x}}\,,$$

where P_n has degree $\lceil n/2 \rceil$ and satisfies the recursion

$$P_{n+2}(s) = -\frac{2n+3}{2} s P_n(s) + s^2 P'_n(s) + \frac{1}{4} P_n(s)\,.$$

¿From this recursive definition it can be seen that the absolute values of the coefficients in P_n are bounded by $(2\sqrt{\pi})^{-1}n!!$, and consequently

$$|F_{n,\gamma}(e^{x\pm id})| \le (2\sqrt{\pi})^{-1}\gamma^{n+1}n!!e^{-\frac{\gamma^2\cos d}{4}e^{-x}}\sum_{k=0}^{\lceil n/2\rceil}\gamma^{-2k}e^{-(n+\frac{3}{2}-k)x}\,. \tag{3.38}$$

By the assumption $d < \pi/2$, we obtain that $F_{n,\gamma}(e^z)$ is holomorphic with respect to z in the strip $\mathscr{D}_d$. Concerning the integrability condition (3.35), for the integrals over the positive real axis we obtain

$$\int_0^\infty e^{-(\frac{1}{4}+\frac{\ell}{2}+n-k)x}e^{-\frac{\gamma^2\cos d}{4}e^{-x}} \le \Big(\frac{1}{4}+\frac{\ell}{2}+n-k\Big)^{-1}\,.$$

For the integrals over the negative real axis, note that for $\alpha > 0$,

$$\begin{aligned}\int_{-\infty}^0 e^{-\alpha x}e^{-\frac{\gamma^2\cos d}{4}e^{-x}}\,\mathrm{d}x &= \int_0^\infty e^{\alpha x}e^{-\frac{\gamma^2}{4}e^x\cos d}\,\mathrm{d}x\\ &= \int_1^\infty s^{\alpha-1}e^{-\frac{\gamma^2}{4}s\cos d}\,\mathrm{d}s\\ &\le \Big(\frac{4}{\gamma^2\cos d}\Big)^\alpha\Gamma(\alpha)\,.\end{aligned}$$

Applying this to each term in (3.38) with $\alpha = \frac{3}{4}+\frac{\ell}{2}+n-k$ for each k, we obtain (3.35).

Concerning the decay condition (3.36), on the one hand, for $x \ge 0$ we have

$$|F_{n,\gamma}(e^x)| \lesssim n!!\max\{n,\gamma^n\}e^{-(\lfloor\frac{n}{2}\rfloor+\frac{3}{2})x}\,,$$

which leads to the choice of μ_ℓ in the hypothesis. The choice of $\hat{x}_\ell$, on the other hand, ensures that

$$e^{(\frac{3}{4}+\frac{\ell}{2}+n)x}e^{-\frac{\gamma^2}{4}e^x} \le e^{-\mu_\ell x}$$

for $x \ge \hat{x}_\ell$, which yields the required estimate for negative x, and hence (3.36). □ □

With the two above lemmas, we are now ready to prove Theorem 3.2.

Proof of Theorem 3.2 Let the even-tempered Gaussian approximation of u be

$$v_\delta(\mathbf{r}) = \check{v}_\delta(r,\theta,\phi) = \sum_{\substack{0\le\ell\le L\\ |m|\le\ell}}\sum_{k=0}^N c_{k\ell m}\chi_k(r)r^\ell Y_{\ell m}(\theta,\phi) \;\in\; V_N$$

with $\chi_k(r) = e^{-\eta_k r^2}$ $(k = 0,1,\cdots,N)$ and $c_{k\ell m}$ the approximation coefficients. Since for u we have

$$u(\mathbf{r}) = \check{u}(r,\theta,\phi) = \sum_{\substack{0\le\ell\le L\\ |m|\le\ell}} P_{\ell m,M}(r)e^{-\gamma_\ell r}\mathcal{Y}_{\ell m}(r,\theta,\phi),$$

we obtain

$$\|u - v_\delta\|_{H^1(\mathbb{R}^3)} \;\le\; \sum_{\substack{0\le\ell\le L\\ |m|\le\ell}}\Big\|\big(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{k=0}^N c_{k\ell m}\chi_k(r)\big)r^\ell Y_{\ell m}(\theta,\phi)\Big\|_{H^1(\mathbb{R}^3)}\,. \tag{3.39}$$

The Laplace operator can be expressed in polar coordinates as

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi},$$

where the last two terms multiplied by r^2 are the total angular momentum operator Δ_{S^2} on the sphere (i.e., the Laplace-Beltrami operator). It can thus be verified by a simple calculation (see, e.g., [11]) that

$$\|f(r)Y_{\ell m}(\theta,\phi)\|^2_{H^1(\mathbb{R}^3)} = \int_0^\infty r^2\left(f^2(r) + \left(\frac{\partial f(r)}{\partial r}\right)^2 + \frac{\ell(\ell+1)}{r^2}f^2(r)\right)dr\int_{S^2}Y^2_{\ell m}(\theta,\phi)d\theta d\phi.$$

Therefore, each term of the right hand side of (3.39) can be estimated as

$$\begin{aligned}
&\|\big(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{k=0}^N c_{k\ell m}\chi_k(r)\big)r^\ell Y_{\ell m}(\theta,\phi)\|^2_{H^1(\mathbb{R}^3)}\\
=\;& \|r^{\ell+1}(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{j=0}^N c_k\chi_k(r))\|^2_{L^2([0,\infty))}\\
&+\ell^2\|r^\ell(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{k=0}^N c_k\chi_k(r))\|^2_{L^2([0,\infty))}\\
&+\|r^{\ell+1}\partial_r(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{j=0}^N c_k\chi_k(r))\|^2_{L^2([0,\infty))}\\
&+\ell(1+\ell)\|r^\ell(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{j=0}^N c_k\chi_k(r))\|^2_{L^2([0,\infty))}.
\end{aligned}$$

Applying Lemma 3.1 and Lemma 3.2, where we choose a fixed $d\in(0,\frac{\pi}{2})$, we obtain

$$\begin{aligned}
&\Big\|\big(P_{\ell m,M}(r)e^{-\gamma_\ell r} - \sum_{k=0}^N c_{k\ell m}\chi_k(r)\big)r^\ell Y_{\ell m}(\theta,\phi)\Big\|_{H^1(\mathbb{R}^3)}\\
&\qquad\le C\sqrt{\frac{(2\ell+3)!}{2^\ell}}M!!\big(\max\{M,\gamma_\ell^M\}\\
&\qquad\qquad + \gamma_\ell^{-\ell-M}b_d^{\frac{\ell}{2}+M}\lceil\ell/2+M\rceil!\big)e^{-2c\sqrt{N}}, \quad (3.40)
\end{aligned}$$

where $b_d := 4/\cos d$, C is a constant depending only on d and the coefficients of the polynomial $P_{\ell m,M}$, and c is a constant determined by d and μ_ℓ in Lemma 3.1. Summing up (3.40) over the indices ℓ and m in (3.39), we obtain (3.28), where

$$C_{M,L}\sim(L+1)^2\sqrt{\frac{(2L+3)!}{2^L}}M!!\left(\max\{M,\overline{\gamma}^M\} + \underline{\gamma}^{-L-M}b_d^{\frac{L}{2}+M}\lceil L/2+M\rceil!\right)$$

with $\overline{\gamma} = \max\{\gamma_0,\cdots,\gamma_L\}$ and $\underline{\gamma} = \min\{\gamma_0,\cdots,\gamma_L\}$. This completes the proof. □

Remark 3.3. *The above theorem gives a priori error estimates for approximations of Slater-type functions. More general wavefunctions can in turn be approximated by sums of Slater-type orbitals*

$$\psi^{\mathrm{STO}}_{n\ell m}(r,\theta,\varphi) = L^{\alpha}_{n}(r)\, e^{-\gamma_\ell r} Y_{\ell m}(\theta,\varphi), \qquad n = 0, 1, \ldots, \tag{3.41}$$

where α, γ_ℓ are constants and L^{α}_{n} are Laguerre polynomials. Since each $\psi^{\mathrm{STO}}_{n\ell m}$ as defined in (3.41) *is of the form* (3.27) *in Theorem 3.2, from this one can obtain estimates for more general wavefunctions for which the Laguerre function expansion coefficients of radial parts have sufficiently rapid decay.*

The regularity result of Proposition 2.2, however, only yields superalgebraic decay of the Laguerre function coefficients of the wavefunctions, which is insufficient considering the rapid growth in L and M of the constants $C_{L,M}$ in Theorem 3.2 (see also our numerical tests in Example 3). In an extension of Theorem 3.2 to general wavefunctions, additional regularity assumptions may thus be required to ensure semi-exponential convergence rates of even-tempered GTO approximations.

Remark 3.4. *Kutzelnigg [30, 31, 33] has shown the error of ground state energy expectation value for the Hydrogen atom obtained by certain even-tempered Gaussian bases goes as $e^{-c\sqrt{n}}$. However, it is not clear whether these results can be extended to a priori H^1-error estimates for general wavefunctions in $\mathbb{R}^3$.*

4 Numerical Experiments

All the numerical results in this section are given in atomic units.

Example 1. We simulate a Hydrogen atom by Gaussian bases as a simple example to support the theory in this paper. Solve the linear eigenvalue problem: Find $\lambda \in \mathbb{R}$ and $u \in H^1(\mathbb{R}^3)$ such that

$$-\frac{1}{2}\Delta u - \frac{1}{|\mathbf{r}|}u = \lambda u.$$

We consider only the first two states of this system (the corresponding exact energies are -0.5 and -0.125).

We first use the Hermite Gaussian basis functions (3.18) by taking $\zeta = 0.2$ with and without one odd order polynomial. The numerical errors of the first two states energies are presented in Figure 4.1 and 4.2 respectively. We observe that the convergence rates of the energy errors are consistent with our theoretical results. We also exploit the even-tempered Gaussian basis functions for this example. The numerical errors of the first two state energies are presented in Figure 4.3, which decay semi-exponentially and are consistent with our theoretical results. We compare the wavefunctions obtained by Hermite Gaussian basis and even-tempered Gaussian basis in Figure 4.4 using the same discretization, say $N = 5$. We observe that the even-tempered Gaussian basis capture the cusp of the wavefunction at the nuclear position much better than Hermite Gaussian basis, even though neither of these bases have the cusp property.

Example 2. We use the package Molpro [41] to simulate a water molecule H_2O using even-tempered Gaussian bases. Molpro is a system of ab initio programs for molecular electronic structure calculations, based on which we perform an all-electron DFT calculations with the Lee, Yang and Parr correlation functional [34] and a self-consistent field iterations. For angular momentums, we include *spdf* types for the oxygen atom and *spd* types for the Hydrogen atoms. Since we do not have the analytic solution, the numerical results obtained

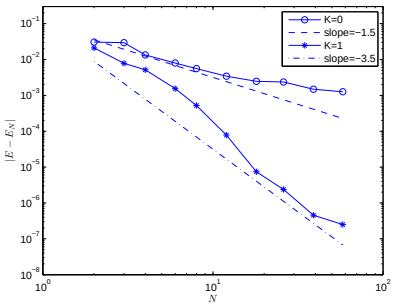

Figure 4.1: Numerical errors of Hermite Gaussian bases for the first state energy (exact value $E = -0.5$).

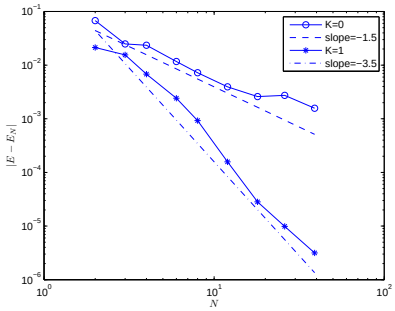

Figure 4.2: Numerical errors of Hermite Gaussian bases for the second state energy (exact value $E = -0.125$).

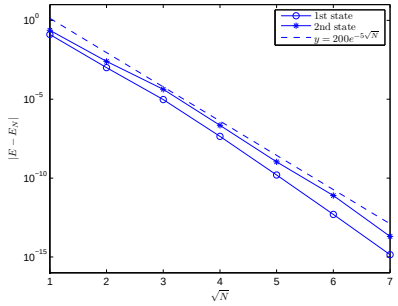

Figure 4.3: Numerical errors of even-tempered Gaussian basis for the first two state energies.

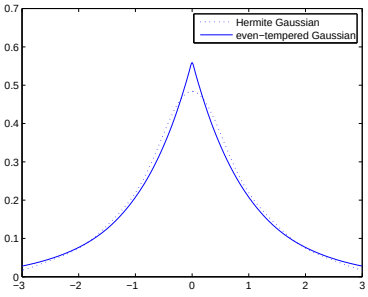

Figure 4.4: Comparison of radial wavefunctions obtained by Hermite Gaussian bases and even-tempered Gaussian bases.

by the default basis of the package, say the VDZ basis [41], are taken to be the exact ones. The numerical errors of the ground state energy per electron are presented in Figure 4.5, from which we observe a semi-exponential decay of the ground state energy error.

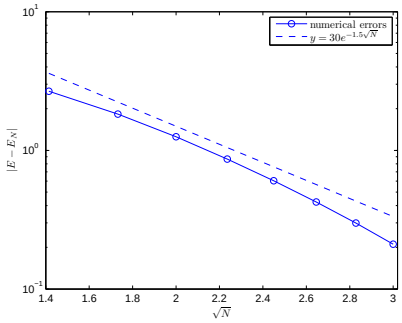

Figure 4.5: Numerical errors per electron of the ground state energy for H_2O by the Molpro package using even-tempered basis.

Example 3. We consider the H^1-error for the approximation of $f(r) := r^n e^{-r}$ as in (3.29), i.e.,

$$\varepsilon_N := \|r^\ell (f - f_N)\|_{L^2([0,\infty))} + \|r^\ell \partial_r (f - f_N)\|_{L^2([0,\infty))}$$

for $n = 0, \ldots, 4$ and $\ell = 0, 2$. Here the approximations f_N are constructed as in Lemma 3.1. Note that in this construction, the value of h depends on the choice of a free parameter $d > 0$, which also enters in the error estimates. This parameter is chosen as follows: for given n, ℓ, and N, we first symbolically evaluate ε_N as a function of d using Maple, and then perform a numerical minimization of ε_N with respect to d, using extended precision. The results are shown in Figure 4.6. We observe the expected growth of the constants in the error estimates with increasing n (in particular for the larger value of ℓ), but also an increase in the convergence rate for larger values of n.

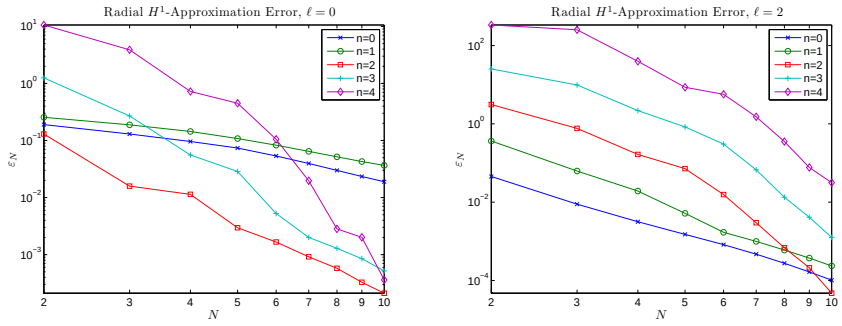

Figure 4.6: H^1-errors (in double logarithmic scale) for approximation of $r^n e^{-r}$ as in Example 3.

5 Concluding remarks

In this paper we have given a numerical analysis for two types of Gaussian approximation in electronic structure calculations. We have obtained a priori error estimates for Hermite Gaussian basis and even-tempered Gaussian basis respectively, which illustrate the efficiency of Gaussian bases in molecular simulations. Our analysis is not restricted to Kohn-Sham theory, but can be extended to various wavefunction methods.

Although several good and flexible Gaussian basis sets have been developed for molecular calculations, such as even-tempered bases, it has not been possible to construct a single, universal molecular basis set that is applicable under all circumstances. In particular, the requirements for accurate excited states, different wavefunction models, and correlated treatment are more severe [21]. Besides, since a relatively large number of Gaussian basis functions are needed to represent the wavefunctions, basis sets are usually constructed from fixed linear combinations of several Gaussians as in the contracted GTOs (3.25) (e.g. for STO-kG and Huzinaga basis sets [20, 25]), instead of using single Gaussian basis functions individually. In this paper we have not considered this additional aspect of atomic bases used in practice, but restricted ourselves to the basic primitive Gaussian approximations. Our work may thus be viewed as a step towards a more complete understanding of Gaussian bases from a numerical point of view.

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