Decay behavior of least-squares coefficients in auxiliary basis expansions

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Many quantum chemical methods, both wave function and density based, rely on an expansion of elements of the electron density in an auxiliary basis. However, little is known about the analytical behavior of the expansion coefficients and, in particular, about their rate of decay with distance. We discuss an exactly solvable model system and characterize the expansion coefficients for various fitting metrics and various dimensionalities of the auxiliary basis. In the case of Coulomb fitting, we find that the decay rate depends critically on the effective dimensionality $D$ of the auxiliary basis, varying from $O(r^{-1})$ to $O(r^{-3})$ to $O(e^{-\gamma r})$ for $D=1, 2, 3$. © 2005 American Institute of Physics.

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I. INTRODUCTION

It has long been recognized that one of the ingredients of an efficient computer program for quantum chemical calculations is a powerful scheme for projecting elements of the electron density into an auxiliary basis set $\{\phi_k\}$. Commonly, this is achieved by minimization of the difference,

$$\chi^2 = \int \int \left[ (\rho(r_1) - \hat{\rho}(r_1)) \hat{\rho}(r_2) - \hat{\rho}(r_2) \right] d\mathbf{r}_1 d\mathbf{r}_2,$$

(1)

between the density element $\rho(r)$ and the model density

$$\hat{\rho}(r) = \sum_k c_k \phi_k(r),$$

(2)

to obtain the matrix equation

$$\sum_k a_{ik} c_k = b_i,$$

(3)

where $a_{ik} = \langle \phi_i | g | \phi_k \rangle$ and $b_i = \langle \phi_i | g | \rho \rangle$.

The two-electron projection operator $g$ must be positive definite and it is common to choose either $g(x)=\delta(x)$ (which fits $\rho$ itself and is called “overlap fitting”) or $g(x)=1/x$ (which fits the norm of the electric field of $\rho$ and is called “Coulomb fitting”). The second of these is favored by many chemists. Some years ago, it was shown that $g(x)=-x$ generates a fit to the electrostatic potential of $\rho$ and we have recently examined the merits of the attenuated Coulomb operator $g(x)=\text{erfc}(\alpha x/x)$.

However, although such fitting procedures are used widely, in both density-functional and wave-function calculations, the analytical behavior of the expansion coefficients has received little attention and, in particular, the relationship between the magnitude of $c_k$ and the distance between $\rho$ and $\phi_k$ has not been studied. The aim of this Communication is to address this oversight.

In order to obtain insight into the decay behavior of the expansion coefficients $c_k$, it is useful to find models that are complex enough to resemble a real system but simple enough to be exactly solvable. Here we exploit the properties of circulant matrices to devise such a model.

II. AN EXACTLY SOLVABLE MODEL

Suppose that the density element $\rho$ is normalized and radially symmetric about the origin and that the auxiliary basis consists of an infinite array of identical normalized radial basis functions $\phi_k$ centered at lattice points $k \in \mathbb{Z}^D$. If the $\phi_k$ are nonoverlapping, if $\rho$ overlaps only with $\phi_0$, and if $g(x)$ is either $\delta(x)$ or $1/x$ or $e^{-\gamma x}/x$, we obtain the circulant system,

$$\sum_{k \in \mathbb{Z}^D} a_{j-k} c_k = b_j,$$

(4)

$$a_k = \begin{cases} \langle \phi_0 | g | \phi_0 \rangle & k = 0 \\ \alpha g(k) & \text{otherwise} \end{cases}$$

(5)

$$b_k = \begin{cases} \langle \phi_0 | g | \rho \rangle & k = 0 \\ \beta g(k) & \text{otherwise} \end{cases}$$

(6)

If $g(x)=\delta(x)$ or $1/x$, then $\alpha=\beta=1$. If $g(x)=e^{-\gamma x}/x$, it can be shown that $\alpha=[C(\phi_0)]^2$ and $\beta=C(\phi_0)C(\rho)$ where $C(F) = (2\pi/\gamma) \int_0^\infty (e^{\gamma r} - e^{-\gamma r}) F(r) dr$. 

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The dependence of the $c_k$ on $\rho$ is trivial and it is convenient to introduce reduced coefficients $d_k$ defined by

$$c_k = \sum_{\ell} d_{\ell} b_{\ell} = \frac{\beta}{\alpha} \delta_{k0} + \left( b_0 - \frac{\beta}{\alpha} a_0 \right) d_k,$$  \hspace{1cm} (7)

which are independent of $\rho$ and satisfy

$$\sum_{k \in \mathbb{Z}^D} a_{j-k} d_k = \delta_{j0}. \hspace{1cm} (8)$$

The $a_k$ are the Fourier coefficients

$$a_k = \frac{1}{(2\pi)^D} \int_{\mathbb{V}^D} f(r) e^{ikr} dr, \hspace{1cm} (9)$$

of the generating function

$$f(r) = a_0 + \alpha \sum_{k \in \mathbb{Z}^D} \rho(k) e^{-ikr}, \hspace{1cm} (10)$$

where $\mathbb{V}^D = [-\pi, \pi]^D$ and the prime indicates that $k = 0$ is excluded. It is convenient to use the Gaussian transform,

$$g(k) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} h(u) e^{-u^2} du, \hspace{1cm} (11)$$

in order to write the generating function as

$$f(r) = a_0 + \frac{2\alpha}{\sqrt{\pi}} \int_{0}^{\infty} \left[ \prod_{i=1}^{D} \theta(r_i) - 1 \right] h(u) du, \hspace{1cm} (12)$$

where the $r_i$ are the Cartesian components of $r$ and

$$\theta(z) = \sum_{n=-\infty}^{\infty} e^{-n^2 \pi^2} \cos nz$$

is a Jacobi theta function.\(^{30}\)

Although we have not specified the detailed form of the $\phi_k$, the positive definiteness of the operator $g(x)$, which is reflected by the positiveness of $f(r)$, implies

$$a_0 > -\inf_{r} \left[ \alpha \sum_{k \in \mathbb{Z}^D} \rho(k) e^{-ikr} \right], \hspace{1cm} (14)$$

and, since the generating function achieves its minimum value when $r = \pi$, we have

$$a_0 > -\frac{2\alpha}{\sqrt{\pi}} \int_{0}^{\infty} \left[ \theta(\pi)^D - 1 \right] h(u) du. \hspace{1cm} (15)$$

By the convolution property of circulant systems,\(^{31}\) the $d_k$ are simply the Fourier coefficients

$$d_k = \frac{1}{(2\pi)^D} \int_{\mathbb{V}^D} \rho(r) e^{ikr} dr \hspace{1cm} (16)$$

of the reciprocal of $f(r)$. Although it is usually difficult to obtain these in closed form, some of their properties can be deduced directly from the Fourier integrand. In particular, their asymptotic decay (as $k \to \infty$) is determined by the region in which $1/f(r)$ varies most rapidly. Additionally, the total charge of $\rho(r)$ is given by

$$q = \sum_{k \in \mathbb{Z}^D} c_k = \frac{\beta}{\alpha} + \frac{b_0}{\alpha} g(0) f(0)$$

showing that, when $\alpha = \beta = 1$, the projection conserves charge only if either $\Sigma'q(k)$ is unbounded or $a_0 = b_0$.

\section{III. YUKAWA FITTING}

We now focus on the Yukawa operator $g(x) = e^{-\gamma x}/x$. By varying the shielding parameter, one can move smoothly from Coulomb fitting ($\gamma = 0$) to overlap fitting ($\gamma = \infty$) and thereby study the effects of attenuation.

For $D=1$ (e.g., where the $\phi_k$ lie at all lattice points on an axis), the generating function can be found directly

$$f(x) = a_0 + 2\alpha \sum_{k=1}^{\infty} e^{-yk}/k \cos kx$$

$$= a_0 - \alpha \ln(1 + e^{-2\gamma} - 2e^{-\gamma} \cos x). \hspace{1cm} (18)$$

Positive definiteness implies that $a_0/\alpha > 2\ln(1 + e^{-\gamma})$. The asymptotic behavior of the Fourier integral (16) is governed by the complex singularities of $1/f(x)$ closest to the real axis. If $a_0/\alpha > \ln[2(1 + e^{-\gamma})]$, these occur at $x = \pm i \gamma$, where the argument of the logarithm vanishes. If $\gamma$ is chosen so that $\gamma < \gamma_0$, where $\gamma_0 = \cosh^{-1}(e^{\eta/\alpha}/2e^{-\gamma} - \cosh \gamma)$, 1/f is analytic in the rectangle between $-\pi, \pi, -\pi+i\gamma, \pi+i\gamma$, except for a branch cut of the logarithm along $[i\gamma, i\gamma]$. Consequently,

$$d_k = \frac{1}{2\pi} \int_{i\gamma}^{i\gamma} f(x) \frac{e^{ikx}}{f(x)} dx + \frac{1}{2\pi} \int_{-\pi+i\gamma}^{\pi+i\gamma} f(x) \frac{e^{ikx}}{f(x)} dx, \hspace{1cm} (19)$$

where $f_s$ denotes the limiting value of $f$ on the branch cut $[i\gamma, i\gamma]$ when approaching from the right and left half plane, respectively. The second integral is negligible, $O(e^{-\gamma k})$, and the first can be analyzed as follows: Set $x = i(y+i\gamma)$, $y \in [0, \gamma_0 - \gamma]$; substitute $f_s(x) = a_0 - \alpha \ln[(1 + e^{-\gamma})^2 \pm i \pi + O(\gamma^2)]$; neglect the $O(\gamma^2)$ term; change variables $s = ky$; replace the integrand by its limiting form. This gives

$$d_k \sim -\frac{e^{-yk}}{k \ln^2 k}, \hspace{1cm} (20)$$

which is consistent with, although more specific than, the $O(e^{-\gamma k})$ result predicted by the analysis of Boyd.\(^{32}\) Finally, we note that a similar analysis to that above also predicts exponential decay in cases where $2 \ln(1 + e^{-\gamma}) < a_0/\alpha < \ln[2(1 + e^{-\gamma})]$.

For $D=2$ (i.e., where the $\phi_k$ lie at all lattice points in a plane) or $D=3$ (i.e., where the $\phi_k$ lie at all lattice points in three space), we have been unable to evaluate the generating function in closed form but we would also anticipate exponential decay.

\section{IV. OVERLAP FITTING}

In the $\gamma \to \infty$ limit, one obtains an “overlap fit” and the generating functions for $D=1,2,3$ are simply
\[ f(x) = f(x,y) = f(x,y,z) = a_0. \]  

(21)

The total charge of \( \hat{\rho} \) is \( q = b_0/a_0 \), confirming that this type of fit conserves charge only if \( a_0 = b_0 \). The Fourier integral is also trivial and yields

\[ d_k = \delta_{k0}/a_0 \]  

(22)

showing that, when such a short-sighted projection operator is used, only \( \phi_0 \) contributes to the model density.

V. COULOMB FITTING

In the \( \gamma \rightarrow 0 \) limit, one obtains a “Coulomb fit” and \( h(u) \rightarrow 1 \). Positive definiteness leads to the bound

\[ a_0 > -\frac{2}{\sqrt{\pi}} \int_0^\infty \left[ \theta(\pi t^0 - 1) \right] du, \]  

(23)

where the right-hand side is the negative of the Madelung constant for the \( D \)-dimensional NaCl lattice. Its value is 2 log 2 = 1.386 29 \((D=1)\), 4 \( \pi \)(1/2)\( \beta(1/2) = 1.615 54 \((D=2)\), 30,33 and = 1.747 56 \((D=3)\). \(34 \)

For \( D=1 \), the generating function reduces to

\[ f(x) = a_0 - \ln(2 - 2 \cos x) = -2 \ln x + O(1), \]  

(24)

but the Fourier integral (16) is intractable, even for \( k=0 \). However, the asymptotic decay of the \( d_k \) is governed by the logarithmic singularity of \( f(x) \) at the origin and can be deduced by a four-step approach: integrate by parts; substitute \( s = kx \); replace \( 1/f \) in the integrand by its limiting form; integrate over \( s \). In this way, we find

\[ d_k = \frac{1}{\pi} \int_0^{\pi} \frac{\cos kx}{f(x)} dx = -\frac{1}{\pi k} \int_0^{k\pi} \frac{\partial}{\partial s} \left[ \frac{1}{f(s/k)} \right] \]  

\[ \times \sin s ds \sim -\frac{1}{2\pi k} \int_0^{\pi} \frac{\sin s}{s} ds = -\frac{1}{4\pi k^2}, \]  

(25)

which may be compared with the \( \gamma > 0 \) case (20).

For \( D=2 \), the generating function cannot be found in closed form but it can be shown that, near the origin,

\[ f(r) = \frac{2\pi}{r} + a_0 + \lambda_2 + O(r), \]  

(26)

where \( \lambda_2 = 2/\sqrt{\pi} f(0)(\partial f(0)/\partial r)^2 - 1 - \pi/r^2 \) \( du = -3.9003 \). The resulting cusp in \( 1/f(r) \) at \( r = 0 \) governs the asymptotic decay of the \( d_k \) and our four-step approach reveals

\[ d_k \sim -\frac{1}{4\pi k^2}. \]  

(27)

For \( D=3 \), the generating function cannot be found in closed form but it can be shown that, near the origin,

\[ f(r) = \frac{4\pi}{r^2} + a_0 + \lambda_3 + O(r^2), \]  

(28)

where \( \lambda_3 = 2/\sqrt{\pi} f(0)^3(\partial f(0)/\partial u)^2 - 1 - \pi^{3/2}/u^3 \) \( du = -2.8373 \). As a result, \( 1/f(r) \) is smooth at the origin and our four-step approach is not useful in this case. However, a bound for the decay rate can be obtained by considering the analyticity of \( f \), via its Laplacian,

\[ \nabla^2 f(r) = \frac{1}{\sqrt{\pi}} \int_0^\infty \nabla^2 w(r,t) \frac{h(\sqrt{t})}{\sqrt{t}} dt, \]  

(29)

\[ w(r,t) = \prod_{i=1}^{3} n_{\nu t} e^{-\nu^2 t} \cos n_{\nu t} - 1. \]  

(30)

It is clear that \( v = \nabla^2 w \) satisfies the heat equation

\[ \frac{\partial v}{\partial t} = \nabla^2 v, \]  

(31)

with the initial condition

\[ v(r,0) = (2\pi)^3 \sum_{n \in Z^3} \nabla^2 \delta(r - 2\pi n). \]  

(32)

Substituting the solutions of (31) and (32), viz,

\[ v(r,t) = (2\pi)^3 \sum_{n \in Z^3} \nabla^2 \left( e^{-|r-2\pi n|^2/4t} \right) \frac{4\pi}{(4\pi)^{3/2}} \]  

(33)

into (29) and integrating yields

\[ \nabla^2 \left( f(r) - \frac{4\pi}{r^2} \right) = 8\pi \sum_{n \in Z^3} \nabla^2 \left( |r - 2\pi n|^2 \right). \]  

(34)

and therefore

\[ \nabla^2 \left( f(r) - \frac{4\pi}{r^2} \right) = 8\pi \sum_{n \in Z^3} \left| \frac{1}{r - 2\pi n} \right|^2. \]  

(35)

The right-hand side of this equation converges uniformly and is analytic in a complex neighborhood \( N \) of \( V^3 \). It is known that solutions of Poisson’s equation \( \nabla^2 F = -4\pi \rho \) are analytic if \( \rho \) is analytic, and therefore \( f(r) - 4\pi/r^2 \) is also analytic on \( N \). We also know that \( f(r) > 0 \) for \( r \in V^3 \) and continuity implies that \( 4\pi + r^2 F(r) \neq 0 \) in some complex neighborhood of \( V^3 \). Thus

\[ l(r) = 1/f(r) = \frac{r^2}{4\pi + r^2 F(r)}. \]  

(36)

is an analytic function on a complex neighborhood \( N' \) of \( V^3 \) and is also a 2\( \pi \) periodic function of \( r \) in \( N' \). If we let \( \zeta \) be such that \( s_j = \zeta \) for \( j = 1, 2, 3 \) implies \( r + is \in N' \), then the analyticity and periodicity of \( l \) allows us to write the Fourier coefficients as

\[ d_k = \frac{1}{(2\pi)^3} \int_{V^3} e^{ik(r+is)} l(r+is) dr. \]  

(37)

Choosing \( s_j = \zeta \) if \( k_j \geq 0 \) and \( -\zeta \) otherwise, we see that

\[ |d_k| \leq M e^{-|\zeta|(|k_1|+|k_2|+|k_3|)} \leq M e^{-|\zeta|k}. \]  

(38)

and the asymptotic coefficient decay is exponential.

VI. DISCUSSION

In typical chemical applications, the \( \phi_k \) are anchored to the nuclear framework, which is unlikely to resemble our model’s regular lattice, and one may ask whether our results
shed much light on the behavior of expansion coefficients in “real-life” density fits. However, numerical experiments suggest that the decay patterns given by (25), (27), and (38) remain essentially unchanged even when the lattice is distorted or defects are introduced. To the extent that this is true, it follows that we may apply these equations, interpreting $k$ as the distance between an expansion function and a target density, in arbitrary molecular contexts.

With that perspective, (25), (27), and (38) explain the empirical discovery that distant expansion functions have significant coefficients in quasilinear systems but that their importance rapidly diminishes as the effective dimensionality of the auxiliary basis set increases. This is qualitatively reasonable because, for example, a three-dimensional grid of basis functions should be able to model the field around a fragment of charge density much better than a one-dimensional grid. However, the fact that polynomial decay in the one-dimensional and two-dimensional cases becomes exponential in the three-dimensional case is unexpected and is probably the most important result in this Communication.

A quantitative understanding of the behavior of expansion coefficients is important for the development of highly efficient computational algorithms. For example, to develop the so-called “local” methods, which presuppose that spatially distant subsystems interact negligibly, it is essential to be able to determine a priori the radius of the “sphere of influence” of each subsystem. The decay behaviors established in this Communication should be useful for such purposes.

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