Singular limit in the optimized effective potential with finite basis sets.

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Most finite-basis set implementations of the optimized effective potential (OEP) method leave the potential undetermined, when the auxiliary basis set for the potential is sufficiently large. We discover that finite-basis OEP also exhibits previously unknown singular behaviour. We expect similar anomalous behaviour to be a general feature of single-particle theories where the response function, or the orbital Green's function, is truncated with a finite orbital basis set and then inverted. Imposing continuity, we derive new well-behaved finite-basis-set OEP equations that determine OEP for any auxiliary basis set and adopt an analytic solution via matrix-inversion.

The Optimized Effective Potential (OEP) theory [1–4] offers a promising route for improved accuracy in Density Functional Theory (DFT) [5–7]. Using the OEP methodology, the optimal local exchange potential is determined exactly. Furthermore, implicit (i.e. orbital) density functionals for the correlation energy [8, 9] may yield accurate local correlation potentials $v_c(\mathbf{r})$ and play a significant role in the near future.

Unfortunately, implementations of OEP with the orbitals and the local potential expanded in finite basis sets are marred with mathematical problems [10]. Several attempts have been made to overcome these issues [11–18] but with limited success so far.

We review briefly the OEP theory, focusing on exact-exchange OEP (x-OEP) as a concrete example. The OEP is determined by a Fredholm integral equation of the first kind,

$$\int d\mathbf{r}' \chi_v(\mathbf{r}, \mathbf{r}') v(\mathbf{r}') = b_v(\mathbf{r}) \tag{1}$$

where, $\chi_v(\mathbf{r}, \mathbf{r}')$ is the density-density response function,

$$\chi_v(\mathbf{r}, \mathbf{r}') = 2 \sum_{i,a} \frac{\phi_{v,i}(\mathbf{r})\, \phi_{v,a}(\mathbf{r})\, \phi_{v,a}(\mathbf{r}')\, \phi_{v,i}(\mathbf{r}')}{\epsilon_i - \epsilon_a}, \tag{2}$$

and $b_v(\mathbf{r})$ is a quantity with units of density. Indices i and a run respectively over occupied and unoccupied orbitals in the OEP Slater determinant. For x-OEP,

$$b_v(\mathbf{r}) = 2 \sum_{i,a} \frac{\langle a | \mathcal{J}_v - \mathcal{K}_v | i \rangle}{\epsilon_i - \epsilon_a} \, \phi_{v,i}(\mathbf{r})\, \phi_{v,a}(\mathbf{r}). \tag{3}$$

$\phi_{v,p}(\mathbf{r})$, are orbitals of a single-particle hamiltonian, $h_v \phi_{v,p} = \epsilon_{v,p} \phi_{v,p}$, with the local potential $v(\mathbf{r})$ representing the Hartree and exchange potentials:

$$h_v(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{\text{en}}(\mathbf{r}) + v(\mathbf{r}). \tag{4}$$

$v_{\text{en}}(\mathbf{r})$ is the electron-nuclear attraction potential. $\mathcal{J}_v(\mathbf{r})$ is the direct Coulomb (or Hartree) local potential operator and $\mathcal{K}_v$ is the Coulomb exchange non-local operator. We use the shorthand $\langle i | \cdot | a \rangle$ for the matrix element

$\langle \phi_{v,i} | \cdot | \phi_{v,a} \rangle$. From the definition of the response function, Eq. (1) gives the response, $b_v(\mathbf{r})$, of the density when the effective potential $v(\mathbf{r})$ in Eq. (4) changes by $v(\mathbf{r})$.

To solve the x-OEP Eq. (1), we start with the orbitals $\phi_{u,i}, \phi_{u,a}$ and eigenvalues $\epsilon_{u,i}, \epsilon_{u,a}$ of a Hamiltonian h_u (4) with a trial x-OEP potential u. Keeping the orbitals and energies fixed (i.e. u fixed), we seek among v the potential v_{oep} which solves the intermediate x-OEP equation $\chi_u v_{oep} = b_u$. The potential v_{oep} depends on u. Having obtained $v_{oep}[u]$, we update the potential u in the Hamiltonian $h_u \to h_{v_{oep}[u]}$, we find the occupied orbitals and energy levels of the updated Hamiltonian and we iterate until at convergence, $v_{oep}[u] = u$.

Hirata and co-workers [11] proved that, for a complete orbital basis set, the products $\phi_{v,i}(\mathbf{r})\,\phi_{v,a}(\mathbf{r})$ form a complete set bar a constant. Hence, in the vector space of functions orthogonal to the constant function, the response function (2) is invertible and OEP is determined within a constant.

On the other hand, with a finite orbital basis set and a finite auxiliary basis set $\{\xi_n(\mathbf{r})\}$ for the potential, the straightforward search for OEP may yield an infinity of solutions [10]: from Eqs. (1-3) we see that the potential is undetermined in the null-space of χ_v. With a finite orbital basis set, the dimensionality of the null-space of χ_v increases from unity (constant function) to infinity, resulting in indeterminacy of the potential for functions of the auxiliary space in the null-space of χ_v.

Interestingly, several approximations to the finite basis OEP approach [19–23], which invariably employ the Unsöld approximation [24], determine the approximate OEP fully. The Unsöld approximation amounts to a common energy denominator approximation for the static orbital Green's function, together with the closure or completeness relation. The reason is that with the closure relationship the orbital basis set becomes effectively complete and the null space of χ_v reduces to the constant function. Consequently it is no longer possible for an auxiliary basis function to have a component in the null-space of χ_v.

Returning to OEP, the remedy appears readily. Consider the overlap matrix of χ_v with the auxiliary basis

functions, $A_{kn} \doteq -1/2 \iint \xi_k(\mathbf{r})\chi_v(\mathbf{r},\mathbf{r}')\xi_n(\mathbf{r}')$. A singular value decomposition (SVD) of A_{kn}, in order to truncate auxiliary functions in the null-space of χ_v, should remove any arbitrariness in the potential. Unfortunately, this truncation is in general ambiguous because the singular eigenvalues of the matrix are not always separated unambiguously from the non-zero ones. Then, the inversion of A_{kn} is ill-posed.

Nevertheless, sometimes, the singular eigenvalues of A_{kn} can be identified a priori, unambiguously, *with a clear gap of many orders of magnitude separating them from the rest, as shown in Fig. 1*. In such a case, the resulting potential after truncation of the singular eigenvectors and inversion of A_{kn} is unique. However, depending on the finite basis sets, the resulting unique potential may not look healthy with unphysical oscillations appearing near the nuclei; in the case of atoms, these oscillations make the potential look very different from the exact x-OEP potential obtained on the grid. See $v_x^{\lambda=0}$ in the inset of Fig. 2(a).

So far, the underlying reason for this anomaly has remained elusive as it is usually confused with the ill-posedness of the inversion of A_{kn}, the two problems appearing as one.

In this Letter, we distinguish between the anomalous behaviour of the unique potential, appearing even when a SVD allows the truncation and inversion of A in the space of its non-singular eigenfunctions, and the general ill-posedness of choice of cut-off for the truncation and inversion of A. In the following, we first focus on the former clear-cut problem and we analyse and sort out the anomaly. Then, we discuss the general case, where the anomaly appears entangled with the ill-posedness of the inversion of the matrix of the response function.

We shall base our analysis on the solution $v_{oep}[u]$ of the intermediate x-OEP equation $\chi_u v_{oep} = b_u$, with u fixed. Since u will be fixed, we shall omit the dependence on u in the rest of the section.

For simplicity, we shall analyse the consequence of a finite orbital basis set in the special case where the finite orbital set is composed of the occupied orbitals ϕ_i and of a subset of the (mostly lower lying) virtual orbitals ϕ_a of h_u. The virtual orbitals of h_u (4) that are outside the orbital basis form the the complement basis, and will be denoted by $\tilde{\phi}_a$ and their energies by $\tilde{\epsilon}_a$.

To study the effect of the finite orbital basis we split χ and b in Eqs. (1-3): $\chi(\mathbf{r},\mathbf{r}') = \chi^0(\mathbf{r},\mathbf{r}') + \tilde{\chi}(\mathbf{r},\mathbf{r}')$, $b(\mathbf{r}) = b^0(\mathbf{r}) + \tilde{b}(\mathbf{r})$, where χ^0, $\tilde{\chi}$ and b^0, $\tilde{b}$ are given by Eqs. (2), (3) but the sum over virtual states are restricted in the orbital finite basis and its complement respectively.

Let us denote by v^λ the potential which satisfies the equation, for $\lambda \geq 0$, (we drop the subscript oep)

$$\int d\mathbf{r}' \left[\chi^0(\mathbf{r},\mathbf{r}') + \lambda\,\tilde{\chi}(\mathbf{r},\mathbf{r}')\right] v^\lambda(\mathbf{r}') = b^0(\mathbf{r}) + \lambda\,\tilde{b}(\mathbf{r}). \quad (5)$$

The exact x-OEP is obtained for $\lambda = 1$. In a finite basis set implementation the unknown $\tilde{\chi}$ is always omitted, and $v^{\lambda=0}$ is calculated in place of $v^{\lambda=1}$. However, note that for finite $\lambda > 0$, the response function in (5) is invertible and v^λ is determined up to a constant, while for $\lambda = 0$, χ^0 has an infinite-dimensional null-space where $v^{\lambda=0}$ is undetermined. Hence, the complete omission of $\tilde{\chi}$ is a singular operation and v^λ is not a continuous function of λ at $\lambda = 0$, $v^{\lambda\to0} \neq v^{\lambda=0}$.

In the following we derive $v^{\lambda\to0}$ for a finite orbital basis set. We aim to investigate the interplay of finite orbital and auxiliary basis sets and expand the potential $v^\lambda(\mathbf{r})$ in an auxiliary basis, $v^\lambda(\mathbf{r}) = \sum_n v_n^\lambda \xi_n(\mathbf{r})$. Multiplying through by $-(1/2)\xi_k(\mathbf{r})$ and integrating, we obtain the matrix equation for v^λ:

$$\sum_n (A_{kn} + \lambda\,\tilde{A}_{kn})\, v_n^\lambda = b_k + \lambda\,\tilde{b}_k\,, \quad (6)$$

with,
$A_{kn} = -1/2 \iint \xi_k(\mathbf{r})\chi^0(\mathbf{r},\mathbf{r}')\xi_n(\mathbf{r}')$, $b_k = -1/2 \int \xi_k(\mathbf{r})b^0(\mathbf{r})$,
$\tilde{A}_{kn} = -1/2 \iint \xi_k(\mathbf{r})\tilde{\chi}(\mathbf{r},\mathbf{r}')\xi_n(\mathbf{r}')$, $\tilde{b}_k = -1/2 \int \xi_k(\mathbf{r})\tilde{b}(\mathbf{r})$.

Obviously, we cannot have $\tilde{\chi}$, $\tilde{b}$ exactly. We approximate [24] the energy differences in the denominators of $\tilde{\chi}$, $\tilde{b}$ by a constant, $\Delta \simeq \tilde{\epsilon}_{u,a} - \epsilon_{u,i}$ and then use the closure relation. The matrix elements become, for small λ:

$$A_{kn} = \sum_{i,a} \frac{\langle i|\xi_k|a\rangle\langle a|\xi_n|i\rangle}{\epsilon_a - \epsilon_i} \quad (7)$$

$$\tilde{A}_{kn} = \sum_i \langle i|\xi_k\xi_n|i\rangle - \sum_{i,j}\langle i|\xi_k|j\rangle\langle j|\xi_n|i\rangle \quad (8)$$

$$b_k = \sum_{i,a} \frac{\langle i|\xi_k|a\rangle\langle a|\mathcal{J}_u - \mathcal{K}_u|i\rangle}{\epsilon_a - \epsilon_i} \quad (9)$$

$$\tilde{b}_k = \sum_i \langle i|\xi_k(\mathcal{J}_u - \mathcal{K}_u)|i\rangle - \sum_{i,j}\langle i|\xi_k|j\rangle\langle j|\mathcal{J}_u - \mathcal{K}_u|i\rangle \quad (10)$$

With definitions (8,10), λ in Eq. (6) stands for λ/Δ. In the limits $\lambda \to 0$ and $\lambda \to \infty$ our results are independent of Δ. For fixed λ the solution of Eq. (6) is

$$v_n^\lambda = \sum_k (A + \lambda\tilde{A})_{nk}^{-1}\,(b_k + \lambda\tilde{b}_k) \quad (11)$$

For $\lambda \to \infty$, we recover the ELP equations $v^\infty = \tilde{A}^{-1}\tilde{b}$ [22, 23]. As we change λ, from large values towards zero, the potential v^λ tends to the required limit $v^{\lambda\to0}$. To derive this limit, we need the eigenvectors $\{c^i\}$ of A with non-vanishing eigenvalues, $g^i \neq 0$,

$$\sum_n A_{kn} c_n^i = g^i \sum_n \langle\xi_k|\xi_n\rangle c_n^i\,, \quad (12)$$

and an orthonormal basis $\{c^\mu, c^\nu, \ldots\}$ in the null space of A, $\sum_n A_{kn} c_n^\mu = 0$. After some algebra we obtain:

$$v^{\lambda\to0} = v^{\lambda=0} + \bar{v}, \quad (13)$$

$$\text{where,} \quad v_n^{\lambda=0} = \sum_i \frac{c_n^i}{g^i}\sum_k c_k^i\, b_k\,, \quad (14)$$

$$\bar{v}_n = \sum_{\mu,\nu,k} c_n^\mu \, \tilde{A}_{\mu\nu}^{-1} \, c_k^\nu \, \tilde{b}_k - \sum_{i,\mu,\nu} c_n^\mu \, \tilde{A}_{\mu\nu}^{-1} \, \tilde{A}_{\nu i} \frac{\sum_k c_k^i \, b_k}{g^i} \; . \quad (15)$$

$\tilde{A}_{\mu\nu}^{-1}$ is the inverse of the non-singular matrix $\tilde{A}_{\mu\nu} = \sum_{k,n} c_k^\mu \, \tilde{A}_{kn} \, c_n^\nu$ and $\tilde{A}_{\nu i} = \sum_{k,n} c_k^\nu \, \tilde{A}_{kn} \, c_n^i$.

The finite basis x-OEP Eqs. (13-15) are the main result of this Letter. In these equations, the discontinuity of the potential v^λ as a function of λ at $\lambda = 0$ is evident. Until now, the potential $v^{\lambda=0}$ played the role of finite basis x-OEP. It is obtained by truncating the singular eigenvectors of A and subsequently inverting A in the space of non-singular eigenvectors. The component $\bar{v}$ of $v^{\lambda\to 0}$ determines x-OEP in parts of the auxiliary space where $v^{\lambda=0}$ is undetermined. For example, the first term on the rhs of Eqn. (15) is the projection of v^∞ in the null space of A. Also if the null-space of A artificially included all the eigenvectors of A, then from Eqs. (13-15), we would have $v^{\lambda=0} = 0$ and $v^{\lambda\to 0} = \bar{v} = v^\infty$.

The total energy as a function of λ is continuous, i.e., the total energy of $v^{\lambda\to 0}$ is the same as that of $v^{\lambda=0}$.
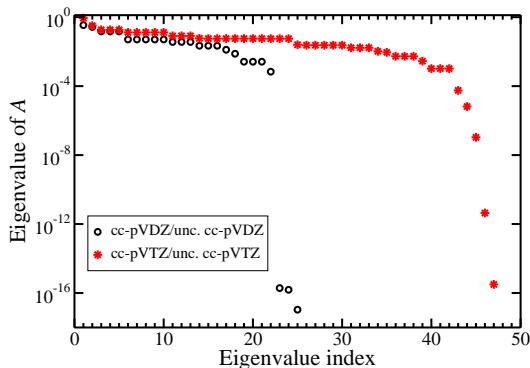

Figure 1: The eigenvalues of matrix A, for the Ne atom with cc-pVDZ/uncontracted cc-pVDZ and cc-pVTZ/uncontracted cc-pVTZ orbital and auxiliary basis sets respectively.

The eigenvalue spectrum of A for the Ne atom, using two different basis set combinations for orbital and auxiliary basis sets, is shown in Fig. 1. In our calculations, we use HF orbitals in place of $\phi_{u,i}, \phi_{u,a}$. A gap separates the zero from the nonzero eigenvalues for the cc-pVDZ basis set. For this case, the limiting potential $v^{\lambda\to 0}$ appears in Fig. 2(a), together with the potentials $v^{\lambda=0.0001}$ (which lies on top of $v^{\lambda\to 0}$), v^∞ (ELP[22, 23], or CEDA[21], or LHF[20]) and for reference the full numerical grid result from Ref. 13. For this basis set, the total energy is identical for Hartree-Fock (HF) and for x-OEP, when $\lambda = 0$ and $\lambda \to 0$.

In general, it will not be possible to identify a priori the null from the non-singular eigenvalues of A [18, 25], as is shown in Fig. 1 for the Ne atom and for orbital/auxiliary basis sets cc-pVTZ/cc-pVTZ uncontracted. One way to obtain the cut-off for the null space of A is to start from too large values for the cut-off (with correspondingly too large null space), and to reduce the cut-off value grad-

ually, removing one by one eigenvalues and eigenvectors from the null space of A. The resulting x-OEP from (13-15) converges to a limiting value and remains unchanged, until a truly singular eigenvalue is reached. When the latter is removed from the null space, the potential changes abruptly. For the previous example, the smallest non-singular eigenvalue of A turns out to be 1.04×10^{-3}. The exchange potential $v_x^{\lambda\to 0}$ is shown in Fig. 2(b). Here, "$\lambda \to 0$" merely implies use of Eqs. (13-15) with an appropriate cut-off.

An alternative approach has been proposed by Heaton-Burgess et al [18], who introduce in the energy expression under minimisation, a Tikhonov regularising term that penalises oscillations of the potential. The main question with Tikhonov's regularisation theory [26] is the choice of regularising function. In Ref. [18], minimisation of the penalty term alone, for strong coupling, leads to a constant potential, which is clearly not the most appropriate choice. To obtain a naturally suited regularising term, we follow the definition of x-OEP in Ref. [27] and consider the second-order energy difference, (the sum is over *all* virtual states a)

$$T_u[v] = \sum_{i,a} \frac{|\langle i|\mathcal{J}_u - \mathcal{K}_u - v|a\rangle|^2}{\epsilon_{u,a} - \epsilon_{u,i}} > 0 \, . \quad (16)$$

For fixed u, the minimising potential of $T_u[v]$ satisfies the x-OEP equation $\chi_u \, v_{oep} = b_u$ [27]. We introduce the λ-dependence:

$$T_u[v](\lambda) = T_u^0[v] + \lambda \, \tilde{T}_u[v] \quad (17)$$

$T^0[v], \tilde{T}_u[v]$ are given by (16) but the sums over virtual states are in the orbital basis set and the complement respectively. Setting the functional derivative of $T_u[v](\lambda)$ equal to zero, yields Eq. (5). Using the Unsöld approximation to approximate $\tilde{T}_u[v]$, we obtain for small λ:

$$T_u[v](\lambda) = T_u^0[v] + \lambda \, S \, , \quad (18)$$

$$S = \sum_i \langle i|(\mathcal{J}_u - \mathcal{K}_u - v)^2|i\rangle - \sum_{ij} |\langle i|\mathcal{J}_u - \mathcal{K}_u - v|j\rangle|^2. \quad (19)$$

λ in Eq. (18) stands for λ/Δ. S is the quantity considered by Staroverov et al [22, 23] in the derivation of ELP. We keep the same symbol as credit to their work. Expanding the potential in a basis set, $v = \sum_n v_n \, \xi_n$, and varying v_n we obtain the finite-basis x-OEP Eqs. (6-10).

From Eq. (18) the energy expression $T_u^0[v]$ coupled with the regularising term S, arise as a natural choice for Tikhonov's regularisation method to yield the finite-basis x-OEP equations when the inversion of A is ill-posed. For example, even for infinite coupling λ, minimisation of the regularising term S gives ELP which is a meaningful approximation to x-OEP.

In Fig. 2(b) we show several potentials for cc-pVTZ and uncontracted cc-pVTZ orbital and potential basis sets. In the inset of Fig. 2(b), we show S versus $T_u^0[v]$
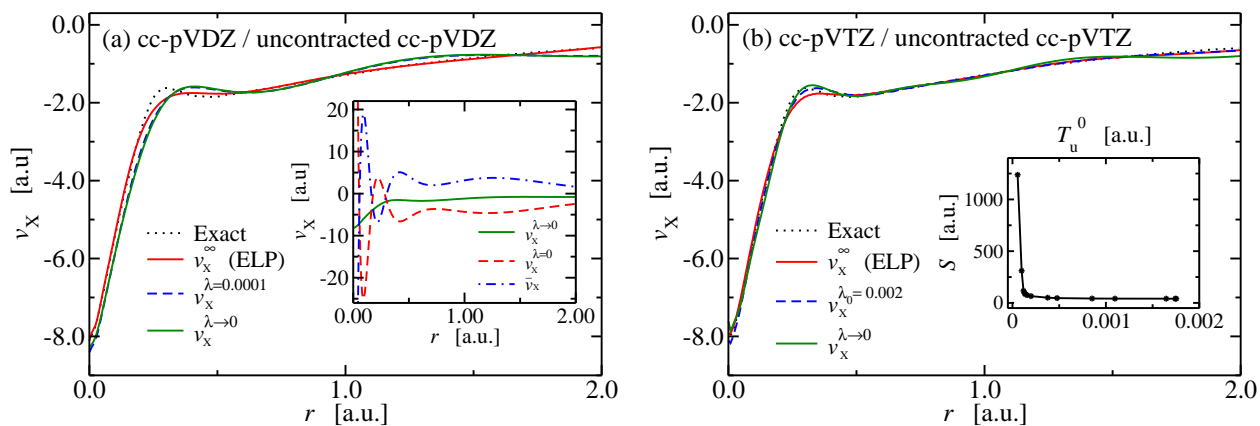
Figure 2: Exchange potentials of the Ne atom using two different combinations for the basis sets for the orbitals and the potential respectively: cc-pVDZ/cc-pVDZ uncontracted in (a) and cc-pVTZ/cc-pVTZ uncontracted in (b). In (a), we show the potentials for $\lambda \to \infty$ (ELP, or CEDA, or LHF), $\lambda = 0.0001$, as well as the limit $\lambda \to 0$ using Eqs. (13-15). In the inset, the two wildly oscillating components of Eq. (13) are shown. In (b), we show the potentials for $\lambda \to \infty$ and $\lambda = 0.002$ (optimal value from Tikhonov regularization), and the potential $v^{\lambda \to 0}$, using such cut-off that the smallest non-singular eigenvalue of A is 1.04×10^{-3}. The L-curve is shown in the inset; S and T_u^0 are shifted by a constant.

for various λ's, and the characteristic L-curve [18, 28], the apex of which gives the optimal $\lambda_0 = 0.002$ which corresponds to the regularised potential v^{λ_0} (11). The total energies of x-OEP for both $\lambda_0 = 0.002$ and $\lambda \to 0$ are 3×10^{-4} Hartrees higher than HF.

In conclusion, we have unveiled a discontinuity in the OEP, as a function of λ, at $\lambda = 0$. This discontinuity is expected to be a general feature of single-particle theories, where the response function (or the orbital Green's function) is truncated with a finite orbital basis set and

then inverted. Such instances arise in linear response in time-dependent density functional theory [29, 30] and in the Dyson equation. Using the Unsöld approximation, we managed to restore continuity and to derive amended finite basis set x-OEP Eqs. (13-15) that determine the limiting potential $v^{\lambda \to 0}$ completely for the whole auxiliary basis set. In the general case, where the truncation and inversion of A is ill-posed, we proposed an appropriate Tikhonov regularisation term that leads to a physical potential even in the limit of infinite coupling.

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