Reply to "Comment on 'Nonanalyticity of the optimized effective potential with finite basis sets' "

Nikitas I. Gidopoulos[1] and Nektarios N. Lathiotakis[2]
[1]*Department of Physics, Durham University, South Road, Durham DH1 3LE, United Kingdom*
[2]*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, GR-11635 Athens, Greece*
(Received 8 May 2013; published 15 October 2013)

The Comment by Friedrich *et al*. does not dispute the central result of our paper [Phys. Rev. A **85**, 052508 (2012)] that nonanalytic behavior is present in long-established mathematical pathologies arising in the solution of finite basis optimized effective potential (OEP) equations. In the Comment, the terms "balancing of basis sets" and "basis-set convergence" imply a particular order towards the limit of a large orbital basis sets where the large-orbital-base limit is always taken first, before the large-auxiliary-base limit, until overall convergence is achieved, at a high computational cost. The authors claim that, on physical grounds, this order of limits is not only sufficient, but also necessary in order to avoid the mathematical pathologies. In response to the Comment, we remark that it is already written in our paper that the nonanalyticity trivially disappears with large orbital basis sets. We point out that the authors of the Comment give an incorrect proof of this statement. We also show that the order of limits towards convergence of the potential is immaterial. A recent paper by the authors of the Comment proposes a partial correction for the incomplete orbital basis error in the full-potential linearized augmented-plane-wave method. Similar to the correction developed in our paper, this correction also benefits from an effectively complete orbital basis, even though only a finite orbital basis is employed in the calculation. This shows that it is unnecessary to take, in practice, the limit of an infinite orbital basis in order to avoid mathematical pathologies in the OEP. Our paper is a significant contribution in that direction with general applicability to any choice of basis sets. Finally, contrary to an allusion in the abstract and assertions in the main text of the Comment that unphysical oscillations of the OEP are supposedly attributed to the common energy denominator approximation, in fact, such anomalies arise with the full treatment of the small eigenvalues of the density response function. This characteristic of the finite basis OEP is well known in the literature but also is clearly demonstrated in our paper.

DOI: 10.1103/PhysRevA.88.046502 PACS number(s): 31.15.eg, 71.15.Mb

I. INTRODUCTION

It is well known to the theoretical electronic structure community that the optimized effective potential (OEP) method shows pathological behavior for finite basis sets. Understanding this pathological behavior is the aim of our paper [1] that is criticized in the Comment by Friedrich *et al*. [2]. This pathological behavior was demonstrated by several authors in the past [3–8].

Friedrich *et al*. explain the motivation for the Comment was that our paper [1] "casts doubt" on a number of numerical OEP calculations with finite basis sets [9], and as such, it "calls for rapid clarification". However, the presence of the mathematical problem outlined above was already known for a long time, and of course, we do not unveil a new mathematical pathology in our paper. Instead, our paper contributes to the understanding of the mathematical problem [10] by showing that the truncation of the orbital Hilbert space with a finite orbital basis amounts to a nonanalytic procedure changing the resulting potential discontinuously. In addition, our paper proposes a possible way to alleviate the problem.

In our paper [1], we study the effect of a finite orbital basis by introducing a small scaling parameter λ multiplying the part of the density-density response function omitted with the truncation of the orbital Hilbert space. We approximate this term with the Unsöld approximation [11]. Then, we show that the OEP v^λ, as a function of λ, is discontinuous at $\lambda = 0$, i.e., the potential $v^{\lambda\to 0}$ differs from the potential v^0. One step further, we propose that the limiting potential $v^{\lambda\to 0}$ offers a better approximation for the OEP than the truncated potential v^0. In that way, the truncated part of the orbital Hilbert space is included in an effective way, and the amended finite basis OEP equations are well behaved.

The discontinuity in the potential $\bar{v} \doteq v^{\lambda\to 0} - v^0$ may vanish for some combinations of orbital and auxiliary basis sets. In Ref. [1], we provide an equation that determines $\bar{v}$, and the discontinuity can be calculated and can be assessed either analytically with the help of this equation or numerically by calculating the potentials v^0 and v^λ for a series of small values of λ.

II. LARGE BASIS-SET LIMIT

The main point of the Comment is that, on the grounds that the electron density must be sufficiently flexible to respond to any potential change, it follows that a finite basis OEP calculation can only be performed with "converged basis sets", regardless of the dramatically increased computational cost. The procedure to obtain such "basis-set convergence" requires first taking the large-orbital-base limit, before the large-auxiliary-base limit. At this point, it is useful to review two different ways of obtaining the large basis-set limit for both the orbital and the auxiliary basis sets.

A. Sequence of finite auxiliary basis sets—large orbital basis limit

One way is to take a sequence of increasingly larger auxiliary basis sets; for each member of this sequence to

employ a sufficiently large orbital basis so that any change in the potential, restricted in the auxiliary space, gives rise to a nonzero change in the electronic density. Each auxiliary basis in the sequence gives rise to a finite basis OEP characterized by the auxiliary basis alone since the limit of an infinitely large orbital basis is used, i.e., if the orbital basis was expanded further, the potential would not change. In such a way, a converging sequence of finite auxiliary basis OEPs is generated. This particular order of limits is termed by Friedrich *et al*. as basis-set convergence and "balancing of basis sets". They deem that this order of limits is necessary in order to obtain the OEP.

We point out that Friedrich *et al*. determine a condition for basis-set convergence that is too strict and is not satisfied exactly with a finite auxiliary basis. In addition, Gaussian orbital basis sets, unlike plane waves, are not systematically improved upon enlargement since a small Gaussian basis set is not a subset of a larger one. This complicates the application of the procedure towards the large orbital basis limit.

B. Sequence of finite orbital basis sets

Another way to reach the large basis-set limit is to use a sequence of fixed orbital basis sets of increasing size; for each orbital basis set in this sequence, employ a sufficiently large auxiliary basis such that any change in the density (representable with the given orbital basis) corresponds to some change in the potential in the large auxiliary space. Obviously, the auxiliary space can be too large, and a singular-value decomposition (SVD) must be used to truncate functions, in the auxiliary space, that describe potential changes with vanishing density responses. These auxiliary functions are in the null space of the density-density response function χ_0 corresponding to the fixed orbital basis. The nonsingular eigenfunctions of χ_0 compose the effective auxiliary basis that is actually used for the expansion of the potential. Note that, with respect to this effective auxiliary basis, the orbital basis is also converged in the sense of the previous order of limits. Each orbital basis in the sequence gives rise to a finite orbital basis OEP. Thus, a converging sequence of finite orbital basis OEPs can be generated. A technical difficulty is how to separate the null from the nonsingular eigenvalues of the response function in order to perform the SVD.

Friedrich *et al*. argue that, because the electron density must be flexible to respond to any potential change, it is necessary to employ the first order of limits. However, there is no reason why the same physical principle cannot be satisfied with either order of limits since for both, any potential change within the effective auxiliary space leads to a nonzero change in density. In fact, a number of finite basis OEP calculations, including the introductory example in our paper, has been routinely performed with a fixed orbital basis [4,12,13].

Next, we show that a sequence of finite auxiliary basis OEPs cannot converge fully in a finite number of steps.

C. Convergence of a sequence of finite auxiliary basis OEPs

Friedrich *et al*. seem to assume that a sequence of finite auxiliary basis OEPs may converge fully in a finite number of steps. To resolve possible confusion with regard to this point, we critically examine the relevant analysis in the Comment. In Ref. [27] of the Comment, Friedrich *et al*. make the (weaker) assumption that a well-behaved OEP is always representable, at least, approximately, by a finite number of auxiliary functions. Mathematically, this statement is difficult to understand without specifying the auxiliary basis. For example, any potential is trivially representable by a single auxiliary function if the potential function itself happens to belong to the auxiliary basis.

In Ref. [1], we argued that the nonsingular eigenfunctions $c^\alpha(\mathbf{r})$ of $\chi_0(\mathbf{r},\mathbf{r}')$ form a natural basis to expand the potential. In practice, even when a different auxiliary basis set $\{\xi_n(\mathbf{r})\}$ is used, it turns out that the auxiliary basis $\{\xi_n(\mathbf{r})\}$ is employed to expand a subset of the functions $\{c^\alpha(\mathbf{r})\}$ [14], and in effect, the potential is actually expanded in this subset of the $\{c^\alpha(\mathbf{r})\}$. The question about the finite or infinite number of auxiliary basis functions required to represent the potential is meaningful for the basis $\{c^\alpha(\mathbf{r})\}$, and we will use this auxiliary basis set in our analysis.

Friedrich *et al*. specify that, at orbital basis convergence, the potential that solves the finite basis OEP equation *for a finite auxiliary basis* also satisfies the OEP equations for the larger auxiliary basis obtained after augmenting the previous basis by any arbitrary function $\xi^\nu(\mathbf{r})$ orthogonal to the initial auxiliary basis.

To see that this requirement for basis-set convergence is too restrictive, we consider the simplest case that, at convergence, the orbital basis is complete. If the criterion for basis-set convergence fails for a complete orbital basis, it will have to fail for any finite orbital basis too as two basis sets cannot be converged when they are both finite but cease to be converged after the orbital basis (assumed converged to the large basis limit) is enlarged even further to completion.

With a complete orbital basis, the density response function $\chi(\mathbf{r},\mathbf{r}')$ has no zero eigenvalues, except for the constant function. As discussed, we take that the initial auxiliary basis is composed from a subset of the eigenfunctions $\{c^\alpha(\mathbf{r})\}$ of $\chi(\mathbf{r},\mathbf{r}')$ and that the extra auxiliary basis function ξ^ν is an eigenfunction of $\chi(\mathbf{r},\mathbf{r}')$ with eigenvalue g^ν. Then, from Eq. (16) in Ref. [1], the potentials v^0,u^0 that solve the finite basis OEP equations in the two auxiliary basis sets do not coincide in general since

$$u^0(\mathbf{r}) - v^0(\mathbf{r}) = \frac{b_\nu \xi^\nu(\mathbf{r})}{g^\nu}. \tag{1}$$

b_ν is defined in Eq. (17) of our paper [1]. Numerical results in the Comment (Fig. 3) and in Fig. 1 show that the ratio b_ν/g^ν does not vanish for all ν. It follows that, in general, the condition for the basis-set convergence of Friedrich *et al*. is not satisfied, even with a complete orbital basis.

Basis-set convergence can be defined in either a less general sense or less strongly. For example, an orbital basis can be converged in relation to a specific fixed auxiliary basis when the orbital basis is large enough such that, after increasing the size of the orbital basis, the results of the calculation no longer change. It is then possible for an orbital basis to be converged with regard to one auxiliary basis but not converged with respect to another.

In principle, a weaker condition can be determined for the convergence of the sequence of the finite auxiliary basis OEPs in a finite number of steps within a certain numerical tolerance. Perhaps, Friedrich *et al*. have in mind this weak

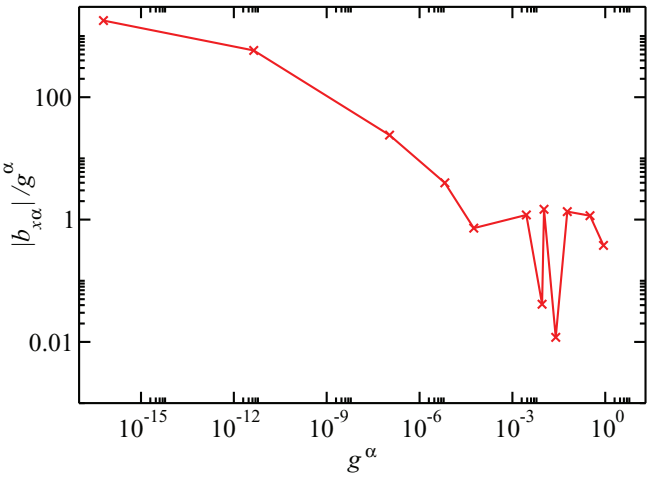

FIG. 1. (Color online) The fraction $v_{x\alpha} = |b_{x\alpha}|/g^{\alpha}$ for the contributing eigenvalues of the response function (i.e., those with $b_{x\alpha} \neq 0$). The magnitude of the contributions diverges out of control for the small eigenvalues.

basis-set convergence. However, the attempted proof (Sec. IV of the Comment) that the discontinuity correction vanishes exactly or, approximately, does not go through using the weak condition for convergence.

III. RESPONSE TO THE COMMENT

Our paper is criticized primarily because our analysis of the OEP equations is not based on the supposedly necessary procedure to construct a sequence of finite auxiliary basis OEPs, taking the limit of a large orbital basis for each potential in the sequence. Friedrich *et al*. argue that, when such converged basis sets are used, all mathematical anomalies, including the nonanalyticity, are avoided. However:

(a) Friedrich *et al*. fail to acknowledge that, in our paper, we had already mentioned that the nonanalyticity vanishes with large orbital basis sets. Specifically, we had written that our "new finite basis OEP equations, give meaningful results (i.e., nonvanishing discontinuity) for a finite auxiliary basis as long as the latter is large enough to overlap with the null space of χ_0". In the limit of large orbital basis sets, the domain of χ_0 completely covers the auxiliary space so that the latter has zero overlap with the null space of χ_0.

(b) A corollary is that, in the limit of large orbital basis sets, our discontinuity correction $\bar{v}$ vanishes since it is expanded in the intersection of the auxiliary space with the null space of χ_0, and in this limit, the intersection is reduced to the empty set.

The attempted proof by Friedrich *et al*. is flawed since it is based on the impossible condition that the potential does not change upon augmenting the auxiliary basis from one step of the sequence to the next. In fact, the discontinuity correction vanishes exactly for every term of the sequence of fixed auxiliary basis OEPs by taking the large orbital basis limit each time.

(c) In Sec. II, Friedrich *et al*. write that the first order of limits is necessary for the OEP but do not explain what is wrong with the second order of limits, other than that it leads to too small eigenvalues of the matrix of χ_0, which poorly approximate the physical eigenvalues of the response function; the latter are important and should not be ignored according to the Comment.

Friedrich *et al*. confuse the small but physically important eigenvalues of the full response function with the null eigenvalues of the matrix of χ_0. These must be truncated because they only reflect the fact that the auxiliary space has more dimensions than the space of the orbital products. Hence, there are always directions in the auxiliary space orthogonal to any orbital product, and these give a zero density response by definition. The null eigenvalues cannot offer any kind of approximation for the small but physical eigenvalues of the full response function. In our theory, they are treated approximately and not exactly, not because they are unimportant, but because, with the exact treatment, the potential is undetermined along them. In Fig. 1, we demonstrate this point by plotting the fraction $v_{x\alpha} = |b_{x\alpha}|/g^{\alpha}$ for the contributing eigenvalues ($b_{x\alpha} \neq 0$) of the matrix of the response function shown in Fig. 1 in Ref. [1] [Ne atom with orbital and auxiliary basis sets correlation-consistent polarized valence triple-ζ (cc-pVTZ) and uncontracted cc-pVTZ]. It is seen that their contribution diverges out of control when their size becomes too small. If one treats them exactly, the resulting potential is pathological and does not converge. If one truncates them with a SVD, the resulting converged finite basis OEP v^0 (Fig. 2, Ref. [1]) is different from the full OEP because there is a discontinuity correction separating the two. By treating them with the Unsöld approximation, we obtain a smooth potential that converges smoothly to the full OEP.

(d) On the same point, Friedrich *et al*. mistakenly attribute oscillatory behavior of the potential in an example in our paper and in the plot of the potential v_x^* in Fig. 5(b) of Ref. [1] to the use of the Unsöld approximation. In this example, the transfer of an eigenvector of χ_0 from the null space (where the eigenvector is treated with the Unsöld approximation) to the nonsingular space (where the eigenvector is treated fully) gives rise to strong oscillations. We do not see how the authors of the Comment infer from this that the oscillatory behavior is attributed to the approximate treatment of the small eigenvalues of the response function.

The example in our paper is clear and reads the opposite, showing that spurious oscillations are produced not by the approximate but by the full treatment of the eigenvectors with small eigenvalues. In fact, this behavior is a trademark of the mathematical pathologies: Various finite basis approximations of OEP (Krieger-Li-Iafrate [15], localized Hartree-Fock [16], common energy denominator approximation [17], and effective local potential [18,19]) employing the Unsöld approximation [11] for all the eigenvectors of the response function, are invariably well behaved and give smooth potentials. The underlying reason is that the δ function in the closure relation [11] has a complete set of eigenfunctions and its use makes the finite orbital basis effectively complete.

(e) Friedrich *et al*. comment that the discontinuity correction requires the "careful classification of the eigenvalues of the response function into singular and nonsingular", a classification that we "admit to be an ill-posed problem". In response, we emphasize that the technical problem of how to distinguish between singular and nonsingular eigenvalues of the response function is separate from the nonanalyticity of

the solution of finite basis OEP equations. The conceptual differentiation between these two issues is an important contribution of our paper. These two issues usually are both present in finite basis OEP calculations and, until our paper, they were confused as one and the same problem. The need to separate null from nonsingular eigenvalues of χ arises in order to analytically calculate the expression for the discontinuity correction $\bar{v}$. Instead, one could directly calculate the limiting potential $v^{\lambda\to 0}$ (Eq. (43), Ref. [1]) for various finite values of λ when the matrix of the response function is always invertible. In Figs. 4, 5(a), and 5(b) of Ref. [1] and in Fig. 1 in Ref. [20], we show that the numerical limit coincides with the analytic limit.

(f) Friedrich *et al*. criticize a pedagogical example in the Introduction of our paper that it shows supposedly false convergence (see Figs. 1 and 2 in Ref. [1]) because we employ an "underconverged" orbital basis set and because we use a small cutoff of 0.001 to truncate small eigenvalues of the density response function.

The criticism is based on the false assumption that we intended to take the limit of an infinite orbital basis. However, it is clearly explained that the opposite order of limits is taken: Using a fixed orbital basis, we converge the OEP for a number of auxiliary basis sets of increasing size. Also, we chose the particular example because there is a gap of several orders of magnitude in the eigenvalue spectrum of the matrix of χ_0 separating null from nonsingular eigenvalues, see Fig. 1 in Ref. [1]. The cutoff in that example can be any number in the range between about 10^{-5} and 10^{-13}.

(g) Although the finite basis OEP equations are solved for fixed orbital basis sets in the examples in our paper, Friedrich *et al*. use terminology meaningful only in calculations employing the large-orbital-base limit. They characterize the orbital basis sets and the density response functions in our examples as underconverged, without making reference to an auxiliary basis. The term underconverged, in this case, is doubly unfortunate because it implies that orbital basis sets that have been employed for decades to optimally represent the electronic orbitals and density are not fit for purpose when we consider the OEP.

In our view, if OEP calculations could only be carried out in the large orbital basis limit, they would be impractical. On this point, we agree with Staroverov *et al*. [18] who write that the large orbital basis procedure "is useless for practical calculations where the orbital basis is fixed", and they continue: "What is needed is a reliable and computationally inexpensive method for constructing the Kohn-Sham potential for a given orbital functional in any finite orbital basis set, be it Gaussian functions, plane waves, or grids. Friedrich *et al*. readily accept [2,21] that the basis set balancing leads to "slow convergence" requiring "uneconomically large orbital basis sets" rendering the method "cumbersome" and partly impractical due to "high computational costs".

IV. CONCLUDING REMARKS

An interesting implication of our discovery is that a sequence of finite orbital basis potentials v^0 is obviously prevented from converging smoothly towards the full OEP by the discontinuity correction $\bar{v}$. With increasing the size of the orbital basis set, the correction $\bar{v}$ is expected to shrink gradually, allowing in the end, convergence of the potential but for large orbital basis sets. In this sense, the cost of converging the finite orbital basis OEP equations for v^0 towards the full OEP becomes comparable, eventually, to the high cost of basis-set convergence. Hence, although the order of limits of basis sets is immaterial, the nonanalyticity of finite basis OEP implies that, with the (old) finite basis OEP equations that determine only v^0, but no correction $\bar{v}$, it is necessary to use rather large orbital basis sets in order to achieve a smooth converged potential.

However, with the amended OEP equations proposed in our paper, it is possible to use standard routine orbital basis sets with a correspondingly low computational cost. As explained in Ref. [1], "with the closure relation, the orbital basis set becomes effectively complete", and a sequence of finite orbital OEPs from the solution of the amended equations in Ref. [1] is expected to converge smoothly to the full OEP.

[1] N. I. Gidopoulos and N. N. Lathiotakis, Phys. Rev. A **85**, 052508 (2012).

[2] C. Friedrich, M. Betzinger, and S. Blügel, preceding paper, Phys. Rev. A **88**, 046501 (2013).

[3] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, J. Chem. Phys. **124**, 141103 (2006).

[4] S. Hirata, S. Ivanov, I. Grabowski, R. J. Bartlett, K. Burke, and J. D. Talman, J. Chem. Phys. **115**, 1635 (2001).

[5] A. Görling, A. Heßelmann, M. Jones, and M. Levy, J. Chem. Phys. **128**, 104104 (2008).

[6] C. Kollmar and M. Filatov, J. Chem. Phys. **127**, 114104 (2007)

[7] C. Kollmar and M. Filatov, J. Chem. Phys. **128**, 064101 (2008)

[8] T. Heaton-Burgess, F. A. Bulat, and W. Yang, Phys. Rev. Lett. **98**, 256401 (2007).

[9] It is actually the Comment that casts doubt on many of these calculations as they do not employ the supposedly necessary "balancing" procedure by taking the infinite orbital basis limit.

[10] G. J. Iafrate and J. B. Krieger, J. Chem. Phys. **138**, 094104 (2013)

[11] A. Unsöld, Z. Phys. **43**, 563 (1927).

[12] S. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).

[13] S. Hamel, M. E. Casida, and D. R. Salahub, J. Chem. Phys. **116**, 8276 (2002).

[14] For the subset of those functions that lie in the auxiliary space, see Eq. (29) in Ref. [1].
[15] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).
[16] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).
[17] M. Grüning, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **116**, 6435 (2002).
[18] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, J. Chem. Phys. **125**, 081104 (2006).
[19] A. F. Izmaylov, V. N. Staroverov, G. E. Scuseria, E. R. Davidson, G. Stoltz, and E. Cancès, J. Chem. Phys. **126**, 084107 (2007).
[20] N. I. Gidopoulos and N. N. Lathiotakis, J. Chem. Phys. **136**, 224109 (2012).
[21] M. Betzinger, C. Friedrich, A. Görling, and S. Blügel, Phys. Rev. B **85**, 245124 (2012).