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REGULAR ARTICLE

On finite basis set implementation of the exchange-only optimized effective potential method

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Abstract In this paper, we analyze a structure of the basis set optimized effective potential (OEP) equations from the Fredholm alternative point of view and present one of possible numerical schemes to solve the OEP equation in a stable manner. The solution is constructed as a sum of a unique solution on the subspace of eigenfunctions of the response matrix with non-zero eigenvalues and a non-unique solution on a counterpart subspace with singular eigenvalues. Non-uniqueness of a solution is exploited to obtain a local effective potential that satisfies the condition for the highest occupied molecular orbital (HOMO) without restricting the variational freedom of the optimization procedure. Unlike the existing methods we implement the HOMO condition using the functions of the null-subspace. Numerical results for the total and orbital energies based on the proposed scheme are close to the corresponding literature data.

Keywords Optimized effective potential · Fredholm alternative · Basis set optimization

1 Introduction

A local exchange potential was originally proposed by Slater [1] to simplify the Hartree–Fock equations. This idea has been developed to the optimized effective potential (OEP) based methods [2, 3] which are considered to be a promising technique for constructing local potentials of density functional theory (DFT) [4, 5] in its orbital-dependent implementation. In addition, the exchange-only OEP (xOEP) can be partitioned into the Slater potential and a response correction part (e.g., [6, 7]).

It is known that in the xOEP method, one seeks for a local potential $V_{\mathrm{eff}}(\mathbf{r})$ such that the eigenfunctions $\phi_i(\mathbf{r})$ of the one-particle Schrödinger equation [the Kohn–Sham (KS) equation]

$$-\frac{1}{2}\nabla^2\phi_i^s(\mathbf{r}) + V_{\mathrm{eff}}^s(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i^s\phi_i^s(\mathbf{r}), \tag{1}$$

where $s = \uparrow, \downarrow$ and, in general, the effective potential $V_{\mathrm{eff}}^{\uparrow}(\mathbf{r})$ is different from $V_{\mathrm{eff}}^{\downarrow}(\mathbf{r})$, minimize the same energy functional as the Hartree–Fock (HF) approach, i.e.,

$$E^{\mathrm{OEP}} = -\frac{1}{2}\sum_s\sum_i^{\mathrm{occ}}\int \phi_i^{s*}(\mathbf{r})\nabla^2\phi_i^s(\mathbf{r})\mathrm{d}^3\mathbf{r} + \int \rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r})\mathrm{d}^3\mathbf{r} + \frac{1}{2}\int \rho(\mathbf{r})\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3\mathbf{r}\mathrm{d}^3\mathbf{r}' + E_x[\{\phi_i^s\}] \tag{2}$$

where V_{ext} represents the external potential, $\rho(\mathbf{r}) = \sum_s\sum_i^{\mathrm{occ}}|\phi_i^s(\mathbf{r})|^2$ is the electron density and $E_x[\{\phi_i^s\}]$ is the orbital-dependent exchange HF energy.

This definition leads to the OEP integral equation which can also be obtained using a perturbation theory along the adiabatic connection between the non-interacting model system and the real many-electron system [8]. In particular the xOEP equation may be written in the form:

$$\frac{\delta E^{\mathrm{OEP}}}{\delta V_{\mathrm{eff}}} = \sum_s\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}}\phi_i^s(\mathbf{r})\phi_a^s(\mathbf{r})\frac{\langle\phi_a^s|F^s|\phi_i^s\rangle}{\varepsilon_i^s - \varepsilon_a^s} = 0, \tag{3}$$

where F^s is the Fock operator based on the OEP orbitals.

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Although a large number of practical calculations has been carried out based on this methodology, the solution of the OEP equations is not straightforward (e.g., [9–14] and references therein). Numerical grid techniques have been proposed to solve the OEP equations [3], but this had been feasible only for atomic systems. For molecules practical solutions of the KS equation (1) and the OEP equation (3) are based on a finite basis set implementation. An orbital basis set is used to represent the orbitals $\phi_i(\mathbf{r})$ and an auxiliary basis set is needed to expand the local effective potential $V_{\mathrm{eff}}(\mathbf{r})$.

As pointed out in Ref. [14], it is difficult to give mathematical formulation of the (infinite dimensional) OEP optimization problem, and also to build consistent finite dimensional approximations of the OEP problem. On the one hand, for a fixed auxiliary basis and in the limit of a complete orbital basis set the response matrix has no eigenvalues equal to zero except the trivial one belonging to a constant function. In this case the OEP problem is well-defined and the HF energy must be lower than OEP one [15]. On the other hand, for any finite orbital basis set with increasing an auxiliary basis set one obtains more and more eigenvalues with too small magnitude and the OEP equations become ill-conditioned. It was demonstrated [13], in particular, that this may lead to: (1) the collapse of the unconstrained exchange-only search to the corresponding HF solution and (2) the existence of infinitely many multiplicative exchange potentials. In addition the basis set OEPs are characterized by unphysical oscillations around the nuclei.

Considerable efforts have been expended to understand the cause of the problem (e.g., [16–24] and reference therein). A detailed analysis of the mathematical properties of various local approximations to the nonlocal HF exchange operator is given in [14]. Gorling et al. [16] showed that the HF ground state energy can be only obtained via a finite basis set xOEP scheme in the case that all products of occupied and unoccupied orbitals emerging from employed orbital basis set are linearly independent of each other. When the products are linearly dependent the OEP energy is greater than the HF one. The problem of non-uniqueness seems to be more difficult. In fact, for any finite orbital basis set we are no longer dealing with the original response operator but only with its part on a finite subspace spanned by a basis set consisting of the orbital products (some discussion of the effects of the truncation can be found in [19]). Therefore, if an auxiliary subspace does not coincide with the space spanned by the orbital products we shall deal with an ill-posed problem and a non-unique solution. When the number of basis functions goes to infinity, in general, it is difficult to prove that the solution of the finite-dimensional problem converges to a solution of the original OEP problem. It is easier to devise mathematical regularization procedures to remedy singularities. The corresponding OEP problems were discussed at various places in the literature. Several methods for generating local exchange potential in a numerically stable manner have been proposed. Some of them use the OEP based techniques [17, 20, 23–27]. Other approaches develop an alternative non-OEP based methodology [28–30]. It was established that numerical stability can be achieved if the auxiliary basis set is carefully balanced for a given orbital basis set. As a rule, basis non-linear parameters adjusted for an orbital basis set are employed to construct auxiliary basis sets.

In this paper, we analyze the structure and a solvability condition of the basis set xOEP equations from the Fredholm alternative point of view and present one of possible numerically stable schemes to solve the OEP equation. The solution is constructed as a sum of a unique solution on the subspace of eigenfunctions of the response matrix with non-zero eigenvalues and a solution on a counterpart subspace of eigenfunctions with singular eigenvalues. In addition, a general solution depends on arbitrary constants. In our implementation the non-uniqueness has been partly fixed by imposing restrictions that must be satisfied by the exact OEP, in particular, we have examined the condition for the highest occupied molecular orbital (HOMO) using the functions of the null-subspace. Opportunities to achieve a balancing of the orbital and auxiliary basis set were investigated using a simple reoptimization of the exponents for auxiliary functions.

The paper is organized as follows: a general outline of the basis set OEP equation is considered in Sect. 2, where we derive optimization equations for non-linear orbital and auxiliary basis set parameters and show that orbital basis set equations are similar to those of the HF method. In Sect. 3 an operator form of the xOEP equations is presented and their analysis based on the Fredholm alternative is given. In Sect. 4 we discuss an algorithm and numerical results for the Be atom and several test diatomic molecules. Finally, Sect. 5 contains our concluding remarks.

2 Optimization equations for orbital and auxiliary basis sets

Below we shall derive the xOEP equations determining the parameterized effective potential $V_{\mathrm{eff}}(\mathbf{r})$ expressed in terms of an auxiliary basis functions $f_k(\mathbf{r}), k = 1, 2, \ldots, M_{\mathrm{aux}}$, which, in general, can depend on a set of non-linear variational parameters $\{\alpha_m\}$

$$V_{\mathrm{eff}}(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{m=1}^{M_{\mathrm{aux}}} b_m f_m(\mathbf{r}) \qquad (4)$$

The effective potential is written as the sum of a reference potential $V_0(\mathbf{r})$ and a remainder which is expanded in terms of the auxiliary basis set.

For the reference potential, rather than the Fermi–Amaldi potential obtained in the local density approximation [31] or the self-consistent Slater potential [11], we choose an analytical potential proposed in Refs. [32, 33] for atoms and in Refs. [34–36] for molecules, where $V_0(\mathbf{r})$ is expressed as a direct mapping of the external potential $V_{\text{ext}}(\mathbf{r})$. For molecules, the expansion is

$$V_0(\mathbf{r}) = -\sum_k \frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|} + \frac{N-1}{Z} C \sum_k Z_k \frac{1-\exp(-d_k|\mathbf{r}-\mathbf{R}_k|)}{|\mathbf{r}-\mathbf{R}_k|} \tag{5}$$

where $Z = \sum_k Z_k$ and summations in Eq. 5 are over the nuclei.

This representation provides correct asymptotic behavior for $V_{\text{eff}}(\mathbf{r})$ and has proven to be useful for the ground and excited state DFT calculations of atoms and simple molecules [34–38].

In our implementation before using the potential Eq. 4, first we solve the KS equations with the reference potential V_0 alone, in order to determine the variational parameters C and d_k in Eq. 5 by minimizing E^{OEP} and subsequently we fix $V_0(\mathbf{r})$ (in practice these parameters were taken from [36]). This procedure makes it possible to get a spectrum of the response matrix with a good accuracy. Then the coefficients b_m are varied to minimize the OEP energy.

As mentioned, in practice for the solutions of Eq. 1, one applies the finite basis set implementation, i.e., the solutions are sought by expanding the orbitals ϕ_i in terms of a finite orbital set of basis functions χ_p, $(p = 1, 2, \ldots, M^{\text{orb}})$, i.e.,

$$|\phi_i\rangle = \sum_{p=1}^{M^{\text{orb}}} a_{ip} |\chi_p\rangle = P|\phi_i\rangle \tag{6}$$

where P is the orthoprojector onto the finite-dimensional subspace determined by the chosen basis set, i.e.,

$$P = \sum_{p,q}^{M^{\text{orb}}} |\chi_p\rangle (S^{-1}_{pq}) \langle \chi_q| = \sum_{p}^{M^{\text{orb}}} |\chi_p\rangle (\chi_p|, \tag{7}$$

where $\mathbf{S}$ is the overlap matrix with elements $\langle \chi_p|\chi_q\rangle$ and $\mathbf{S}^{-1}$ is its inverse. The vectors $(\chi_p| = \sum_q^{M^{\text{orb}}} S^{-1}_{pq}\langle\chi_q|$, $(p = 1, 2, \ldots, M^{\text{orb}})$, form an orbital basis set biorthogonal to the origin one so that $(\chi_p|\chi_q\rangle = \delta_{pq}$. Here δ_{pq} is the Kronecker symbol.

Thus, the solution of Eq. 1 is replaced by the solution of the equation

$$P(H_{\text{eff}} - \varepsilon_i)P|\phi_i\rangle = 0, \tag{8}$$

where

$$H_{\text{eff}} = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}) \tag{9}$$

For simplicity, the formalism described will be considered in the case of a closed-shell system with a non-degenerate ground state. The Hamiltonian of a system with N electrons has the standard form

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{k}^{\text{nuclei}} \frac{Z_k}{|\mathbf{r_i}-\mathbf{R}_k|} + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r_i}-\mathbf{r}_j|} \tag{10}$$

The expectation value (total energy in the xOEP method) $E = \langle\Phi|H|\Phi\rangle, \langle\Phi|\Phi\rangle = 1$, of the Hamiltonian H with a Slater determinant Φ constructed from spin–orbitals (Eq. 8) becomes a functional of such a potential, i.e., $E = E[\{\phi_i\};V_{\text{eff}}]$ and the effective potential is varied to minimize the total energy. We start from the stationary condition

$$\delta E[\{\phi_i\}; V_{\text{eff}}] = \delta\langle\Phi|H|\Phi\rangle = 0 \tag{11}$$

The transformation of (Eq. 11) from a many-particle expression to the one-particle orbitals yields

$$\delta E = \sum_i^{\text{occ}} \langle\delta\phi_i|(I - P_N)F|\phi_i\rangle + \text{c.c.} = 0 \tag{12}$$

where I is identity and $P_N = \sum_i^{\text{occ}} |\phi_i\rangle\langle\phi_i|$ is the orthoprojector on the subspace of occupied orbitals. The Fock operator F is based on orbitals of Eq. 8. The explicit form of this operator depends on the occupation scheme of the shells.

Taking Eq. 6 into account the variations of the orbitals can be divided into the following parts

$$|\delta\phi_i\rangle = P_N|\delta\phi_i\rangle + (P - P_N)|\delta\phi_i\rangle + \sum_a (\partial_a P)|\phi_i\rangle\delta\gamma_a, \tag{13}$$

Here, γ_a, $a = 1, 2, \ldots, n^{\text{orb}}$, represents the orbital basis set parameters (the orbital exponents and the positions, i.e., we assume that basis functions can be distributed along a molecular axis) and $\partial_a P \equiv \frac{\partial P}{\partial \gamma_a}$ are the derivatives of the projection operator P with respect to the basis set parameters. The first term in Eq. 13 does not lead to any change in the total energy because it is invariant under any orthogonal transformation of the occupied orbitals among themselves. The second term corresponds to variations within the finite-dimensional subspace spanned by the chosen orbital basis set, whereas the last term allows this subspace to be rotated within the Hilbert space of one-particle states to attain the deeper minimum with respect to the total energy.

Substituting Eq. 13 in Eq. 12 and taking into account the independence of the variations expressed by the second and third terms in Eq. 13 and also arbitrariness of γ_a we obtain the following equations:

$$\sum_i^{\mathrm{occ}} \langle \delta\phi_i|(P-P_N)F|\phi_i\rangle + \mathrm{c.c.} = 0 \tag{14}$$

and

$$\sum_i^{\mathrm{occ}} \langle \phi_i|(\partial_a P)F|\phi_i\rangle + \mathrm{c.c.} = 0, \quad a = 1,2,\ldots,n^{\mathrm{orb}} \tag{15}$$

Equation 15 are optimization equations for non-linear parameters (exponents and positions) of an orbital basis set. It is useful to note that these equations in their present form coincide with the basis set optimization equations for the HF method [39, 40]. Hence, a basis set optimized for the HF orbitals is a good approximation for the OEP orbitals and vice versa. The left side of the Eq. 15 presents gradient components of E^{OEP} with respect to the orbital basis set parameters and can be used to construct minimization procedures.

Let us now examine Eq.14. Unlike the HF equations the variations $(P-P_N)|\delta\phi_i\rangle$ in Eq. 14 are not arbitrary, because they are restricted by Eq. 8 and should be determined by the equation:

$$P(H_{\mathrm{eff}}-\varepsilon_i)P|\delta\phi_i\rangle = -P[\delta(V_{\mathrm{eff}}(\mathbf{r})-\varepsilon_i)]P|\phi_i\rangle, \tag{16}$$

Then after some transformations we get

$$\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\phi_i|[\delta V_{\mathrm{eff}}]|\phi_a\rangle\langle\phi_a|(V_{\mathrm{HF}}-V_{\mathrm{eff}})|\phi_i\rangle}{\varepsilon_i-\varepsilon_a} + \mathrm{c.c.} = 0 \tag{17}$$

where summations are over spin–orbitals and $V_{\mathrm{HF}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_x^{\mathrm{HF}}(\mathbf{r})$ with the Hartree potential V_{H} and a non-local exchange potential V_x^{HF} of the form of the HF exchange operator.

In our representation V_{eff} (Eq. 4) depends on a set of variational parameters $\{\mu\}$, i.e., $V_{\mathrm{eff}} = V_{\mathrm{eff}}(\{\mu\})$, where $\{\mu\} \Rightarrow \{b_m,\alpha_m\}$. Therefore

$$\delta V_{\mathrm{eff}} = \sum_\mu (\partial_\mu V_{\mathrm{eff}})\delta\mu \tag{18}$$

and Eq. 17 can be reduced to a system of algebraic equations with respect to the variational parameters $\{\mu\}$, which is divided into two parts:

1. for linear coefficients $\{b_m\}$:

$$\sum_{n=1}^{M^{\mathrm{aux}}} A_{mn}b_n = h_m \tag{19}$$

with

$$A_{mn} = 4\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\phi_i|f_m|\phi_a\rangle\langle\phi_a|f_n|\phi_i\rangle}{\varepsilon_i-\varepsilon_a} \tag{20}$$

and

$$h_m = 4\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\phi_i|f_m|\phi_a\rangle\langle\phi_a|(V_{\mathrm{HF}}-V_0)|\phi_i\rangle}{\varepsilon_i-\varepsilon_a} \tag{21}$$

2. for non-linear auxiliary basis parameters $\{\alpha_m\}$:

$$4\sum_{m=1}^{M^{\mathrm{aux}}} b_m \sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\phi_i|\frac{\partial f_m}{\partial \alpha_m}|\phi_a\rangle\langle\phi_a|F|\phi_i\rangle}{\varepsilon_i-\varepsilon_a} = 0 \tag{22}$$

Eq. 19 is identical to that employed in [23] (Eq. 15) and [17] (Eq. 33). It is worth also noting that Eq. 22 makes it possible to carry out calculations with flexible basis sets for V_{eff} and is similar to Eq. 6 obtained by Yang and Wu [31].

3 A structure of the basis set xOEP equations and its analysis based on the Fredholm alternative

In this section, we analyze the solvability of Eq. 19 from the Fredholm alternative point of view and show how to apply this alternative to construct a solution of the basis set OEP equation. It is known and discussed in the literature that the matrix representation of the OEP equation has a unique solution only if the response matrix has no eigenvalues equal to zero and otherwise has none or infinitely many solutions. Nevertheless, in our opinion, the Fredholm alternative presents a natural and unified tool to analyze ill-conditioned problems and their solvability conditions.

3.1 Operator form of the basis set OEP equation and the Fredholm alternative

The xOEP equation (19) presents a system of linear equations with respect to coefficients $\{b_n\}$ for a finite-dimensional symmetric response matrix A_{mn}, (Eq. 20), $m,n = 1,2,\ldots,M^{\mathrm{aux}}$. For further analysis, we rewrite this system in an operator-vector form.

$$A|u\rangle = |h\rangle \tag{23}$$

where

$$|u\rangle = \sum_{n=1}^{M^{\mathrm{aux}}} b_n|f_n\rangle \tag{24}$$

A is the corresponding response operator

$$A = \sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{|\phi_i\phi_a\rangle\langle\phi_a\phi_i|}{\varepsilon_i-\varepsilon_a} \tag{25}$$

and

$$|h\rangle = \sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{|\phi_i\phi_a\rangle\langle\phi_a|(V_{\mathrm{HF}}-V_0)|\phi_i\rangle}{\varepsilon_i-\varepsilon_a} \tag{26}$$

It is useful to note that $h_m = \langle f_m|h\rangle, A_{mn} = \langle f_m|A|f_n\rangle$ and the expression $\langle f_m|\phi_i\phi_a\rangle$ should be considered as

$$\begin{aligned}\langle f_m|\phi_i\phi_a\rangle &= \int f_m(\mathbf{r})\phi_i(\mathbf{r})\phi_a(\mathbf{r})\mathrm{d}\mathbf{r}\\ &= \int \phi_i(\mathbf{r})f_m(\mathbf{r})\phi_a(\mathbf{r})\mathrm{d}\mathbf{r} = \langle \phi_i|f_m|\phi_a\rangle \qquad (27)\end{aligned}$$

A solvability condition of Eq. 23 can be treated by the Fredholm alternative, which presents a general result from the theory of equations. The alternative may be formulated in the following particular form appropriate for our finite-dimensional case (e.g., [41]):

1. either the homogeneous equation
   $$A|u\rangle = 0 \qquad (28)$$
   has only the trivial solution $|u\rangle = 0$ and then the non-homogeneous equation
   $$A|u\rangle = |h\rangle \qquad (29)$$
   is uniquely solvable for any right-hand side $|h\rangle$, or
2. Equation 28 has $r > 0$ linearly independent solutions $\theta_j, j = 1,2,...,r$, and then Eq. 29 is solvable if and only if $\langle h|\theta_j\rangle = 0,\ j = 1, 2, \ldots, r$. In addition, its solution is not unique and its general solution is $|u\rangle = |u_p\rangle + \sum_{j=1}^{r} c_j|\theta_j\rangle$, where c_j are arbitrary constants and $|u_p\rangle$ is a particular solution of (29).

Below we shall outline how the Fredholm alternative fits the OEP theory.

3.2 Solvability of the finite basis set OEP equations and the Fredholm alternative

Existence of non-trivial solutions of Eq. 28 implies that there exist eigenvectors of the operator A with vanishing eigenvalues. In other words the response matrix A_{mn} is non-invertible in the full space spanned by auxiliary basis functions. Indeed, it has been mentioned repeatedly in the literature (e.g., [12, 13, 15, 24, 25] and references therein) that the basis set OEP method is ill-posed and may lead to infinitely many multiplicative exchange potentials that yield the same energy and density, although these potentials can differ dramatically. Using the Fredholm alternative we realize that such a non-uniqueness originates from arbitrariness of the coefficients c_j in the second part of the alternative.

The full auxiliary space, S^{aux} can be presented as a direct sum of two subspaces which are invariant for a part of the operator A (see Eq. 25) on the auxiliary space:

$$S^{\mathrm{aux}} = S \oplus S^{\perp} \qquad (30)$$

The first of them S with dim $S = M_s$ is defined by eigenvectors of $A\{|\theta_s\rangle\}_1^{M_s}$ with non-zero eigenvalues. The eigenvectors $\{|\theta_s^{\perp}\rangle\}_{M_s+1}^{M^{\mathrm{aux}}}$ corresponding to singular eigenvalues (i.e., eigenvalues whose absolute values are less than some positive threshold σ) form the second so-called null-subspace $S^{\perp}$ with dim $S^{\perp} = M^{\mathrm{aux}} - M_s$.

A solvability condition means that the vectors of the null-subspace must satisfy the orthogonality requirements

$$\langle \theta_s^{\perp}|h\rangle = \sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\theta_s^{\perp}|\phi_i\phi_a\rangle\langle\phi_a|(V_{\mathrm{HF}} - V_0)|\phi_i\rangle}{\varepsilon_i - \varepsilon_a} = 0. \qquad (31)$$

In particular (Eq. 31) is fulfilled if

$$\langle\phi_a\phi_i|\theta_s^{\perp}\rangle = 0 \qquad (32)$$

One can show that Eq. 32 is automatically fulfilled if all products of occupied and virtual orbitals are linearly independent of each other. Equation 32 means also that the null-subspace is orthogonal to the space spanned by the orbital products ($S^{\times}$). If we deal with a finite orbital space then $S^{\times}$ is not complete and there exist infinitely many vectors of the null-subspace. However, in the limit of a complete orbital basis set we deal with the complete $S^{\times}$, i.e., there are no any vectors orthogonal to $S^{\times}$ except a constant function (f_c) so that $\langle\phi_a\phi_i|f_c\rangle = 0$.

The S subspace should be considered as a projection of the auxiliary space on the $S^{\times}$ space and according to the first part of the Fredholm alternative Eq. 29 has a unique solution on S:

$$\Pi_s A \Pi_s|u\rangle = \Pi_s|h\rangle \qquad (33)$$

where $\Pi_s = \sum_{s=1}^{M_s}|\theta_s\rangle\langle\theta_s|$ is the orthoprojector on the subspace S, and $|\theta_s\rangle$ are eigenvectors with non-zero eigenvalues.

A solution of Eq. 29 on the subspace S can be obtained as a result:

$$\Pi_s|u\rangle = \sum_{s=1}^{M_s} c_s|\theta_s\rangle = \Pi_s A^{-1}\Pi_s|h\rangle = \sum_{s=1}^{M_s}|\theta_s\rangle\frac{1}{\omega_s}\langle\theta_s|h\rangle \qquad (34)$$

with

$$c_s = \frac{1}{\omega_s}\langle\theta_s|h\rangle \qquad (35)$$

where ω_s are non-zero eigenvalues corresponding to a set of eigenvectors $\{\theta_s\}$, $s = 1, \ldots, M_s$, and $V_{\mathrm{eff}}(\mathbf{r})$ can be written in the form:

$$\begin{aligned}V_{\mathrm{eff}}(\mathbf{r}) &= V_0(\mathbf{r}) + \sum_{s=1}^{M_s} c_s\theta_s(\mathbf{r})\\ &= V_0(\mathbf{r}) + \sum_{m=1}^{M_{\mathrm{aux}}}\left[\sum_{s}^{M_s} c_s U_{sm}\right]f_m(\mathbf{r}) \qquad (36)\end{aligned}$$

and U_{sm} are components of eigenvectors $|\theta_s\rangle$ in a basis set of auxiliary functions $f_m(\mathbf{r})$. It is clear that the old expansion coefficients $\{b_m\}$ are related to new ones $\{c_s\}$ by the expression:

$$b_m = \sum_s^{M_s} c_s U_{sm}, \quad m = 1, 2, \ldots, M^{\mathrm{aux}}. \tag{37}$$

3.3 Singular value decomposition and optimization for auxiliary basis sets

Above described technique termed as truncated singular value decomposition (TSVD) was considered in literature (e.g., [24–26]) as one of elements to remedy numerical instabilities of the basis set OEP equation and construct its stable solution. In this case practical calculations face the important issue of finding objective criteria for discriminating zero and non-zero eigenvalues (see, e.g., [19]). We solve this problem by analyzing the spectrum of eigenvalues of the response matrix A_{mn}. In the spectrum, there is usually an abrupt jump of several orders of magnitude if $M^{\mathrm{aux}} \geq M^{\mathrm{orb}}$. From Table 1 (where eigenvalues of A_{mn} for a combination $M^{\mathrm{orb}}/M^{\mathrm{aux}}$ = 6s/14s of the Be atom are listed) one can see that starting with the 7th eigenvalue the structure of the spectrum becomes steplike. It is important to note that this specific feature does not depend on a type of an auxiliary basis set. The large gap gives us confidence that all eigenvectors corresponding to eigenvalues before the gap must be included into the S subspace. For example, according to Table 1, we should take the first six vectors. The criterion introduced in this way may appropriately be called a *gap-analysis*. It is worth noting that a similar steplike structure in the A_{mn} spectrum was observed and analyzed in Refs. [23, 25]. However, it was not exploited to divide the full auxiliary space into two parts. The corresponding regularization in these papers was achieved by adding in the OEP minimization procedure of the so-called smoothing term expressed in terms of a steplike structure [24, 26].

Table 1 Eigenvalues (in a.u.) of the response matrix **A** for the different types of auxiliary functions and the element $\langle \theta_m | h \rangle$ for the Be atom

m	$f_m =$ $\exp(-\alpha_m r^2)$ Non-opt	$f_m =$ $\exp(-\alpha_m r^2)$ Opt	$f_m = \frac{1-\exp(-\alpha_m r^2)}{r}$ Non-opt	$\langle \theta_m \| h \rangle$
1	$-0.985E-01$	$-0.162E+00$	$-0.530E+02$	$-0.166E-01$
2	$-0.154E-01$	$-0.245E-01$	$-0.956E+00$	$0.386E-02$
3	$-0.797E-03$	$-0.127E-02$	$-0.161E+00$	$0.200E-02$
4	$-0.132E-03$	$-0.226E-03$	$-0.192E-01$	$-0.131E-02$
5	$-0.224E-04$	$-0.313E-04$	$-0.304E-02$	$-0.272E-03$
6	$-0.603E-05$	$-0.751E-05$	$-0.201E-03$	$0.301E-03$
7	$-0.154E-10$	$-0.842E-09$	$-0.125E-07$	$\mathbf{0.403E-06}$
8	$-0.132E-15$	$-0.118E-11$	$-0.846E-11$	$\mathbf{0.394E-08}$
9	$-0.384E-19$	$-0.220E-17$	$-0.204E-14$	$\mathbf{-0.310E-13}$
10	$-0.451E-21$	$0.151E-21$	$-0.952E-15$	$\mathbf{0.943E-13}$
11	$-0.515E-23$	$0.300E-20$	$-0.236E-15$	$\mathbf{0.171E-12}$
12	$-0.161E-23$	$0.483E-20$	$0.563E-15$	$\mathbf{0.260E-13}$
13	$-0.586E-25$	$0.328E-19$	$0.668E-15$	$\mathbf{-0.375E-13}$
14	$0.650E-24$	$0.290E-17$	$0.162E-14$	$\mathbf{-0.129E-12}$

First 6 rows shows vectors of S subspace and 7–14 rows shows vectors of null-subspace

($M^{\mathrm{orb}} = 6$, $M^{\mathrm{aux}} = 14$)

Nevertheless, as mentioned in the literature (e.g., [17, 26, 42]) the numerical problems of the OEP equation, in general, cannot be solved by methods involving only SVDs. In other words, these schemes, as well as the Tikhonov regularization [23], may not yield a correct OEP unless the auxiliary basis set strikes the right balance with the orbital basis.

We investigated a possibility of a balancing scheme for orbital and auxiliary basis sets via optimization of the exponents for auxiliary functions. Let us clarify this point considering the Be atom as an example. Both auxiliary and orbital basis sets were constructed using s-type Gaussian functions whose the exponents ζ_p were chosen according to an even-tempered prescription [43]

$$\zeta_p = \alpha\beta^p, \quad p = 1, 2, \ldots, M \tag{38}$$

with $M = M^{\mathrm{aux}}$ or $M = M^{\mathrm{orb}}$ for auxiliary and orbital basis sets respectively. In general, the parameters α and β must be taken to be functions of M, the number of basis functions, i.e., $\alpha = \alpha(M)$ and $\beta = \beta(M)$, if the Gaussian sets defined by Eq. 38 are to become complete in the appropriate subspace as $M \to \infty$.

These parameters for orbital basis sets are tabulated for different atoms and can be found in [43]. We performed a simple reoptimization of the α and β parameters to find the exponents for auxiliary basis sets. In our case values $\alpha(6) = 0.542\,448$ and $\beta(6) = 1.607\,563$ were obtained by minimizing the OEP energy with $M^{\mathrm{aux}} = 6$. It is not time consuming procedure as it should be done only for a small auxiliary basis set. The α and β parameters for sizes larger than $M^{\mathrm{aux}} = 6$ were determined using the recursions [44]:

$$\alpha[M] = \left[\frac{\beta[M] - 1}{\beta[M-1] - 1}\right]^a \alpha[M-1] \tag{39}$$

and

$$\ln(\beta[M]) = \left[\frac{M}{M-1}\right]^b \ln \beta[M-1] \tag{40}$$

with $M = M^{\mathrm{aux}}$ and $a = 0.3274$ and $b = -0.5230$ values were taken from [43]. In essence, the reoptimized α and β parameters for auxiliary basis sets can be tabulated for all atoms in a way similar to Ref. [43] and, thus, they may be used with the standard basis sets.

It is known from the literature that one of important steps of a balancing scheme is a removing the most diffuse and some tightest s-type functions in the auxiliary basis set

Table 2 Beryllium atom: exponents ζ_p of even-tempered orbital and auxiliary basis sets of 14s Gaussians

p	Orbital	Auxiliary
1	0.04529	0.61780
2	0.11723	0.83794
3	0.30339	1.13652
4	0.78517	1.54149
5	2.03205	2.09076
6	5.25900	2.83575
7	13.61050	3.84619
8	35.22430	5.21669
9	91.16150	7.07553
10	235.92900	9.59671
11	610.59100	13.01627
12	1,580.23000	17.65429
13	4,089.67000	23.94495
14	10,584.20000	32.47713

(see, e.g., [16] pp. 054102–054114). We would like to note that a similar effect can be achieved by the reoptimization described. A comparison of the exponents of an orbital and auxiliary basis set consisting of 14s functions (see Table 2) confirms our observation. The preliminary calculations carried out for the Be atom showed the effectiveness of such a procedure (see Sect. 4).

Thus, the construction of an auxiliary basis set balanced for a given orbital one comprises the following steps:

1. Choose an orbital basis set and reoptimize its exponents according to the mentioned recipe.
2. Carry out the TSVD regularization using the gap-analysis described above.

This scheme, however, cannot prevent an uncontrolled shift of the orbital energies even, if the reference potentials with correct asymptotic are used. Imposing the so-called HOMO condition improves the quality of the corresponding OEP and partly solves this orbital energy problem. According to this HOMO condition the orbital energy $\varepsilon^{\mathrm{HOMO}}$ obtained from the one-particle equation (8), should be identical to the expectation value $\langle \phi^{\mathrm{HOMO}} | F^{HF} | \phi^{\mathrm{HOMO}} \rangle$ obtained with the Fock operator, based on the OEP orbitals. In Ref. [16], this condition was imposed on a reference potential which is also expanded in the auxiliary basis set, whereas in Refs. [12, 20, 25, 27]) it was enforced via a Lagrange multiplier technique. In the last case the HOMO constraints restrict the variational freedom of the optimization procedure.

Below we will consider how to account the HOMO condition without involving restrictions into the variational procedure. For this the contribution of singular eigenstates of A_{mn} to a local effective potential $V_{\mathrm{eff}}(\mathbf{r})$ will be examined.

3.4 HOMO condition

We will exploit the freedom to choose appropriately the component of the OEP solution $V_{\mathrm{eff}}(\mathbf{r})$ in the null-subspace, in order to ensure that certain conditions [45] of the exact OEP are satisfied by the basis set OEP $V_{\mathrm{eff}}(\mathbf{r})$, thus improving the approximation. These conditions will be applied to fix arbitrary coefficients appearing in the second part of the Fredholm alternative. For example, a constraint arises from the HOMO condition. Other restrictions, for example, can be imposed using the Levy–Perdew virial relation [46] or the correct asymptotic decay.

We shall show how the HOMO condition can be imposed on the basis set OEP solution within the Fredholm alternative. Unlike the existing methods which seek the solution on the subspace S subject to the HOMO constraint, we use for this purpose a solution from the null-subspace $S^{\perp}$ and, therefore, do not involve additional restrictions into the variational procedure.

Let a potential $V(\mathbf{r}) = \sum_{s=1}^{M_s} c_s \theta_s(\mathbf{r})$ be a solution of the OEP equation (23) and $\theta^{\perp}(\mathbf{r})$ be an arbitrary function belonging to the null-subspace $S^{\perp}$. Then $V(\mathbf{r}) + \theta^{\perp}(\mathbf{r})$ represent another solution since $A|\theta^{\perp}\rangle = 0$ and thus, we have an infinite number of such potentials. We may choose an effective potential in the form

$$V_{\mathrm{eff}}(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{s=1}^{M_s} c_s \theta_s(\mathbf{r}) + c^{\perp}_{M_s+1} \theta^{\perp}(\mathbf{r}) \tag{41}$$

As mentioned the coefficients c_s are found via Eq. 33 whereas the unknown coefficient $c^{\perp}_{M\_s+1}$ will be determined with the help of the HOMO condition, which can be written as:

$$\langle \phi^{\mathrm{HOMO}} | V_{\mathrm{eff}} | \phi^{\mathrm{HOMO}} \rangle = \langle \phi^{\mathrm{HOMO}} | V_{\mathrm{HF}} | \phi^{\mathrm{HOMO}} \rangle \tag{42}$$

Substituting Eq. 41 in Eq. 42 we arrive at the relation

$$c^{\perp}_{M_s+1} = \frac{\langle \phi^{\mathrm{HOMO}} | V_{\mathrm{HF}} | \phi^{\mathrm{HOMO}} \rangle - \langle \phi^{\mathrm{HOMO}} | V_0 | \phi^{\mathrm{HOMO}} \rangle - \sum_{s=1}^{M_s} c_s \langle \phi^{\mathrm{HOMO}} | \theta_s | \phi^{\mathrm{HOMO}} \rangle}{\langle \phi^{\mathrm{HOMO}} | \theta^{\perp} | \phi^{\mathrm{HOMO}} \rangle} \tag{43}$$

After determining $c^{\perp}_{M_s+1}$ the one-particle Schrödinger equation (8) is solved with $V_{\mathrm{eff}}(\mathbf{r})$ (Eq. 41) and the procedure has to be repeated until we find self-consistency.

Certainly, we have infinitely many of the potentials (Eq. 41) and all of them will satisfy the HOMO condition by construction. In addition, it is clear that the proposed HOMO procedure is applicable, if the denominator in (Eq. 43) is not equal to zero. However, it is worth noting that the vector $|\phi^{\mathrm{HOMO}}\rangle$ belongs to the null-subspace of the A operator (Eq. 25). Consequently, it has a non-zero projection on this subspace. Therefore, in our implementation we use the only choice for $\theta^{\perp}$:

$$|\theta^{\perp}\rangle = \sum_{s=M_s+1}^{M^{\mathrm{aux}}} |\theta_s^{\perp}\rangle\langle\theta_s^{\perp}|\phi^{\mathrm{HOMO}}\rangle \tag{44}$$

Thus the OEP is presented as a linear combination of M_s functions belonging to the subspace S and the only function (44) from the null-subspace $S^{\perp}$.

4 Algorithm and numerical results

The analysis described above leads to the numerical procedure for constructing effective potentials. In summary, the procedure is the following:

1. Solve the KS equation (8) with the reference potential $V_0(\mathbf{r})$ (Eq. 5), whose variational parameters d and C are determined by minimizing the OEP energy.
2. Pick a set of at least $M^{\mathrm{orb}}+1$ auxiliary functions $\{f_m\}$ and evaluate the matrix elements $\langle\chi_p|f_m|\chi_q\rangle$.
3. Using the KS orbitals construct and diagonalize response matrix A_{mn} to get its eigenvalues $\{\omega\}$ and eigenvectors $\{\theta\}$.
4. Using the gap-analysis select M_s eigenvectors of A_{mn} forming the S subspace and evaluate the coefficients $c_s, s=1,2,\ldots,M_s$ according to Eq. 35.
5. Calculate the coefficient c_{M_s+1} according to Eq. 43 and solve the KS equation with the potential of Eq. 41 keeping the reference potential fixed.
6. Evaluate the total energy using a new set of the KS orbitals.
7. Return after step 6 to step 3 using the current KS orbitals and repeat steps 3–6 until convergence is achieved.

Regarding the computational efficiency of our implementation, it should be noted that matrix elements of $V_{\mathrm{eff}}(\mathbf{r})$ demand analytical evaluation of one-particle integrals only.

The basis set OEP calculations for the Be atom and small diatomics H_2, HeH, LiH, BeH and BH were carried out to examine numerical stability and to evaluate the performance of the proposed procedure.

It is well known that the choice of the finite basis sets is crucial for the success of any ab initio calculations. Therefore before comparing the numerical results obtained here with the literature data we consider the specific features of orbital and auxiliary basis functions employed in our implementation and present illustrative calculations of the response matrix for the Be atom, which has been well studied for the OEP problem from various aspects [11, 13, 16, 27]. In addition, we discuss also how the method in question can be used when the OEP is split as a sum of two or more terms, for example the Hartree potential and the exchange potential.

4.1 Orbital and auxiliary functions for the Be atom

For the Be atom we used orbital basis sets of s-type Gaussian functions

$$\chi_p(r) = \exp(-\zeta_p r^2), \tag{45}$$

where the orbital exponents ζ_p were chosen according to an optimal even-tempered prescription [43].

As far as auxiliary basis functions are concerned, it should be stressed that the basis functions for orbitals and for the potential, in general, have to cover different functional subspaces as they have to satisfy different criteria (see, e.g., [14]). Indeed, the OEP is not an integrable function, because it falls off as $-\frac{1}{r}$ asymptotically. It is therefore impossible to expand it directly in terms of the traditional orbital basis sets. At this stage we will consider two types of auxiliary functions. The first uses the orbital basis set itself, i.e.,

$$f_m(r) = \exp(-\zeta_m r^2) \tag{46}$$

The second choice of auxiliary functions is different from the traditional one and follows the choice of the reference potential $V_0(\mathbf{r})$. In other words we use auxiliary basis functions expressed in terms of the external potential. For atoms auxiliary functions are:

$$f_m(r) = (N-1)\frac{1-\exp(-\zeta_m r^2)}{r} \tag{47}$$

The parameters ζ_m for the potential functions (46) and (47) were determined by the prescription (38) like orbital functions. In addition, auxiliary basis sets of the different quality were constructed. The first type specified as *non-optimal* bases were generated with the exponents ζ_m of an orbital basis set. For the second type of auxiliary bases specified as *optimal* bases the parameters ζ_m were reoptimized in accordance with Sect. 3.3.

Using the basis sets described and the reference potential $V_0(\mathbf{r})$ (Eq. 5), which for atoms takes the form

$$V_0(r) = -\frac{Z}{r} + (N-1)C\frac{1-\exp(-dr)}{r}, \tag{48}$$

the Kohn–Sham equation (8) was solved and the response matrix A_{mn} was constructed for two types of auxiliary functions (46) (non-optimal and optimal) and (Eq. 47) (non-optimal). Values $d = 1.974140$ a.u and $C = 0.917234$ a.u. were determined by minimizing E^{OEP}. Diagonalization of this matrix was performed to check the ill-posedness of this matrix. The corresponding results obtained with orbital basis set ($M^{\mathrm{orb}} = 6$) and auxiliary basis set ($M^{\mathrm{aux}} = 14$) are given in Table 1. As expected, the matrix A_{mn} is pathologically non-invertible in the full space spanned by both functions (46) and functions (47) forming auxiliary basis sets since it has many practically zero eigenvalues. In addition, as mentioned, the singular eigenvalues as well as the element $\langle h|\theta_j\rangle$ show a gap of several orders of magnitude from values whose eigenvectors should be included in the S subspace. The number of these eigenvectors determines the dimension M_s. In our case $M_s = 6$.

4.2 Splitting of the effective potential and auxiliary functions

The previous sections dealt with the problem how to expand the whole OEP in the basis set. However, in the traditional OEP practice V_{eff} is split as a sum of some terms:

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_x(\mathbf{r}) \tag{49}$$

with $V_{\text{ext}}(\mathbf{r}) = -\frac{Z}{\mathbf{r}}$, $V_H(\mathbf{r}) = \int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'$ is the Hartree potential and $V_x(\mathbf{r})$ is a local exchange potential, which is expanded in a set of auxiliary basis functions.

In this subsection we consider how the method in question can be applied to the problem (Eq. 49). In addition, we shall consider atoms although implementation for molecules is straightforward. In our implementation a fixed electronic density $\rho_0(\mathbf{r})$ in V_H $(\mathbf{r})$ was obtained with our reference potential (Eq. 5). Unlike V_{eff}, V_x is finite at the nucleus, so auxiliary functions for V_x, in general, are different from that for V_{eff}. For example, functions (47) employed for the whole OEP cannot be used to expand V_x, because

$$\lim_{r\to 0} \frac{1-\exp(-\zeta_m r^2)}{r} = 0 \tag{50}$$

whereas $\lim_{r\to 0} V_x(r) \neq 0$. To ensure that the potential V_x has the correct asymptotic behavior, one may choose to search the local potential in the form:

$$V_x(r) = V_{0x}(r) + \sum_{m=1}^{M_{\text{aux}}} b_m f_m(r) \tag{51}$$

with Gaussians $f_m = \exp(-\zeta_m r^2)$ and a reference exchange potential $V_{0x}(r)$ which in the spirit of $V_0(r)$ takes the form

$$V_{0x}(r) = (N-1)C_x \frac{1-\exp(-d_x r)}{r}, \tag{52}$$

The KS equations with the potential $V = V_{\text{ext}}(r) + V_H$ $(r) +$ V_{0x} (r) were solved to determine the variational parameters C_x and d_x in Eq. 52 by minimizing E^{OEP} and subsequently we fix $V_{0x}(r)$. For the Be atom they are $C_x = -0.267611$ a.u. and $d_x = 3.346702$ a.u. Then the coefficients b_m are determined in accordance with the algorithm.

Thus the algorithm of constructing $V_x(r)$ is similar to that for the whole effective potential.

4.3 Comparison with other methods for the Be atom

Below we will use potentials with only optimal exponents of auxiliary functions.

For the Be atom calculations were carried out with both the effective potential (Eq. 4) and the splintered potential (Eq. 49). An influence of reoptimization of auxiliary basis sets on a smoothness of the potential is demonstrated in Fig. 1 where the exchange potentials of Be obtained with non-optimal and optimal auxiliary basis sets are shown. We used 6s functions for an orbital basis and 14s functions for an auxiliary basis set (6*s*/14*s* combination). The dotted potential corresponds to non-optimal auxiliary functions and the SVD filtering. We observe a distorted tail near a nucleus, i.e., this TSVD regularization is not sufficient to ensure a physically meaningful solution for the OEP in general. Whereas this regularization in conjunction with the reoptimization procedure leads to a correct behavior (solid line). Figure 2 presents the exchange potentials of Be as a function of the distance from the nucleus. These potentials were determined according to Eq. 51. The dotted line is our result by using 6s gaussians (Eq. 45) for orbitals and an auxiliary basis set of 6s optimal functions. The dashed and solid lines correspond to 14s and 18s auxiliary functions respectively. Unlike V_{eff}, we did not use the HOMO condition for V_x. One can see that our calculated V_x potentials have a smooth behavior near the nuclei and are visually indistinguishable. They produce the total energy E $= -14.535$ 178 hartree which coincides practically with that obtained with the whole OEP (see Table 3).

A comparison in the behavior of the reference potential (Eq. 48) and the V_{eff} potentials (Eq. 4) with HOMO conditions obtained for different combinations $(M^{\text{orb}}/M^{\text{aux}})$ ⇒

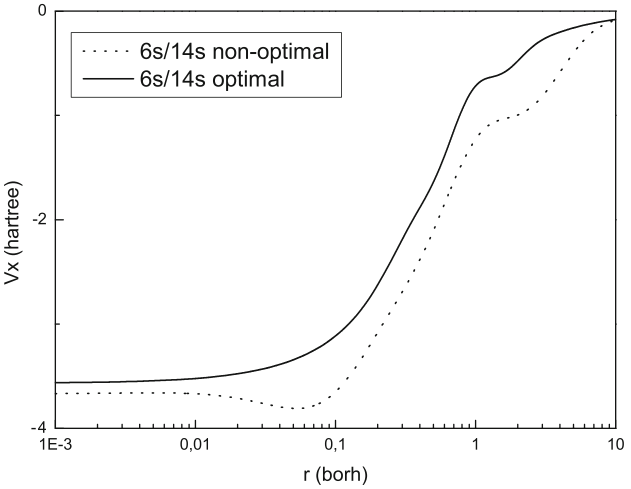

Fig. 1 Exchange potentials of the beryllium atom obtained using even tempered auxiliary basis sets with non-optimal (*dotted line*) and optimal (*solid line*) exponents

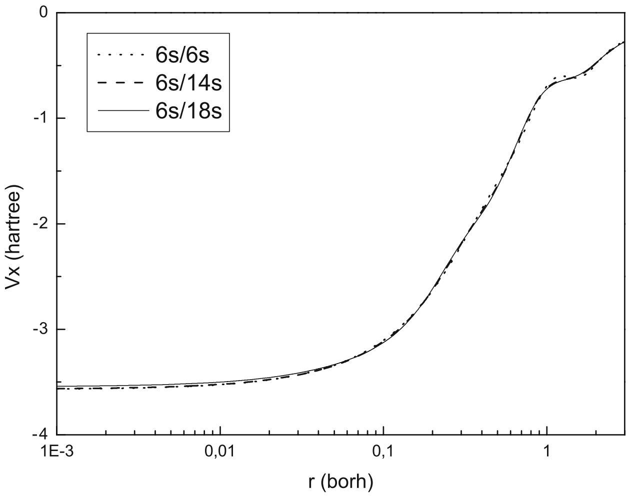

Fig. 2 The exchange potentials of Be obtained with an orbital basis set of 6s functions and different auxiliary basis sets

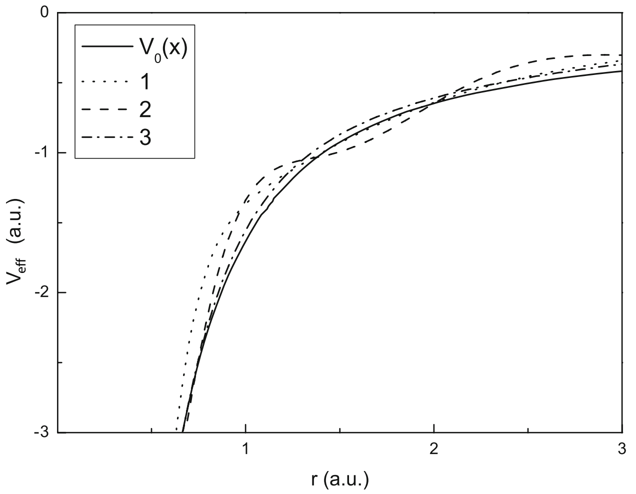

Fig. 3 The reference potential $V_0(\mathbf{r})$ (*solid line*) and the effective potentials of Be, computed with HOMO condition for different combinations ($M^{\mathrm{orb}}/M^{\mathrm{aux}}$): (6s/14s), potential 1; (14s/14s), potential 2 and (14s/6s), potential 3. Auxiliary functions $f_m = \frac{1-\exp(-\zeta_m r^2)}{r}$ are used

(6)/(14), (14)/(14) and (14)/(6) is given in Fig. 3. All the effective potentials were computed with auxiliary functions (47). One can see that our reference potential (Eq. 48) can be considered as a good approximation in some average sense to a more accurate effective potential, missing, however, the peek due to the shell structure (at about 1 a.u.) and correct values of orbital energies. Although it should be noted that the effective potentials in our implementation show a smoothed intershell peek, compared to the exchange potentials presented in Fig. 2. It can be partly explained by including the external potential from scratch to our effective potentials which smooths slightly the peek.

The results listed in Table 3 were obtained with the second type of optimal auxiliary functions (47) of different sizes and without the HOMO condition. One can see that dimension (M_s) of the subspace S is determined by a chosen orbital basis set ($M^{\mathrm{orb}} = 6$) and does not depend on a size of an auxiliary basis set. In addition the OEP energy does not depend practically on the number of auxiliary functions.

Table 3 Total energy (hartrees) of the Be atom obtained with an orbital basis set of 6s functions and the different number of auxiliary basis functions $f_m = \frac{1-\exp(-\alpha_m r^2)}{r}$ (energy difference in mhartrees)

M^{aux}	$M_s + 1$	E^{OEP}	$E^{\mathrm{OEP}} - E^{\mathrm{HFa}}$
10	7	−14.535 173	0.028
14	7	−14.535 174	0.027
18	7	−14.535 175	0.026
22	7	−14.535 178	0.023

[a] The Hartree–Fock energy $E^{\mathrm{HF}} = -14.535\,201$ hartrees was obtained with the same orbital basis set as for the OEP method

Table 4 shows convergence of the OEP energy and differences between OEP and HF energies as a function of an orbital basis set size. The auxiliary basis set of 22 functions (46) and (47) was used for different sizes of orbital basis sets ($M^{\mathrm{orb}} = 6$, 10, 14 and 22). For both types of auxiliary functions we observe that the difference $E^{\mathrm{OEP}} - E^{\mathrm{HF}}$ converges towards the value 0.591 mhartrees, which can be regarded as close to the exact one [16]. In addition, our total OEP energies are in good agreement with the corresponding literature data (see, e.g., the values in footnote taken from [42]).

The energies of occupied orbitals and lower unoccupied orbitals for Be obtained with HF and various local potentials are given in Table 5. The results show that our scheme and the known in literature ELP, SCELP and Yang–Wu OEP methods yield very similar orbital energies. Here it should be stressed that the ELP, SCELP and Yang–Wu OEP spectra are shifted to have the same HOMO energies as Hartree–Fock, whereas our values are obtained directly from a solution of the KS and xOEP equations.

4.4 Implementation for molecules

For the molecules under consideration, unlike the traditional atom-centered basis sets, we used orbital basis functions distributed along the molecular Z axis:

$$\chi_p = \exp\{-\zeta_p[x^2 + y^2 + (z - Z_p)^2]\}, \quad p = 1, 2, \ldots, M^{\mathrm{orb}} \tag{53}$$

The orbital exponents ζ_p and the positions Z_p were determined by invoking the OEP variational principle. Optimization equation (15) were used to construct an effective computational algorithm for their determination. More information about the variationally optimized basis sets can be found in Refs. [39, 40].

Table 4 Beryllium atom: convergence of the OEP energy (hartrees) and differences between OEP and HF energies (mhartrees) as a function of the orbital basis set size

M^{orb}	$M_s + 1$	E^{OEPa}	$E^{\mathrm{OEP}} - E^{\mathrm{HF}}$	$\varepsilon^{\mathrm{HOMO}}_{\mathrm{OEP}}$	$\varepsilon^{\mathrm{HOMO}}_{\mathrm{HF}}$
$f_m = \exp(-\alpha_m r^2)$					
6	7	−14.535 182	0.019	−0.298 354	−0.298 636
10	11	−14.571 530	0.208	−0.309 399	−0.308 872
14	11	−14.572 366	0.585	−0.309 634	−0.309 258
22	12	−14.572 432	0.591	−0.309 573	−0.309 269
$f_m = \frac{1-\exp(-\alpha_m r^2)}{r}$					
6	7	−14.535 178	0.023	−0.298 606	−0.298 636
10	11	−14.571 530	0.208	−0.309 472	−0.308 872
14	15	−14.572 427	0.524	−0.309 533	−0.309 258
22	19	−14.572 435	0.588	−0.309 563	−0.309 269

The 5th and 6th columns display HOMO orbital energies (hartrees) computed with the present OEP implementations and the HF method. The largest auxiliary basis set of $M^{\mathrm{aux}} = 22$ and optimal even-tempered exponents are used

[a] Other results (taken from [42]; a large UGBS basis set was used): (1) Effective localized potential (ELP) method (aux = orb) $E = -14.572\ 280$ hartrees, (2) Yang–Wu OEP method (aux = orb) $E = -14.572\ 426$ hartrees, (3) Numerical OEP method $E = -14.572\ 433$ hartrees

Table 5 Orbital energies (in hartrees) of the Be atom calculated with Hartree–Fock and various local potentials

Orbital	HF	ourOEP	Yang–Wu OEP	ELP	SCELP
1s	−4.732 67	−4.125 26	−4.127 96	−4.117 89	−4.108 20
2s	−0.309 27	−0.309 56	−0.309 27	−0.309 27	−0.309 27
3s	0.077 18	−0.076 43	−0.080 72	−0.074 11	−0.078 67
4s	0.362 93	0.155 74	0.150 13	0.158 15	0.156 07

The ELP, SCELP and Yang–Wu OEP spectra are shifted to have the same HOMO orbital energies as Hartree–Fock [29]. Orbital/auxiliary (22s)/(22s) basis sets are used

To clarify our modifications for auxiliary basis functions (47) it is worth noting that orbital products $\{\phi_i\phi_a\}$ form a suitable basis set to expand a local potential [11, 20]. Let us suppose that for a diatomic molecule **A–B** an occupied molecular orbital is presented by a linear combination of atomic functions centered on the **A** nucleus, whereas an unoccupied orbital is located on the **B** nucleus (the traditional basis sets are atom-centered ones). The orbital product can then be expressed in terms of atomic basis functions:

$$\phi_i(\mathbf{r})\phi_a(\mathbf{r}) = \sum_{p,q} C_{ip}C_{aq}\exp\left\{-\zeta_p[x^2+y^2+(z-Z_A)^2]\right\} \times \exp\left\{-\zeta_q[x^2+y^2+(z-Z_B)^2]\right\} \tag{54}$$

Using the Gaussian product theorem we have

$$\phi_i(\mathbf{r})\phi_a(\mathbf{r}) = \sum_{p,q} C_{ip}C_{aq}K_{pq} \times \exp\left\{-\zeta_{pq}[x^2+y^2+(z-Z_{pq})^2]\right\} \tag{55}$$

where

$$\zeta_{pq} = \zeta_p + \zeta_q, \quad K_{pq} = \exp\left[-\frac{\zeta_p\zeta_q}{\zeta_{pq}}(Z_{\mathrm{A}} - Z_{\mathrm{B}})^2\right] \tag{56}$$

and new positions Z_{pq} are determined by the relation

$$Z_{pq} = \frac{\zeta_p Z_A + \zeta_q Z_B}{\zeta_{pq}} \tag{57}$$

In other words, because of Eq. 57 we deal with an expansion in terms of Gaussians, whose centers Z_{pq}, in general, do not coincide with the nuclei. Therefore, for molecules we employed the following modified auxiliary functions with distributed Gaussians:

$$f_m(\mathbf{r}) = \frac{N-1}{Z}\sum_k Z_k \frac{1-\exp[-\zeta_m(\mathbf{r}-\Re_{\mathbf{m}})^2]}{|\mathbf{r}-\mathbf{R_k}|} \tag{58}$$

In addition, orbital exponents ζ_m and the corresponding positions $\Re_m$ can be determined by minimizing the OEP energy or using the distributed models proposed in [47, 48].

The total OEP energies of simple diatomics in a comparison with the HF energies are presented in Table 6. The energies were computed with variationally optimized orbital basis sets of 18s Gaussians.Auxiliary basis sets contained 14, 18 and 22 functions f_m (Eq. 58). The corresponding gaussian functions in (Eq. 58) were distributed along the molecular axis with the same exponents ζ_m and positions $\Re_m$ as the orbital basis set functions. The parameters of the basis sets are available from the author (V.N.G.) on request.

It is known [15] that the exact exchange-only OEP energy is above HF except closed-shell two-electron systems (H_2 in our case) for which $E^{\mathrm{OEP}} = E^{\mathrm{HF}}$. Our results for the molecules under consideration are in agreement with this statement. In addition, we observe that the difference $E^{\mathrm{OEP}} - E^{\mathrm{HF}}$ for open-shell molecules HeH and BeH is larger than for closed-shell systems: LiH and BH (cf. HeH (0.31 mhartrees) with LiH (0.03 mhartrees) and BeH (0.743 mhartrees) with BH (0.716 mhartrees).

This can be explained by using the same local potential V_{eff} for all electrons, whereas the restricted open-shell HF method deals with different Fock operators for spin-up and spin-down electrons.

To estimate an accuracy of the computed OEP and HF energies and the quality of basis sets employed, we present the HF limits data obtained with the numerical HF method [50]: H_2, $R = 1.4$ bohr, $E^{\mathrm{HF}} = -1.133\ 629\ 57$ hartrees; HeH, $R = 1.5$ bohr, $E^{\mathrm{HF}} = -3.220\ 315\ 12$ hartrees; LiH, $R = 3.015$ bohr, $E^{\mathrm{HF}} = -7.987\ 352\ 14$ hartrees; BeH,

$R = 2.5$ bohr, $E^{\mathrm{HF}} = -15.153\ 182\ 34$ hartrees and BH, $R = 2.3289$ bohr, $E^{\mathrm{HF}} = -25.131\ 639\ 16$ hartrees.

Table 6 The total HF and OEP energies (hartrees) of diatomics computed with orbital basis set of 18*s* functions and different size of auxiliary basis sets of functions f_m (Eq. 58)

Molecule	aux$-14f_m$	aux$-18f_m$	aux$-22f_m$	HF[b]
OEP/auxiliary basis				
H_2^a	−1.133 583	−1.133 583	−1.133 583	−1.133 583
HeH	−3.217 701	−3.217 731	−3.218 021	−3.218 331
LiH	−7.986 013	−7.986 066	−7.986 271	−7.986 301
BeH	−15.149 616	−15.150 181	−15.150 295	−15.151 038
BH	−25.127 439	−25.127 537	−25.127 874	−25.128 590

[a] Orbital basis set of 2 × 9 = 18s functions was used

[b] HF energy computed with the OEP orbital basis set of 18s functions; alternative restricted open-shell HF technique [49] was used for open-shell systems HeH and BeH

5 Conclusions

Using the Fredholm alternative we have analyzed a structure and a solvability condition of the basis set xOEP equations. It has been shown that a solution can be constructed as a sum of a unique solution on the subspace which is a projection of the full auxiliary space on the space spanned by the orbital products and a solution on the null-subspace. Non-uniqueness of a solution has been exploited to obtain a local effective potential $V_{\mathrm{eff}}(\mathbf{r})$ that satisfies the HOMO condition without restricting the variational freedom of the optimization procedure. A simple reoptimization of the basis function exponents together with the TSVD regularization has been examined to construct a balancing scheme for orbital and auxiliary basis sets.

A new form of auxiliary functions expressed in terms of the external potential has been introduced. These functions preserve a symmetry of the external potential and provide a correct asymptotic behavior. The corresponding calculations of the total OEP energies and orbital energies have shown a proper performance of the proposed basis set OEP implementation.

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