

# Rate of Convergence of the Expansion of a Wavefunction in a Gaussian Basis

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## Abstract

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Original reference. [W.K.](#) Int. J. Quantum Chem. **51**, 447 (1994)

# Convergence of basis expansions

Expand the (lowest) eigenstate of a one-electron Schrödinger equation

$$H\psi = E\psi \quad (1)$$

in a  $d$ -dimensional orthonormal set of one-electron functions  $\chi_p$ .

$$\psi_d = \sum_{p=1}^d c_p \chi_p \quad (2)$$

Search for stationary points (minimum) of the energy expectation value

$$E_d = \langle \psi_d | H | \psi_d \rangle = f(c_1, c_2, \dots, c_d) \quad (3)$$

as function of the expansion coefficients  $c_p$ .

This leads to a **matrix eigenvalue problem**.  $\mathbf{H}\vec{c} = E\vec{c}$

Consider a *family of basis sets*  $\{\psi\}_d$ , characterized by its dimension  $d$ . We want that in the limit  $d \rightarrow \infty$  the considered matrix eigenvalues **converge to the corresponding eigenvalues of the Schrödinger equation (1)**.

This has, for a long time been taken for granted. Only in 1977 Klahn and Bingel [1] showed that completeness *in a Hilbert space norm* is not sufficient, but that rather completeness in the *first Sobolev space* is required.

Basis sets used conventionally, in particular *Gaussian* basis sets fulfil this requirement, provided that some, rather weak precautions are taken.

So convergence of conventional basis expansions is guaranteed, however, the **rate of convergence** remains critical.

If a one-electron basis  $\{\chi_p\}_d$  of *spin-orbitals* is given, then the set of all *n*-electron Slater determinants constructable from the  $\chi_p$  is a *basis* for an *n*-electron system.

The expansion of the *n*-electron Hamiltonian in this basis leads to what is usually called *full CI*, where CI stands for *configuration interaction*.

Extrapolation to  $d \rightarrow \infty$ , i.e. from *full CI* to *complete CI*, which is hardly feasible in practice, leads to the exact result under the same condition as for one-electron systems, i.e. for completeness of the basis in the first Sobolev space.

## Different types of convergence

Nobody would consider to evaluate  $\ln(2)$  from the series

$$\ln(1 + x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \dots \quad (4)$$

The error due to truncating the series after  $n$  terms is of  $O(\frac{1}{n})$ , and  $n \approx 10^6$  is needed to get  $\ln(2)$  with 6-figure accuracy. *An inverse-power law for the truncation error means usually poor convergence.*

Much better is the (geometric) series

$$2 = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \dots \quad (5)$$

Here the truncation error  $(\frac{1}{2})^{n+1}$  decreases *exponentially* with  $n$ . *Exponential convergence is desirable, but it cannot always be achieved.*

A third type of convergence behavior appears to gain importance, namely with a truncation error that goes as

$$f - f_n \sim A \exp(-b\sqrt{n}) \quad (6)$$

and that will play an important role in this lecture.

## Fourier series.

Let  $f(x) = f(x + 2\pi)$  be a periodic function. Then the expansion

$$f_n(x) = f_0 + \sum_{k=1}^n a_k \cos(kx) + \sum_{k=1}^n b_k \sin(kx) \quad (7)$$

converges in an  $L^2$ -norm, provided that  $f(x)$  is *piecewise continuous*. However the convergence is *exponential*, i.e. the truncation error goes as

$$\|f - f_n\| \sim A \exp(-cn) \quad (8)$$

*only if*  $f(x)$  and all of its derivatives exist and are continuous. If some derivative is discontinuous, there is only an *inverse-power* law convergence

$$\|f - f_n\| \sim Bn^{-k} \quad (9)$$

with  $k$  determined by the order of the first discontinuous derivative [2].

The rate of convergence of a Fourier-type expansion depends sensitively on the *singularities* of the function to be expanded.

One can speed up the convergence, if one complements the basis by one or more functions (called *comparison functions* by Hill [3]), that contain the 'correct' singularity (thus making the basis formally *overcomplete*).

An alternative is, as we shall see, to care for an *expansion that is less sensitive to the singularities*.

## Properties of exact wave functions (T. Kato)

The  $n$ -electron wave function (for *clamped point nuclei* with charge  $Z_\mu$  at  $\vec{R}_\mu$ ) is bounded everywhere, and the Schrödinger equation is satisfied in any neighborhood of the Coulomb singularities.

The wave function has a **discontinuous first derivative** at the Coulomb singularities. *Nuclear cusp relation* (in Hartree units)

$$\lim_{r_{k\mu} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{k\mu}} \right)_{av} = -Z_\mu \Psi_{\{r_{k\mu}=0\}} \quad (10)$$

with

$$r_{k\mu} = |\vec{r}_k - \vec{R}_\mu| \quad (11)$$

$\vec{r}_k$  the position of the  $k^{\text{th}}$  electron, and *av* meaning spherical averaging.

*Correlation cusp:*

$$\lim_{r_{ij} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{ij}} \right)_{av} = \frac{1}{2} \Psi_{\{r_{ij}=0\}}; \quad r_{ij} = |\vec{r}_i - \vec{r}_j| \quad (12)$$

Also the coalescence of *three particles*, e.g. a nucleus and two electrons has been studied. The **Fock expansion** [5, 6], which contains **logarithmic** terms in  $(r_1^2 + r_2^2)$ , is not yet understood in all details [7].

Behavior for **distances from any nucleus** [11, 12].

$$\sqrt{\varrho(x)} \leq C(1+r)^{(Z-n+1)/\sqrt{2\varepsilon}-1} \exp(-\sqrt{2\varepsilon} r) \quad (13)$$

$r = |x|$ ,  $\varepsilon$ : first ionization potential,  $n$ : number of electrons, and  $Z$  the nuclear charge (or the sum of the nuclear charges for a molecule.)

Exponential decay, determined by the first ionization potential, does not appear to have an impact on the rate of convergence of basis expansions.

## Three types of Gaussian basis sets for s-AOs

- (a)  $\tilde{\psi}_p = r^p e^{-\eta r^2}$ ;  $p = 0, 2, 4, 6, \dots, 2(n-1)$ ; a single  $\eta$
- (b) as (a) but  $p = 0, 1, 2, 3, 4, \dots$
- (c)  $\psi_k = e^{-\eta(k)r^2}$  (14)

Expand the (normalized) wave function  $\psi$  of the ground state of the hydrogen atom, or rather of hydrogen-like ions with nuclear charge  $Z$  (in atomic units)

$$\psi = Z^{-\frac{3}{2}} \pi^{-\frac{1}{2}} \exp(-Zr) \quad (15)$$

in any of the three basis sets.

$$\begin{aligned}
\text{(a)} \quad & \tilde{\psi}_p = r^p e^{-\eta r^2}; \quad p = 0, 2, 4, 6 \dots, 2(n-1); \quad \text{a single } \eta \\
\text{(b)} \quad & \text{as (a) but } p = 0, 1, 2, 3, 4 \dots \\
\text{(c)} \quad & \psi_k = e^{-\eta(k)r^2}
\end{aligned} \tag{16}$$

Two sets (a) and (c), unable to describe the correct  $\psi$  near the nucleus (**no cusp**). All three sets **fail far from a nucleus** (too fast decay).

All three basis sets are *complete* (in the first Sobolev space) in the limit of an infinite basis (for case (c) if the  $\eta(k)$  increase sufficiently fast with  $k$ ), but the **rate of convergence is quite different**.

Klahn and Morgan [14] have studied the ground state of the H atom in a basis of type (a) i.e. a basis of  $1s, 3s, 5s$  etc. Gaussians with the **same** exponential factor. Equivalent to a basis of **Hermite functions**.

The result was **frustrating**. The error of the energy goes as  $\sim n^{-3/2}$  if  $n$  is the dimension of the basis.

$$\begin{aligned}
& \text{(a) } \tilde{\psi}_p = r^p e^{-\eta r^2}; \quad n = 0, 2, 4, 6 \dots, 2(n-1); \quad \text{a single } \eta \\
& \text{(b) as (a) but } p = 0, 1, 2, 3, 4 \dots \\
& \text{(c) } \psi_k = e^{-\eta(k)r^2}
\end{aligned} \tag{17}$$

The rate of convergence can somewhat be improved, if one optimizes the factor  $\eta$  in the exponent as function of the dimension  $d$  [15, 16].

If one **adds a 2s Gaussian** function ( $n = 2$ ), the error is reduced to  $\sim n^{-3}$ , and it is further diminished if one includes 4s, 6s functions etc.

For basis set (b) the convergence becomes **exponential** and this is the best that one can get. Note that basis (a) is complete and (b) is *overcomplete*.

Why is the basis with just even powers of  $r$  in front of  $\exp(-\alpha r^2)$  so much poorer than the basis with even and odd powers (although both basis sets are complete)?

The reason is – as first pointed out by [C. Schwartz](#) [17] in 1962 in a different context and worked out in detail by [R.N. Hill](#) in 1985 [3] based on the work of [Klahn and Morgan](#) [14] – that **exponential (and hence fast) convergence is only possible if the basis set describes the *singularities* of the function to be expanded.**

The correct ground state wave function of the H-atom has a cusp at  $r = 0$  [4], while Gaussians of type (a) and (c) have a vanishing first derivative at  $r = 0$ .

Applying arguments very similar to those current in the theory of Fourier series [2], [Klahn and Morgan](#) [14] were able to demonstrate the origin of the slow convergence in terms of basis (a).

Basis (b) describes the nuclear cusp correctly. However, the molecular integrals for the functions of basis (b) are *considerably more complicated* than for the sets (a) or (c), that basis (b) is of **no practical interest**.

**Basis set (c) behaves quite differently.** The convergence turned out – surprisingly – to be effectively much better than for basis sets (a), although **not as fast as exponential**. There were some numerical studies on the convergence, e.g. rather extensive ones by **Ruedenberg** and coworkers [18, 19] (1979), but these did not lead to very clear-cut conclusions.

Ruedenberg et al. [18, 19]: **Even-tempered** basis sets. For these the orbital exponents  $\eta(n, k)$  are constructed as

$$\eta(n, k) = \alpha(n)\beta(n)^{k-1} \quad (18)$$

i.e. for each dimension  $n$ , the basis is characterized by only two parameters  $\alpha$  and  $\beta$ .

Such basis sets perform a little less well than basis sets with individually optimized orbital coefficients  $\eta(n, k)$  [20], but are **surprisingly good in view of their compactness**.

**Klopper and Kutzelnigg** [15] (1986) studied the error  $\varepsilon$  of the energy of the H atom ground state with **Huzinaga** basis sets [20] of dimension  $d$  and found an excellent numerical fit of the form

$$\varepsilon = A \exp(-b\sqrt{n}). \quad (19)$$

# Discretization of an integral transformation

Start from:

$$e^{-\alpha r} = \frac{\alpha}{2\sqrt{\pi}} \int_0^{\infty} s^{-3/2} \exp\left\{-\frac{\alpha^2}{4s} - sr^2\right\} ds = \int_0^{\infty} f(s, r) ds \quad (20)$$

Exponential function as a *Gaussian integral transform* [21].

**First step:** restrict the integration domain in (20) from  $s_1$  to  $s_2$  [22, 23].

Two cut-off errors:

$$\varepsilon_{c1}(r) = \int_0^{s_1} f(s, r) ds, \quad (21)$$

$$\varepsilon_{c2}(r) = \int_{s_2}^{\infty} f(s, r) ds. \quad (22)$$

Figure 1: Integrand before variable transformation

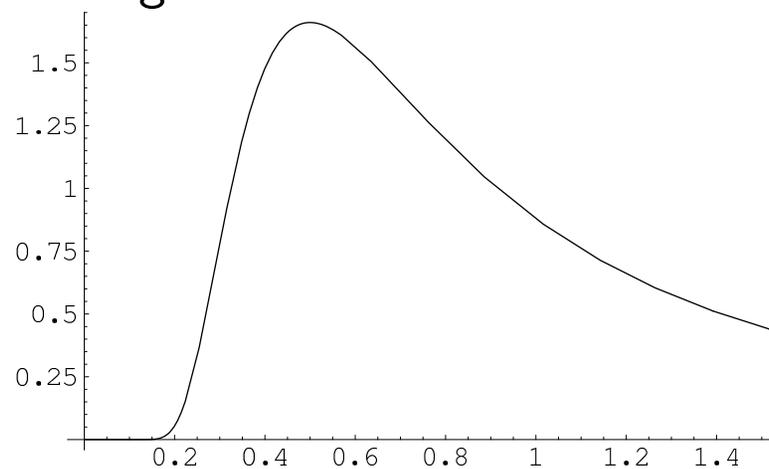
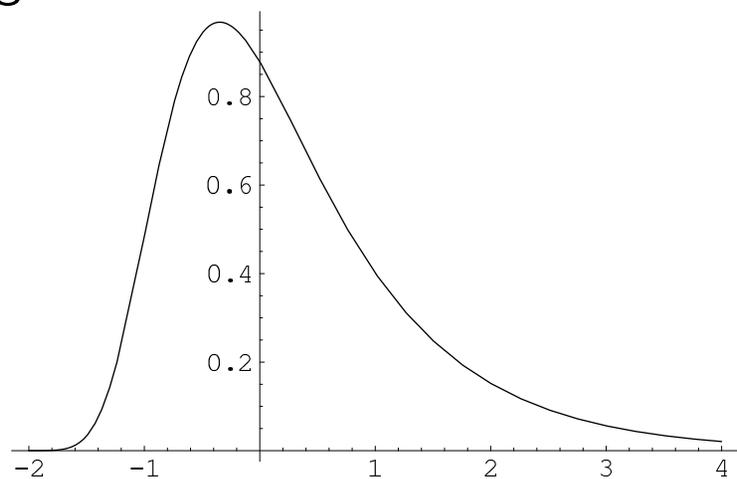


Figure 2: Integrand after variable transformation  $t \rightarrow \exp(u)$



**Second step:** transform the integration variable  $s$  to another variable  $q$ .  
**Final step:** replace the integral over  $q$  is by a sum over an equidistant grid (trapezoid formula).

The **variable transformation** is chosen so that the **grid points sample the integrand in an effective way**. Choose a transformation such hat the grid points correspond to an *even-tempered basis*.

$n$ : number of intervals

$$\int_{s_1}^{s_2} f(s, r) ds = \int_{q(s_1)}^{q(s_2)} f(s[q], r) \frac{ds}{dq} dq = \int_{q_1}^{q_2} g(q, r) dq \approx h \sum_{k=1}^n g(q_k, r)$$

$$q_k = q(s_1) + (k - \frac{1}{2})h; \quad h = \frac{q(s_2) - q(s_1)}{n}; \quad s(q) = \exp(\frac{q}{2}) \quad (23)$$

The total error in the wave function is then the sum of the discretization error  $\varepsilon_d(r)$  and of the two cut-off errors  $\varepsilon_{c1}(r)$  and  $\varepsilon_{c2}(r)$ .

We define an error always as the difference between the exact and the approximate results:

$$\varepsilon_d(r) = \int_{s_1}^{s_2} f(s, r) ds - h \sum_{k=1}^n g(q_k, r) \quad (24)$$

In order to make  $\varepsilon_{c1}(r)$  and  $\varepsilon_{c2}(r)$  as small as possible, one should make  $s_1$  as small and  $s_2$  as large as possible.

For the discretization error  $\varepsilon_d$ , one expects that it becomes smaller as the interval length  $h$  becomes smaller. For a given number  $n$  of points a big  $h$  reduces the cut-off errors, and a small  $h$  reduces the discretization error. The optimum  $h$  will then be some compromise.

We want to measure the error by a single number rather than by a function of  $r$ . There are various possibilities, e.g. :

- (a) The mean square error, i.e. the distance of the expansion to the exact function in a Hilbert space norm.
- (b) The maximum error in a Chebyshev norm.
- (c) The error of the energy expectation value.
- (d) The variance of the energy expectation value.
- (e) The error of the density at the position of the nucleus.

In view of the relation to variational calculations the option (c) looks particularly promising.

For any of these norms the **sum of the two cut-off errors** goes asymptotically as

$$\varepsilon_c \sim A(hn)^k \exp(-ahn) \quad (25)$$

where  $h$  is the interval length,  $n$  the number of intervals, and  $A$  and  $k$  are constants.

The **discretization error**, i.e. the error of using a trapezoid formula has the asymptotic behavior

$$\varepsilon_d \sim Bh^{-l} \exp\left(-\frac{b}{h}\right) \quad (26)$$

with  $B, l$ , and  $b$  constants. As expected, a small  $h$  is good for  $\varepsilon_d$ , while a large  $h$  makes  $\varepsilon_c$  small. **The best compromise is achieved for:**

$$h \sim \sqrt{\frac{b}{an}}; \quad \varepsilon \sim Dn^m \exp(-\sqrt{bn}) \quad (27)$$

While the estimation of the truncation error is trivial, that of the trapezoid approximation looks somewhat **unorthodox**. It does not at all remind the traditional asymptotic expansion of the error [24, 22], based on the Taylor expansion in each interval [22, 23].

$$\varepsilon_d = -\frac{h^2}{24}[g'(q_2) - g'(q_1)] + \frac{7h^4}{5760}[g^{(3)}(q_2) - g^{(3)}(q_1)] + O(h^6) \quad (28)$$

This error estimate is only valid if the integrand allows a power series expansion in  $h$ , but this is obviously not the case here.

The discretization error has even an *essential singularity* at  $h = 0$ . On the other hand an error quadratic in  $h$  would be unacceptably poor anyway. The special kind of a **bell-shaped integrand** decaying very fast both at  $-\infty$  and  $+\infty$  allows a different and more powerful error estimate.

One arrives at a useful asymptotic expansion of the discretization error, if one formulates the discretization in terms of a periodic  $\delta$ -function and then uses the Fourier expansion of the **periodic  $\delta$ -function**. The result is [22]

$$\varepsilon_d = -2 \sum_{l=1}^{\infty} (-1)^l \int_{q_1}^{q_2} g(q) \cos \frac{2l\pi(q - q_1)}{h} dq \quad (29)$$

For the cases that we are interested in, the term with  $l = 1$  **dominates** [22] and determines the leading term in the asymptotic expansion

$$\varepsilon_d \sim 2 \int_{q_1}^{q_2} g(q) \cos \frac{2\pi(q - q_1)}{h} dq \quad (30)$$

One can actually **extend the integration domain to the full range** (usually  $-\infty < q < \infty$ ), i.e. consider

$$\varepsilon_{d\infty} = 2 \int_{-\infty}^{\infty} g(q) \cos \frac{2\pi(q - q_1)}{h} dq \quad (31)$$

This simplifies the evaluation of the integral. Moreover we have completely separated cut-off and discretization errors. The 'coupling' between the two errors, i.e. the difference between (29) and (31), in other words the cut-off error of the discretization error, is usually of higher order and negligible.

The discretization error  $\varepsilon_{d\infty}$  corresponds formally to replacing the integral over an infinite domain by a (countable) infinite sum of terms.

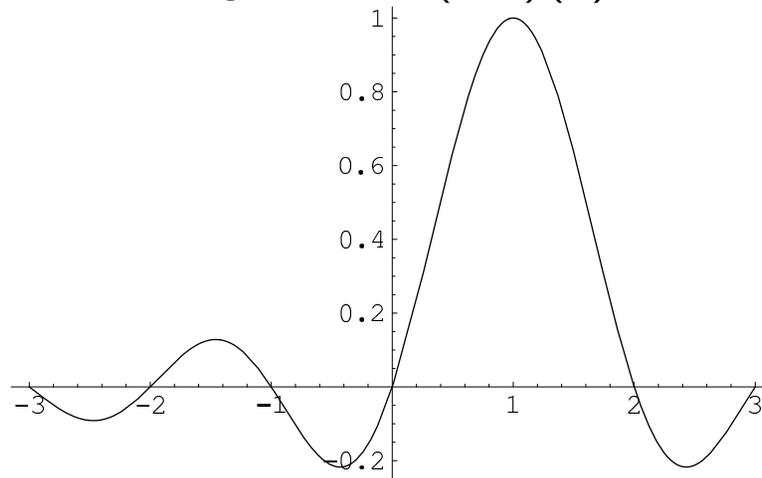
There is one problem with  $\varepsilon_{d\infty}$ . For finite values of  $q_1$  and  $q_2$  the division of the integration domain into intervals of length  $h$  is unique. This is no longer the case if both integration limits are infinite. Then the 'phase'  $\eta = 2\pi q_1$  becomes indefinite and there is no unique limit for  $q_1 \rightarrow -\infty$ . An indefinite phase can be avoided, if one places one grid point at the maximum of the integrand (provided it has a single maximum).

The expression (31) is useful, nevertheless. The indefinite phase has, on one hand, some numerical reality. On the other hand, it is possible to average over the indefinite phase in some simple and meaningful way.

## Theory of Sinc functions (F. Stenger)

$$S(k, h)(x) = \frac{\sin \pi(x - kh)/h}{\pi(x - kh)/h} \quad (32)$$

Figure 3:  $S(1,1)(x)$



A function  $f(x)$  defined at  $x = kh, k$  integer, can be interpolated as

$$\sum_{k=-\infty}^{\infty} f(kh)S(k, h) \quad (33)$$

The integral over this interpolate is equal to the approximation by the trapezoid rule.

The integrands that arise in our context are of the form required for the application of the Sinc function theory.

## Energy expectation value. The truncation error.

Minimize the error  $\varepsilon$  of the energy expectation value for the hydrogen atom

$$\varepsilon = \int f(r)\{H - E_0\}f(r)r^2 dr \quad (34)$$

$$H = -\frac{1}{2}\Delta - \frac{Z}{r}; \quad E_0 = -\frac{1}{2}Z^2 \quad (35)$$

$f(r)$  is an approximation to the exact radial function

$$\psi(r) = 2Z^{3/2}e^{-Zr} = \int_0^\infty \phi(t, r)dt \quad (36)$$

$$\phi(t, r) = \frac{Z^{5/2}}{\sqrt{\pi}}t^{-2} \exp\left(-\frac{Z^2}{4t^2} - r^2t^2\right) \quad (37)$$

Cut-off error of the expectation value:

$$\begin{aligned}
\varepsilon_c &= \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dq \int_0^\infty dr r^2 \phi(t, r) (\hat{H} - E_0) \phi(q, r) \\
&= \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dq F(t, s)
\end{aligned} \tag{38}$$

Integration over  $r$ :

$$\begin{aligned}
F(t, q) &= \int_0^\infty dr r^2 \Phi(t, r) (\hat{H} - E_0) \Phi(q, r) = \\
&= \frac{\exp\left(-\frac{Z^2(q^2+t^2)}{4q^2t^2}\right)}{q^2t^2} \left\{ \frac{Z^7}{2\sqrt{\pi}} \frac{1}{(q^2+t^2)^{3/2}} - \frac{2Z^6}{\pi(q^2+t^2)} + \frac{3Z^5q^2t^2}{\sqrt{\pi}(q^2+t^2)^{5/2}} \right\}
\end{aligned} \tag{39}$$

Final integration in spherical polar coordinates

$$\tilde{t} = \frac{1}{t} = p \cos \varphi = \frac{2u}{Z} \cos \varphi \quad (40)$$

$$\tilde{q} = \frac{1}{q} = p \sin \varphi = \frac{2u}{Z} \sin \varphi \quad (41)$$

$$dt dq = \tilde{t}^{-2} \tilde{q}^{-2} d\tilde{t} d\tilde{q}; \quad d\tilde{t} d\tilde{q} = p dp d\varphi = \frac{4}{Z^2} u du d\varphi \quad (42)$$

$F(t, q)$  is then replaced by

$$G(u, \varphi) = Z^2 e^{-u^2} \left\{ \frac{3u^2}{\sqrt{\pi}} \sin^3 2\varphi - \frac{8u^3}{\pi} \sin^2 2\varphi + \frac{2u^4}{\sqrt{\pi}} \sin^3 2\varphi \right\} \quad (43)$$

Since

$$\int_0^\infty dt \int_0^\infty dq F(t, q) = \int_0^\infty dt \int_{t_1}^{t_2} dq F(t, q) = \int_{t_1}^{t_2} dt \int_0^\infty dq F(t, q) = 0 \quad (44)$$

the cut-off error (38) can be rewritten as

$$\begin{aligned} \varepsilon_c &= - \int_{t_1}^\infty dt \int_{t_1}^\infty dq F(t, q) - \int_{t_2}^\infty dt \int_{t_2}^\infty dq F(x, q) \\ &\quad - \int_0^{t_1} dt \int_{t_2}^\infty dq F(t, q) - \int_{t_1}^\infty dt \int_{t_2}^\infty dq F(t, q) \end{aligned} \quad (45)$$

First term in (45): *lower cut-off error*

$$\varepsilon_{c1} = - \int_{t_1}^\infty dt \int_{t_1}^\infty dq F(t, q) \quad (46)$$

second term in (45): *upper cut-off error*

$$\varepsilon_{c2} = - \int_{t_2}^\infty dt \int_{t_2}^\infty dq F(t, q) \quad (47)$$

Last two terms in (45): coupling between upper and lower cut-off. Small of higher order, don't contribute to the leading term in the asymptotic expansion of the cut-off error.

$$\varepsilon_{c2} = \frac{Z^5}{\sqrt{\pi}} \left( \frac{4}{3} - \frac{5\sqrt{2}}{6} \right) t_2^{-3} + O(t_2^{-4}) \quad (48)$$

$$\varepsilon_{c1} = \frac{Z^3}{\sqrt{2\pi}} t_1^{-1} e^{-Z^2/2t_1^2} [1 + O(t_1)] \quad (49)$$

$\varepsilon_{c2}$  proportional to  $t_2^{-3}$ ,  $\varepsilon_{c1}$  behaves as  $\exp[-a/t_1^2]$ . Much more sensitive dependence on the upper cut-off parameter  $t_2$  than on the lower cut-off parameter  $t_1$ .

For an **even tempered basis**  $t_1$  and  $t_2$  are related as

$$t_2 = t_1 e^{nh} \quad (50)$$

This relation and the minimization  $\varepsilon_c = \varepsilon_{c1} + \varepsilon_{c2}$  with respect to  $t_1$  for fixed  $n$  and  $h$  lead to

$$t_1 = \frac{Z}{\sqrt{6hn}} \left\{ 1 + O\left(\frac{\ln(hn)}{hn}\right) \right\} \quad (51)$$

$$\varepsilon_c = A(hn)^{\frac{3}{2}} e^{-3hn} \left\{ 1 + O(hn) \right\} \quad (52)$$

with  $A$  a numerical constant.

## The discretization error and the final result

The leading term of the discretization error is

$$\varepsilon_d = 4 \int_0^\infty dt \int_0^\infty dq F(t, q) \cos \frac{2\pi g(t)}{h} \cos \frac{2\pi g(q)}{h} \quad (53)$$

For an even-tempered basis with the mapping function

$$g(t) = \ln t \quad (54)$$

the discretization error (53) becomes

$$\begin{aligned} \varepsilon_d &= 2 \int_0^\infty dt \int_0^\infty dq F(t, q) \cos \frac{2\pi \ln t + \eta}{h} \cos \frac{2\pi \ln q + \eta}{h} \\ &= \operatorname{Re} \int_0^\infty du \int_0^{\pi/2} d\varphi G(u, \varphi) \left\{ \left(\frac{2u}{Z}\right)^{4\pi i/h} \left(\frac{\sin 2\varphi}{2}\right)^{2\pi i/h} e^{2i\eta/h} + (\tan \varphi)^{2\pi i/h} \right\} \end{aligned} \quad (55)$$

with  $G(u, \varphi)$  defined by (43) and with  $\eta$  the indefinite phase mentioned previously.

There are two contributions to  $\varepsilon_d$  corresponding to the two terms in braces in the last expression in (55), both of which can be expressed in terms of the Gamma function for a complex variable.

While the first of these contributions is a rapidly oscillating function of  $h$ , the second contribution depends monotonically on  $h$ . Fortunately the second one dominates, going as  $h^{-3} \exp(-\frac{2\pi^2}{h})$  for small  $h$ , while the absolute value (rather than the real part) of the first contribution goes as  $h^{-3/2} \exp(-\frac{2\pi^2}{h})$ .

So for the leading contribution up to  $O(h^{-2} \exp[-\frac{2\pi^2}{h}])$  we only need to consider the second contribution. For this one we get

$$\varepsilon_d \approx \varepsilon_{d2} = \frac{2\pi^4 Z^2}{h^3} e^{-\pi^2/h} [1 + O(h)] \quad (56)$$

We can now minimize the total error  $\varepsilon = \varepsilon_c + \varepsilon_d$  with respect to  $h$  and obtain

$$h = \frac{\pi}{\sqrt{3n}} [1 + O(\frac{\ln n}{\sqrt{n}})] \quad (57)$$

$$\varepsilon = C(n)^{9/8} \exp\{-\pi\sqrt{3n}[1 + O(n^{-1/2})]\} \quad (58)$$

$$t_1 = Dn^{-1/4} [1 + O(n)] \quad (59)$$

The asymptotically (i.e. for large  $n$ ) optimized parameters  $\alpha$  and  $\beta$  of the even-tempered basis in the sense of (18) are

$$\beta = n^{-1/(4n)} \exp(2\pi/\sqrt{3n}) \quad (60)$$

$$\alpha = t_1^2 \beta^{1/2} = \frac{Z^2}{2\pi\sqrt{3n}} \exp \frac{\pi}{\sqrt{3n}} \quad (61)$$

## Comparison with variational calculations

Table 1:  $\frac{\ln |\varepsilon|}{\sqrt{n}}$  for the H atom ground state;  $\varepsilon = E_0 - \langle H \rangle$

n	(a)	(b)	(c)	(d)	(e)	(f)
10	-3.384	-3.338	-3.53	-3.87	3.8671	-4.28
20	-3.813	-3.764	-3.96	-4.07	4.1798	-4.65
30	-4.028	-3.905	-4.17	-3.83	4.3159	-4.84
40	-4.166	-4.119	-4.27	-3.64	4.4382	-5.02
50	-4.265	-4.230	-4.38	-3.49	4.5229	
$\infty$	-5.4414					

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(a)	$\varepsilon = CZ^2 n^{9/8} \exp(-\pi\sqrt{3n})$
(b)	explicit discretization of the integral
(c)	variational calculation with approximate asymptotic even-tempered basis
(d)	variational calculation with extrapolated Schmidt-Ruedenberg basis tempered basis
(e)	variational calculation with optimized even-tempered basis (Helgaker)
(f)	variational calculation with the Morgan-Haywood basis
All variational calculations where done in 128-bit arithmetic	

Table 2: Comparison of asymptotic and variationally optimized parameters of an even-tempered basis for the H atom ground state

$n$	$\alpha$		$\beta$	
	asympt	var-opt	asympt	var-opt
10	0.0516	0.0748	2.973	2.589
20	0.0308	0.0458	2.168	2.021
30	0.0234	0.0274	1.885	1.799
40	0.0193	0.0250	1.734	1.670
50	0.0168	0.0229	1.638	1.587
60	0.0150	0.0210	1.570	1.529

Good agreement between the prediction of the error by means of (58) and use of the trapezoid approximation. Noting that

$$\frac{\ln|\varepsilon|}{\sqrt{n}} = \pi\sqrt{3} - \frac{9\ln n}{8\sqrt{n}} + O(n^{-1/2}) \quad (62)$$

$\frac{\ln n}{\sqrt{n}}$  is not negligible, for the  $n$ -values considered here. Even for  $n = 50$  one is still far from the asymptotic value  $-\pi\sqrt{3}$  for  $\ln|\varepsilon|/\sqrt{n}$ . Actually for  $n$  between  $n = 10$  and  $n = 50$ ,  $\ln n/\sqrt{n}$  varies only between 0.73 and 0.55.

The errors of the results for the variational calculation with the asymptotically optimized basis sets are close to those of an explicit discretization and to the estimate (58).

In view of the  $n - 1$  linear variational parameters, it is not astonishing that the errors of the variational calculation are somewhat smaller, but the effect of this additional flexibility is not very large.

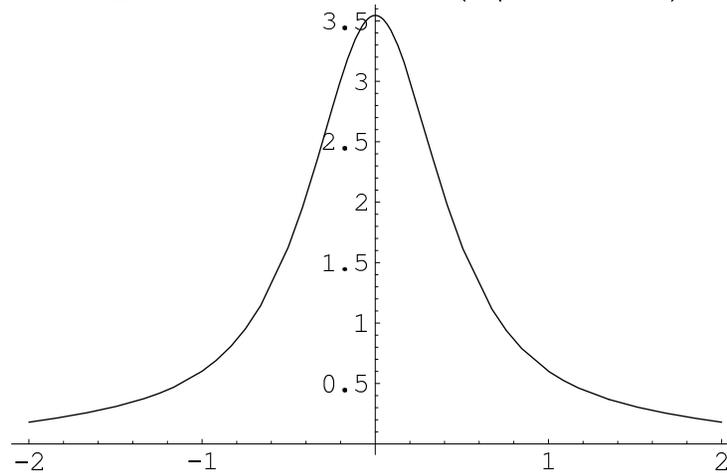
The comparison with the [Schmidt-Ruedenberg](#) basis reveals that the basis optimized individually for each  $n$  gains over the asymptotically optimized basis as long as  $n$  is small. However, for large  $n$  (30 to 50) the extrapolation from the [Schmidt-Ruedenberg](#) fit is rather poor. [Helgaker](#) [32] has recently optimized even-tempered basis sets up to  $n=60$ .

We shall comment later on the errors obtained with the [Morgan-Haywood](#) basis.

## Gamma functions of a complex argument

The discretization integrals lead to Gamma functions of a complex argument. Both real and imaginary parts are rapidly oscillating for large  $x$ , but the absolute value is smooth.

Figure 4:  $2 \operatorname{Re} \Gamma(1/2 + ix)$



$$|\Gamma(1 + ix)|^2 = \pi x / \sinh(\pi x) \approx 2\pi x e^{-\pi x}; \text{ for } x \text{ large} \quad (63)$$

$$|\Gamma(1/2 + ix)|^2 = \pi / \cosh(\pi x) \approx 2\pi e^{-\pi x}; \text{ " - " } \quad (64)$$

$$|\Gamma(k + ix)| \approx \sqrt{2\pi x} x^{k-1/2} e^{-\pi x/2} \quad (65)$$

Figure 5:  $2 \operatorname{Re} \Gamma(1/2 + i/x)$

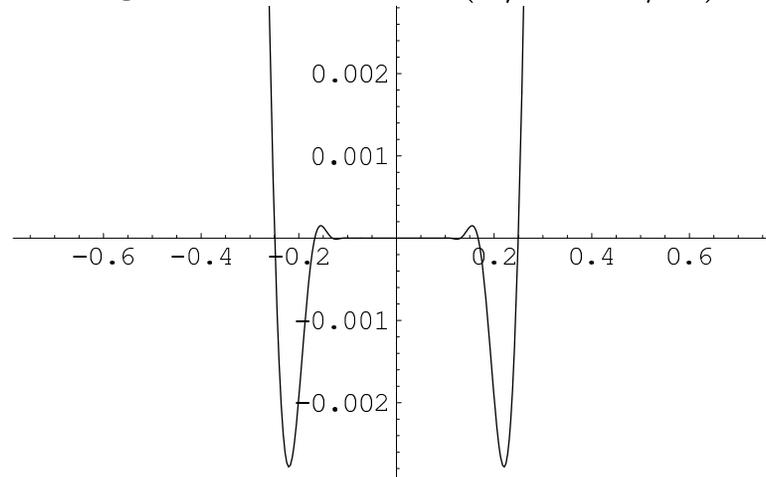
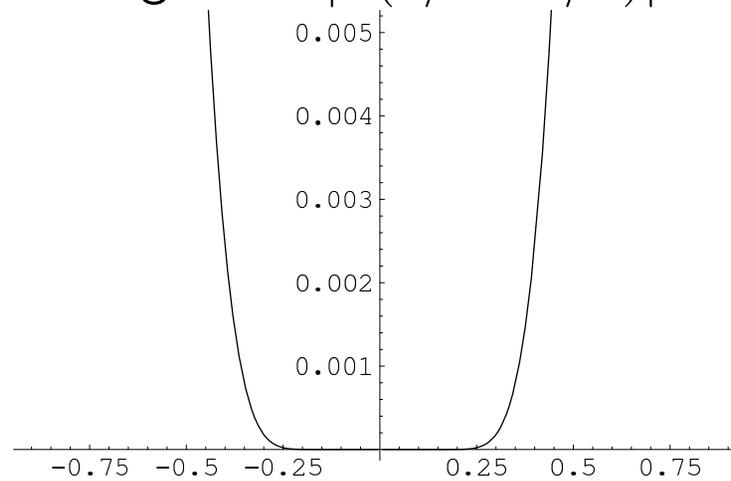


Figure 6:  $|\Gamma(1/2 + i/x)|$



## Other properties than the energy

We have optimized the parameters  $\alpha$  and  $\beta$  of an even-tempered basis such that the error of the energy expectation value is minimized asymptotically for large  $n$ .

There are other possible criteria. One can e.g. try to minimize the **distance in Hilbert space** between the exact and the approximate (expanded) wave function. The integral to be approximated instead of (34) is then

$$\varepsilon = \int [f(r) - \psi(r)]^2 r^2 dr \quad (66)$$

For this quantity the cut-off-errors  $\varepsilon_{c1}$  and  $\varepsilon_{c2}$  behave as

$$\varepsilon_{c1} \sim t_1^{-1} e^{-Z^2/(2t_1^2)} \quad (67)$$

$$\varepsilon_{c2} \sim t_2^{-5} \quad (68)$$

instead of (48), (49). While the lower cut-off error has again a very weak dependence on  $t_1$  as for the energy expectation value, the upper cut-off-error is less sensitive to  $t_2$  as in the example of the energy expectation value (namely  $\sim t_2^{-5}$  rather than  $\sim t_2^{-3}$ ). As a consequence, the optimum  $t_1$  is now

$$t_1 \sim \frac{Z}{\sqrt{10hn}} \quad (69)$$

i.e. the factor 6 in (59) is now replaced by 10: the lower cut-off is somewhat reduced. For the interval  $h$  one now gets

$$h \sim \pi/\sqrt{n} \quad (70)$$

to be compared with (57), i.e.  $h$  and hence  $\beta$  is reduced.

Therefore also the highest exponent  $\eta_n$  is smaller than for minimization of the energy expectation value. Basis functions with large exponents are required less to minimize the distance in Hilbert space than to minimize the error of the energy.

Another possible criterion is to minimize the variance of the energy expectation value. Now the integral that we want to approximate is

$$\varepsilon = \int f(r)(H - E_0)^2 f(r)r^2 dr \quad (71)$$

Instead of (47) we now get

$$\varepsilon_{c2} \sim t_2^{-1} \quad (72)$$

i.e. the variance is extremely sensitive to the upper cut-off, i.e. to the inclusion of large orbital exponents. This means the optimum  $\alpha$  and  $\beta$  are much larger than those needed to minimize the error of the energy.

One may even want to choose the basis such that certain expectation values, say of  $r^k$  are best approximated. This is a different situation from the three ones considered so far.

The error of the energy, the distance in Hilbert space, and the variance are all bounded. A consequence of this is that the terms which are linear in the error of the wave function vanish, and the errors of the respective expressions are determined by terms quadratic in the error of the wave function. This implies that the indefinite phase has no effect on the dominating error terms.

All this is no longer the case for a simple expectation value, say that of the nuclear attraction potential  $-Z/r$  or the kinetic energy  $T$ . The errors of these expectation values have qualitatively a similar behavior as the error of the energy (as suggested by the virial theorem). However, the **discretization error depends on the indefinite phase**, and it can be either positive or negative, such that the overall error does not decrease monotonically with  $n$ , but has a somewhat **irregular dependence** on the basis dimension  $n$ , especially for large  $n$ . This has also been found in computer experiments, and is obviously not a consequence of numerical instabilities.

An important expectation value is that of the delta function  $\delta(r)$ , i.e. the **density at the nucleus**. We cannot go into details, but we mention the following observation.

For the expectation value of  $\delta(r)$  the error depends on the upper cut-off as  $\sim t_2^{-1}$  (somewhat like the variance of the energy). For the expectation value of  $\delta'(r)$  one finds that the cut-off error  $\varepsilon_{c2}$  goes as  $\sim t_2^0$ , i.e. *becomes independent of  $t_2$* , and for  $\delta''(r)$  it even goes as  $\sim t_2^1$ , i.e. *increases with  $t_2$* . This means that the error of  $\langle \delta(r) \rangle$ , i.e. the *value* of the wave function at  $r = 0$  converges to 0 with extension of the basis, while the **error of  $\langle \delta'(r) \rangle$** , i.e. of the first derivative of the wave function at  $r = 0$ , does not go to zero for  $t_2 \rightarrow \infty$ , and the **error of  $\langle \delta''(r) \rangle$  even diverges**.

## Error of the energy vs. mean-square error

Table 3: (Constant factors ignored)

	(a)	(b)
$\varepsilon_{c1}$	$t_1^{-1} \exp(-\frac{Z^2}{2t_1^2})$	<i>same</i>
$\varepsilon_{c2}$	$t_2^{-3}$	$t_2^{-5}$
$\varepsilon_d$	$h^{-3} \exp(-\frac{\pi^2}{h})$	<i>same</i>
$\alpha$	$n^{-1/2} \exp(\frac{\pi}{\sqrt{3n}})$	$n^{-1/2} \exp(\frac{\pi}{\sqrt{5n}})$
$\beta$	$\exp(\frac{2\pi}{\sqrt{3n}})$	$\exp(\frac{2\pi}{\sqrt{5n}})$
$\varepsilon$	$\exp(-\pi\sqrt{3n})$	$\exp(-\pi\sqrt{5n})$

(a) Error of the energy expectation value

(b) Mean square error with respect to exact function

## (1st order) errors of expectation values

Table 4: (Constant factors ignored)

	$\langle r^2 \rangle$	$\langle r^0 \rangle$	$\langle r^{-2} \rangle$	$\langle \delta(r) \rangle$
$\varepsilon_{c1}$	$t_1 \exp(-\frac{Z^2}{4t_1^2})$	<i>same</i>	<i>same</i>	<i>same</i>
$\varepsilon_{c2}$	$t_2^{-6}$	$t_2^{-4}$	$t_2^{-2}$	$t_2^{-1}$
$\varepsilon_d$	$\exp(-\frac{\pi^2}{2h})$	<i>same</i>	<i>same</i>	<i>same</i>
$\alpha$	$n^{-1/2} \exp(\frac{\pi}{2\sqrt{3n}})$	$n^{-1/2} \exp(\frac{\pi}{(2\sqrt{3n})})$	$n^{-1/2} \exp(\frac{\pi}{2\sqrt{5n}})$	$n^{-1/2} \exp(\frac{\pi}{\sqrt{2n}})$
$\beta$	$\exp(\frac{\pi}{\sqrt{3n}})$	$\exp(\frac{\pi}{\sqrt{2n}})$	$\exp(\frac{\pi}{\sqrt{n}})$	$\exp(\frac{\pi\sqrt{2}}{\sqrt{n}})$
$\varepsilon$	$\exp(-\pi\sqrt{3n})$	$\exp(-\pi\sqrt{2n})$	$\exp(-\pi\sqrt{n})$	$\exp(-\frac{\pi\sqrt{n}}{\sqrt{2}})$
$\frac{\ln(\varepsilon)}{\sqrt{n}}$	-5.4414	-4.44288	-3.14159	-2.22144

## Beyond even tempered basis sets

Although even-tempered basis sets are quite good, they are obviously not the best possible choice [25].

The even tempered basis follows automatically from the mapping (54). It appears therefore recommended to study a more general class of mappings and to find an optimum one. In fact one should try to find a mapping such that for an integration domain specified by  $t_1$  and  $t_2$  a smaller number of intervals leads to the same (or a smaller) discretization error.

At first glance it is just a matter of imagination how to choose a more general class of mapping functions. In practice the problem arises that for most mappings that one can think of the integrals which arise cannot be obtained in closed form. However, we do need the explicit dependence on the interval length and the basis dimension in order to derive asymptotic estimates for the optimum basis parameters and the overall error.

The most interesting proposal for a basis determined by a small number of parameters, that is definitely superior to an even-tempered basis is that of Morgan and Haywood [25]. For this basis the large orbital exponents rise faster than exponentially. This is also what one finds if one optimizes the orbital exponents individually. The analytic expression given by Morgan and Haywood looks, nevertheless, somewhat puzzling. In fact the orbital exponents are chosen according to the prescription

$$\eta_k^{(n)} = ck^{-d} \exp[a(n^b - k^b)] \quad (73)$$

The basis contains 4 parameters  $(a, b, c, d)$ , which all should asymptotically be independent of  $n$ .

There is some evidence, but no proof that the error of the energy expectation value obtained with this basis goes as

$$\varepsilon \sim 3n^{1/2} \exp\{-\pi\sqrt{3n}\} \quad (74)$$

## Related methods and problems

A convergence behavior as found here, is probably less exotic than believed not too long ago. In a recent paper Stahl [26] has shown that the error of a rational Chebyshev approximation of order  $(n, n)$  – i.e. for the quotient of two polynomials of degree  $n$  – to the function  $|x|$  in the interval  $[-1, 1]$  goes asymptotically as  $8 \exp(-\pi\sqrt{n})$ .

Using similar techniques Braess [27] studied a problem related to that occurring in the basis expansion reported here. He was able to get rigorous bounds for the error. Unfortunately the problems were not identical, so a direct comparison is not possible. Actually Braess studied the expansion of  $r^{-1}$  and  $\exp(-\alpha r)$  in a weighted  $L_1$  norm, with an exponential weight factor and found a  $\exp(-a\sqrt{n})$  behavior of the error as in Ref. [22].

The same kind of behavior is quite common if one tries to approximate an integral over the entire real axis by a finite sum making use of the theory of Whittaker's cardinal functions or sinc-functions [28, 29, 30, 31]. Stenger [30, 31] points out that the expansion based on the theory of Whittaker's cardinal functions is inferior to an expansion in orthogonal polynomials if the function to be expanded is *nonsingular*, but by far superior in the presence of singularities at the boundaries, to which it is little sensitive.

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