

Finite-basis-set optimized effective potential exchange-only method

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(Received 6 June 2001; accepted 23 October 2001)

The finite-basis-set optimized effective potential (OEP) method is presented from an integral equation point of view. It is shown that the projection method for solving the OEP integral equation provides a consistent and convenient approach for including orbital-dependent functionals and potentials in the finite-basis-set implementations of the Kohn–Sham theory. Different finite-basis-set realizations of the OEP method are introduced and tested within the exchange-only approximation. An exact condition involving the local multiplicative exchange potential and the nonlocal Hartree–Fock exchange potential built from Kohn–Sham orbitals is incorporated in our schemes. Numerical results are presented. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1427712]

INTRODUCTION AND DEFINITIONS

Recent advances^{1–10} in developing computational schemes featuring explicitly orbital-dependent exchange-correlation functionals and potentials within the Kohn–Sham (KS) formalism of density functional theory (DFT) (Refs. 11–13) require a general and consistent approach for solving Fredholm integral equations of the first kind with a real symmetric kernel.^{14,15} These types of integral equations appear within the optimized effective potential (OEP) method,^{1–10,16,17} which presents a computational framework for handling orbital-dependent functionals and potentials rather than just explicit density functionals and potentials. The OEP method provides a computational scheme for an exact exchange treatment within the KS theory. The inclusion of correlation effects requires certain approximations due to the fact that the correlation energy functional $E_c[n]$ is yet unknown in terms of the ground-state KS single determinant in contrast to the exchange energy functional $E_x[n]$, which is known explicitly in terms of the occupied KS orbitals.

The purpose of this work is to present a general basis-set formulation of the OEP method with particular emphasis on the exact exchange-only treatment. In this basis-set formulation, the OEP linear integral equation is solved by means of the projection method.¹⁵ Different choices for projection basis sets built from atomic orbital (AO) basis sets are discussed, and numerical results are presented. An important exact condition,^{1,9,18,19} usually invoked to test the accuracy of numerical results, is incorporated in our computational schemes. It is demonstrated numerically that when sufficiently large projection basis sets are used, the ground-state energies obtained from the basis-set formulations of the Hartree–Fock (HF) and of the OEP exchange-only methods are very close.

The utilization of the explicit form of the exchange energy functional $E_x[n]$ given by

$$E_x[n] = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{i,j=1}^{N_\sigma} \int \int \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \times d\mathbf{r}' d\mathbf{r}, \quad (1)$$

within the KS theory leads to a Fredholm linear equation for the σ -spin component of the corresponding local exchange potential $v_{x\sigma}(\mathbf{r}) (= \delta E_x[n] / \delta n_\sigma)$, where N_σ is the number of electrons of spin σ . The integral equation reads

$$\int X_{s\sigma}(\mathbf{r}, \mathbf{r}') v_{x\sigma}(\mathbf{r}') d\mathbf{r}' = \sum_{i_\sigma}^{\text{occ}_\sigma} \sum_{a_\sigma}^{\text{unocc}_\sigma} \left[\langle \varphi_{a\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{i\sigma} \rangle \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \right], \quad (2)$$

where $v_{x\sigma}^{\text{NL}}(\mathbf{r})$ is the nonlocal HF-type exchange potential built from KS orbitals. In Eq. (2), the kernel of the integral equation can be readily identified^{1,4,5,9} as the static KS linear response function $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$, which is known in terms of KS orbitals and energies, i.e.,

$$X_{s\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{i_\sigma}^{\text{occ}_\sigma} \sum_{a_\sigma}^{\text{unocc}_\sigma} \frac{\varphi_{a\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \quad (3)$$

Here, the orbitals $\varphi_{p\sigma}(\mathbf{r})$, and the energies $\epsilon_{p\sigma}$, are obtained by solving the one-particle KS equations given by

$$\left\{ -\frac{1}{2} \nabla^2 + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r}) + v_o(\mathbf{r}) \right\} \varphi_{p\sigma}(\mathbf{r}) = \epsilon_{p\sigma} \varphi_{p\sigma}(\mathbf{r}), \quad (4)$$

where $v_o(\mathbf{r})$ is the external spin-independent potential for the system of interest, and $n(\mathbf{r})$ is the total ground-state electron density, i.e., $n(\mathbf{r}) = \sum_{\sigma=\alpha,\beta} n_\sigma(\mathbf{r})$, which is uniquely associated with $v_o(\mathbf{r})$ by virtue of the Hohenberg–Kohn theorem.^{20,21} Pure state v -representability is assumed throughout our work.²² The exchange potential $v_{x\sigma}(\mathbf{r})$ is the solution to integral Eq. (2), and $v_{c\sigma}(\mathbf{r})$ is the correlation potential defined formally as the functional derivative of

$E_c[n]$, i.e., $v_{c\sigma}(\mathbf{r}) = \delta E_c[n] / \delta n_\sigma(\mathbf{r})$. The spin density $n_\sigma(\mathbf{r})$ is obtained from the N_σ lowest energy solutions to Eq. (4) through $n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2$.

Throughout our consideration we shall neglect the correlation effects, and focus our attention on the exchange-only formalism. In other words, we shall assume that $E_c[n] = 0$, and $v_{c\sigma}(\mathbf{r}) = 0$. When this assumption is made, $E_x[n]$ is not the exact exchange energy for the system of interest as defined in the KS theory since Eq. (4) with $v_{c\sigma}(\mathbf{r}) = 0$ does not lead to the exact ground-state spin densities $n_\sigma(\mathbf{r})$. This approximate KS method, known as the OEP exchange-only, utilizes the exact orbital dependent form of $E_x[n]$, Eq. (1), but with orbitals which are solutions to Eq. (4) with $v_{c\sigma}(\mathbf{r}) = 0$.

Formula (2) is a Fredholm linear integral equation of the first kind with a real symmetric kernel. We also note that the kernel of Eq. (2) is nondegenerate,¹⁴ when the infinite summation in Eq. (3) is carried out. In other words, $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$ cannot be exactly represented as a finite sum of products of functions of \mathbf{r} and \mathbf{r}' , i.e., $X_{s\sigma}(\mathbf{r}, \mathbf{r}') \neq \sum_{i=1}^M S_i(\mathbf{r}) R_i(\mathbf{r}')$. The nondegeneracy of $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$ is a direct consequence of the fact that the space built from all products of occupied and unoccupied KS orbitals is complete minus a constant function¹⁰ in the limit of an infinite number of orbitals. For such a nondegenerate kernel, the following eigenvalue equation:

$$\Theta_{m\sigma}(\mathbf{r}) = \eta_{m\sigma} \int X_{s\sigma}(\mathbf{r}, \mathbf{r}') \Theta_{m\sigma}(\mathbf{r}') d\mathbf{r}', \quad (5)$$

generates a complete set of eigenfunctions, $\text{span}\{\Theta_{m\sigma}\}$, with real eigenvalues $\eta_{m\sigma}$.¹⁴ Further, due to the specific form of the kernel, the zero eigenvalues are inevitably associated with constant eigenfunctions.^{4,10} As a result, by restricting the domain of the eigenfunctions $\Theta_{m\sigma}(\mathbf{r})$ in Eq. (5) to non-constant ones, we can assume that all $\eta_{m\sigma}$ are nonzero. In terms of the orthonormal eigenfunctions, the known function on the right-hand side of Eq. (2) can be expressed as

$$\begin{aligned} & \sum_{i\sigma}^{\text{occ}_\sigma} \sum_{a\sigma}^{\text{unocc}_\sigma} \langle \varphi_{a\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{i\sigma} \rangle \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r})}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \\ & = \sum_{m=1}^{\infty} A_{m\sigma} \Theta_{m\sigma}(\mathbf{r}). \end{aligned} \quad (6)$$

Note that the expansion is exact even with the restriction imposed upon the domain of eigenfunctions $\Theta_{m\sigma}(\mathbf{r})$. If the unknown $v_{x\sigma}(\mathbf{r})$ is expanded in the complete orthonormal set of eigenfunctions of $X_{s\sigma}(\mathbf{r}, \mathbf{r}')$, $\text{span}\{\Theta_{m\sigma}\}$, each of the unknown coefficients $C_{m\sigma}$ in the representation of $v_{x\sigma}(\mathbf{r})$,

$$v_{x\sigma}(\mathbf{r}) = \sum_{m=1}^{\infty} C_{m\sigma} \Theta_{m\sigma}(\mathbf{r}), \quad (7)$$

is given by

$$C_{m\sigma} = \eta_{m\sigma} \sum_{i\sigma}^{\text{occ}_\sigma} \sum_{a\sigma}^{\text{unocc}_\sigma} \langle \varphi_{a\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{i\sigma} \rangle \frac{\langle \varphi_{i\sigma} | \Theta_{m\sigma} | \varphi_{a\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.} \quad (8)$$

Since $\eta_{m\sigma}$ is not zero, unless $\Theta_{m\sigma}(\mathbf{r}) = \text{const.}$, it follows that the solution to Eq. (2) is determined within an additive constant. The unknown constant is further determined by the requirement that the unknown potential $v_{x\sigma}(\mathbf{r})$ must vanish at the boundaries, i.e., $|\mathbf{r}| \rightarrow \infty$. This finding is consistent with previous work by Görling and Levy,⁴ Grabo *et al.*,^{9,18} and Hirata *et al.*,¹⁰ showing that the solution of the OEP equations is unique given the boundary condition that $v_{x\sigma}(\mathbf{r})$ vanishes as $|\mathbf{r}| \rightarrow \infty$.

FINITE-BASIS-SET OEP METHOD

The practical implementation of any OEP method hinges on the efficient approach for solving integral Eq. (2). The numerical grid-based realization of the OEP method presents limitations in its applicability to many-electron molecular systems without high symmetry. With this in mind, we present convenient finite-basis-set algorithms directed toward solving Eq. (2).

In the typical basis set realization of the KS theory, the one-particle orbitals are expanded in an AO basis set of finite size. As a result, the kernel of integral Eq. (2) is approximated with a finite number of products of occupied and unoccupied KS orbitals, and thus becomes degenerate.¹⁴ The fundamental domain of the degenerate kernel is restricted to functions, which are not orthogonal to each pair of occupied and unoccupied orbitals, i.e., $\varphi_{i\sigma}(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r})$. In this case, the kernel is highly singular since the zero eigenvalues are associated not only with constant functions, but also with all functions orthogonal to each pair $\varphi_{i\sigma}(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r})$. Consequently, integral Eq. (2), when expressed in a finite basis set, cannot determine the potential uniquely within an additive constant.

One of the methods for solving integral equations with degenerate kernels is the projection method.¹⁵ The projection of integral Eq. (2) onto a finite real orthonormal M -dimensional space $\text{span}\{\xi_m\}$ yields a set of linear equations given in a matrix form by

$$\tilde{\mathbf{X}}_{s\sigma} \tilde{\mathbf{C}}_\sigma = \tilde{\mathbf{A}}_\sigma, \quad (9)$$

where the projection of $X_{s\sigma}(\mathbf{r}', \mathbf{r})$ is described by a real symmetric matrix whose elements are

$$(\tilde{X}_{s\sigma})_{ml} = \int \xi_m(\mathbf{r}') X_{s\sigma}(\mathbf{r}', \mathbf{r}) \xi_l(\mathbf{r}) d\mathbf{r}' d\mathbf{r}. \quad (10)$$

The elements of the vector-column $\tilde{\mathbf{A}}_\sigma$ are given by

$$(\tilde{A}_\sigma)_m = \sum_{i\sigma}^{\text{occ}_\sigma} \sum_{a\sigma}^{\text{unocc}_\sigma} \langle \varphi_{a\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{i\sigma} \rangle \frac{\langle \varphi_{i\sigma} | \xi_m | \varphi_{a\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} + \text{c.c.}, \quad (11)$$

and the unknown $v_{x\sigma}(\mathbf{r})$ is represented by

$$v_{x\sigma}(\mathbf{r}) = \sum_{m=1}^M (\tilde{C}_\sigma)_m \xi_m(\mathbf{r}), \quad (12)$$

where $(\tilde{C}_\sigma)_m$ is the m th element of the unknown $\tilde{\mathbf{C}}_\sigma$.

The matrix Eq. (9) can be solved by obtaining the inverse of $\tilde{\mathbf{X}}_{s\sigma}$, or the pseudoinverse of $\tilde{\mathbf{X}}_{s\sigma}$ when $\tilde{\mathbf{X}}_{s\sigma}$ is singular. The pseudoinverse of $\tilde{\mathbf{X}}_{s\sigma}$ is obtained by singular value decomposition, i.e., for an eigenvalue of $\tilde{\mathbf{X}}_{s\sigma}$, whose

absolute value is less than some positive threshold, the inverse is set to zero. The solution of Eq. (9) is given by

$$\tilde{\mathbf{C}}_{\sigma} = \text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1} \tilde{\mathbf{A}}_{\sigma}, \quad (13)$$

where $\text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1}$ is the pseudoinverse (PI) of $\tilde{\mathbf{X}}_{s\sigma}$.

In order to demonstrate certain connections between the integral equation consideration outlined in the previous section and our finite-basis-set implementation, we note that the matrix $\text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1}$ is obtained by the following two-step procedure. In the first step, the real symmetric nonpositive matrix $\tilde{\mathbf{X}}_{s\sigma}$ is diagonalized through an orthogonal transformation \mathbf{U}_{σ} , i.e., $\tilde{\mathbf{X}}_{s\sigma} = \mathbf{U}_{\sigma} \mathbf{\Omega}_{\sigma} \mathbf{U}_{\sigma}^{-1}$, where $\mathbf{\Omega}_{\sigma}$ is a diagonal matrix that contains the nonpositive eigenvalues and \mathbf{U}_{σ} contains the eigenvectors. This step is analogous to solving Eq. (5) for $\Theta_{m\sigma}(\mathbf{r})$, and η_m . In the second step, $\text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1} = \mathbf{U}_{\sigma} \text{IP} \mathbf{\Omega}_{\sigma}^{-1} \mathbf{U}_{\sigma}^{-1}$. Each element of the diagonal $\text{IP} \mathbf{\Omega}_{\sigma}^{-1}$ is the reciprocal of the corresponding eigenvalue when the eigenvalue is smaller than or equal to a prespecified negative threshold, and is set to zero if the eigenvalue is greater than the threshold. This replacement with zero is similar to excluding the eigenfunctions with zero eigenvalues, i.e., constant functions, from the representation given by Eq. (7).

Recently, a finite-basis-set formulation and implementation of the OEP method for atoms and molecules have been reported.^{7,8,10} Two possible projection basis sets for solving the OEP equations have been discussed: orthonormal Gaussian basis sets^{7,10} and biorthogonal Gaussian basis sets with explicit $1/r$ asymptotic term.^{8,10} It shall be shown that the orthonormal-basis-set formulation is very similar to the biorthogonal approach, when a specific choice for the projection basis set is made. Different choices for the projection basis set shall be discussed and numerical results shall be presented. A specific exact condition will be considered and its incorporation in our finite-basis-set OEP schemes, denoted by EXX, will be presented.

DIFFERENT CHOICES FOR PROJECTION BASIS SETS AND EXACT CONDITIONS

In the following, we consider only real basis sets, and all equations in the rest of our paper reflect this fact. We also make use of the following exact condition^{1,9,18,19} to assess the quality of $v_{x\sigma}(\mathbf{r})$ obtained from EXX calculations, i.e.,

$$\langle \varphi_{N\sigma} | v_{x\sigma} | \varphi_{N\sigma} \rangle = \langle \varphi_{N\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{N\sigma} \rangle, \quad (14)$$

where $\varphi_{N\sigma}(\mathbf{r})$ is the highest occupied molecular orbital (HOMO) of spin σ . Constraint (14), named in this work the HOMO condition, is closely related to the asymptotic decay of $v_{x\sigma}(\mathbf{r})$. When finite Gaussian basis sets are used, $v_{x\sigma}(\mathbf{r})$ may not satisfy Eq. (14) due to the unphysical exponential decay of the potentials as opposed to the correct $-1/|\mathbf{r}|$ decay despite that $v_{x\sigma}(\mathbf{r})$ correctly vanishes at infinity by construction since it is expanded in a basis set whose functions vanish at infinity. Alternatively, when the biorthogonal projection basis sets are used, $v_{x\sigma}(\mathbf{r})$ vanishes either as a constant/ $|\mathbf{r}|$,¹⁰ or as $-1/|\mathbf{r}|$ when this asymptotic decay is enforced via a Lagrange multiplier.⁸ Even though condition (14) is intimately connected with the correct asymptotic decay of $v_{x\sigma}(\mathbf{r})$, our numerical results suggest that the ap-

proach advanced by Görling⁸ does not lead to the direct obedience of the HOMO condition. The ground-state energies obtained from Görling's approach are generally higher than the ones obtained via the implementations presented in this work. As a result, we shall only consider different computational schemes in which Eq. (14) is exactly satisfied without explicitly enforcing $-1/|\mathbf{r}|$ decay of $v_{x\sigma}(\mathbf{r})$.

To arrive at schemes in which the HOMO condition is attained, we consider two general realizations. In the first one, a constant is added to $v_{x\sigma}(\mathbf{r})$ in such a way that Eq. (14) holds. The orbital energies are shifted by this constant, but the final form of the KS orbitals is not effected by the additive constant. As a result, the ground-state energies are unchanged. This constant is viewed as an approximation to the projection of $v_{x\sigma}(\mathbf{r})$ onto the function space orthogonal to the eigenfunctions of a finite-basis-set representation, and it must vanish in the limit of an infinitely large projection basis set.

In order to alleviate the undesired asymptotic behavior of $v_{x\sigma}(\mathbf{r})$ when a constant is added to the potential to satisfy Eq. (14), we incorporate the HOMO condition via a Lagrange multiplier technique. According to this approach, Eq. (9) is modified to include Eq. (14), and takes the following form:

$$\tilde{\mathbf{X}}_{s\sigma} \tilde{\mathbf{C}}_{\sigma} = \tilde{\mathbf{A}}_{\sigma} + \nu_{\sigma} \mathbf{L}_{\sigma}, \quad (15)$$

where \mathbf{L}_{σ} is a vector with elements $(L_{\sigma})_m = \langle \varphi_{N\sigma} | \xi_m | \varphi_{N\sigma} \rangle$, and the Lagrange multiplier ν_{σ} is defined as

$$\nu_{\sigma} = (\langle \varphi_{N\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{N\sigma} \rangle - \mathbf{L}_{\sigma}^T \text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1} \tilde{\mathbf{A}}_{\sigma}) / (\mathbf{L}_{\sigma}^T \text{PI} \tilde{\mathbf{X}}_{s\sigma}^{-1} \mathbf{L}_{\sigma}). \quad (16)$$

If the expansion coefficients of the unknown $v_{x\sigma}(\mathbf{r})$ are determined through Eq. (15), then $v_{x\sigma}(\mathbf{r})$ vanishes at infinity and constraint (14) is satisfied. We also note that Eq. (15) provides a general formulation for determining $v_{x\sigma}(\mathbf{r})$, subject to specific constraints. When a specific choice for the projection basis set is made and the exact asymptotic decay of $v_{x\sigma}(\mathbf{r})$ is ensured by means of a Lagrange multiplier technique, Eq. (15) leads to similar matrix elements as those defined by Eqs. (5) and (6) in Ref. 8.

Next, we turn our attention to the choice of projection basis sets that shall be used for the practical implementation of Eqs. (9) and (15). The projection basis set has to be carefully chosen. It has to not only adequately represent any product of $\varphi_i(\mathbf{r})$ and $\varphi_a(\mathbf{r})$ formed from combinations of occupied and unoccupied KS orbitals in $X_{s\sigma}(\mathbf{r}', \mathbf{r})$, but also provide functions with the correct asymptotic behavior needed for expansion of the exchange potential. In order to keep our method self-contained, we consider only projection basis sets built from the AO basis set used to represent the KS orbitals. We choose four different projection basis sets for our calculations. These four options are:

I. Direct use of the AO basis set, i.e., $\text{span}\{\xi_k\} = \text{span}\{\chi_p\}$, where χ_p represents an AO basis function. The implementation of EXX with this projection basis set will be denoted by EXX- χ .

II. Construction of a function space built from products of all possible pairs of the AO basis functions. We denote this computational scheme by EXX- χ^2 .

III. Asymptotically correct projection basis set with the same dimension as the original AO basis set, built from

$$\bar{\xi}_m(\mathbf{r}) = \int \frac{\chi_m^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (17)$$

IV. Asymptotically correct product projection basis set built from

$$\bar{\xi}_m(\mathbf{r}) = \int \frac{\chi_p(\mathbf{r}')\chi_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (18)$$

In Eqs. (17) and (18), the bar sign indicates that the projection basis functions are not orthonormalized. The orthogonalization procedure shall be discussed in the next section. The computational schemes based on choices (III) and (IV) will be denoted by EXX- χ/r and EXX- χ^2/r , respectively. We note that when these asymptotically-correct orthonormal projection basis sets are used in Eqs. (10) and (11), one obtains a matrix formulation very similar to the one within biorthogonal basis sets. Further, if one imposes the constraint that $v_{x\sigma}(\mathbf{r})$ approaches zero at infinity as $-1/|\mathbf{r}|$ by means of Eq. (15) with the appropriate choices for \mathbf{L}_σ and v_σ , one obtains the analog of the approach introduced by Görling.⁸

IMPLEMENTATION AND NUMERICAL RESULTS

The actual implementation of the computational schemes based on Eq. (9) or Eq. (15) with the projection basis sets corresponding to choices I and II is straightforward within any standard HF program. The only new elements needed for these schemes are three and four-index overlap integrals which can be computed analytically. Once these integrals are available, Eq. (9) or Eq. (15) is solved by finding the pseudo-inverse of $\tilde{\mathbf{X}}_{x\sigma}$, as outlined in Sec. II.

The implementation of choices (III) and (IV) is more complex since it requires an orthonormal projection basis functions which are given by Eqs. (17) and (18). For the orthogonalization of the projection space, one needs the following general type of integrals:

$$\langle \bar{\xi}_m | \bar{\xi}_k \rangle = \int \int \int \frac{\chi_p(\mathbf{r}')\chi_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \frac{\chi_s(\mathbf{r}'')\chi_t(\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}. \quad (19)$$

Since the above integrals are not readily available, we re-express Eq. (19) by means of the resolution of identity, i.e., $I = \sum_{l=1}^{\infty} |\zeta_l\rangle\langle\zeta_l|$ as

$$\begin{aligned} & \sum_{l=1}^{\infty} \langle \bar{\xi}_m | \zeta_l \rangle \langle \zeta_l | \bar{\xi}_k \rangle \\ &= \sum_{l=1}^{\infty} \int \int \frac{\chi_p(\mathbf{r}')\chi_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \zeta_l(\mathbf{r}) d\mathbf{r}' d\mathbf{r} \\ & \quad \times \int \int \zeta_l(\mathbf{r}) \frac{\chi_s(\mathbf{r}'')\chi_t(\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|} d\mathbf{r}'' d\mathbf{r}. \quad (20) \end{aligned}$$

In our finite basis implementation, we approximate the infinite summation in the representation of the identity by a finite sum of orthonormal auxiliary basis functions formed from the AO basis set. When choice (III) for the projection

basis set is made, the auxiliary basis set is given by $\text{span}\{\chi_p\chi_p\}$. This choice features projection and auxiliary basis sets with dimensionality which in turn is equal to the dimensionality of the AO basis set. When choice (IV) is made, the auxiliary basis set used for the resolution of the identity is given by $\text{span}\{\chi_p\chi_q\}$. The dimensionality of the projection basis set is equal to the number of unique combinations between two AO basis functions. The advantage of the auxiliary basis sets used with choices (III) and (IV), is that all integrals are analytically available. The only new element is the calculation of four-index overlap integrals. However, these four-index overlap integrals are the same as the ones needed for implementation of choice (II) for the projection basis set. Hence, the realization of choices (III) and (IV) does not require any substantial extra programming effort once choice (II) is implemented.

We also note that our implementation of choices (III) and (IV) becomes very similar to the biorthogonal projection-basis-set method.^{8,10} In both formulations, the same types of two-center four-index electron-electron integrals are required. In addition, the exchange potential $v_{x\sigma}(\mathbf{r})$ in both approaches takes the following general expansion:

$$v_{x\sigma}(\mathbf{r}) = \sum_{m=1}^M (D_\sigma)_m \int \frac{f_m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (21)$$

According to the present work, $f_m(\mathbf{r}) = \chi_p(\mathbf{r})\chi_p(\mathbf{r})$ [choice (III)] or $f_m(\mathbf{r}) = \chi_p(\mathbf{r})\chi_q(\mathbf{r})$ [choice (IV)], and $(D_\sigma)_m$ is the m th element of the vector-column \mathbf{D}_σ given by $\mathbf{D}_\sigma = \mathbf{W}^{-1}\mathbf{C}_\sigma$, where \mathbf{W}^{-1} is the inverse of the transformation matrix \mathbf{W} , which orthonormalizes the basis functions given by Eqs. (17) or (18). The form of $f_m(\mathbf{r})$ in the biorthogonal projection basis set is effectively the same. The expansion coefficients $(D_\sigma)_m$ are similar and reflect the different normalization conditions of the basis functions in the biorthogonal and the orthonormal projection basis sets.

In Table I, we compare results for the Ar atom obtained from four different realizations of EXX denoted by EXX- χ , EXX- $\chi-L$, EXX- χ/r , and EXX- $\chi/r-L$ against numerical grid-based OEP results taken from Ref. 9. The suffix L indicates that constraint (14) is introduced via a Lagrange multiplier. When the suffix L is omitted, the HOMO condition is satisfied by adding a constant to the exchange potential, respectively to all orbital energies. The HF results from numerical grid-based and basis set schemes are also reported. The basis used in the calculations is the even-tempered Gaussian Partridge-3 basis set.²³ When the projection space built from AO functions is used without any constraint, EXX leads to a slightly lower ground-state energy than the one from numerical grid-based OEP. The agreement between the orbital energies is also excellent, supporting the viability of the approach based on adding a constant to $v_{x\sigma}(\mathbf{r})$. The significant negative shift can be attributed to the faster decay of $v_{x\sigma}(\mathbf{r})$, when represented as a linear combination of Gaussian functions, than the correct $-1/|\mathbf{r}|$.

The negative constant shift in $v_{x\sigma}(\mathbf{r})$ obtained from EXX- χ is substantially reduced by considering projection basis sets capable of capturing the correct asymptotic form of $v_{x\sigma}(\mathbf{r})$, namely choice (III), method EXX- χ/r . When this

TABLE I. Comparison of numerical HF and OEP calculations against HF and different EXX realizations for Ar atom in even-tempered Gaussian Partridge-3 basis set. All values in a.u.

Method Functions used for $v_{x\sigma}(\mathbf{r})^a$	HF ^b	OEP	EXX- χ (65)	EXX- χ - L (65)	EXX- χ / r (19)	EXX- χ / r - L (19)
Total energy	-526.8175	-526.8122	-526.8123	-526.8112	-526.7859	-526.7859
HOMO shift ^c			-0.208	-0.002		
1s	-118.6103(4)	-114.5424	-114.4514	-114.4521	-113.9914	-113.9881
2s	-12.3222(1)	-11.1534	-11.1539	-11.1552	-11.0004	-10.9981
2p	-9.5715	-8.7339	-8.7343	-8.7355	-8.6031	-8.6010
3s	-1.2774(3)	-1.0993	-1.0993	-1.0959	-1.1023	-1.1020
3p	-0.5910	-0.5908	-0.5908	-0.5876	-0.5943	-0.5939

^aIn parentheses, number of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$.

^bBasis set calculations. In parentheses are given the last figures corresponding to numerical grid-based calculations. Numerical results for HF and OEP from Ref. 9.

^c $\langle \varphi_{N\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{N\sigma} \rangle - \langle \varphi_{N\sigma} | v_{x\sigma} | \varphi_{N\sigma} \rangle$.

computational approach is tested, the ground-state energy is higher than the one obtained by means of EXX- χ . This result is not particularly surprising given the fact that $v_{x\sigma}(\mathbf{r})$ is represented with only 23 projection basis functions. The inclusion of the HOMO condition through Eq. (15) leads to slightly higher ground-state energies than the corresponding schemes featuring constant shifts in $v_{x\sigma}(\mathbf{r})$.

We do not present results corresponding to choices (II) and (IV) since the basis sets formed from products of two AO basis functions contain very large numbers of linear dependencies. The AO basis set used in the calculations is nearly complete with respect to s - and p -functions. We have also implemented the condition on the correct asymptotic decay of $v_{x\sigma}(\mathbf{r})$ as proposed by Görling within choices (III) and (IV) for projection basis sets. In all calculations this scheme leads to higher ground-state energies when compared to any other realization of EXX. In addition, we have observed slower self-consistent field convergence, and condition (14) is not well satisfied in our implementation for the chosen AO basis sets. We do not present further results obtained by means of that scheme, even though the exchange potential $v_{x\sigma}(\mathbf{r})$ has the correct asymptotic behavior and decays as $-1/|\mathbf{r}|$. In our choices (III) and (IV) for projection basis sets, $v_{x\sigma}(\mathbf{r})$ decays as a constant/ $|\mathbf{r}|$ rather than $-1/|\mathbf{r}|$. However, we choose not to enforce the correct value of -1 , but rather ensure that Eq. (14) is satisfied.

In Tables II–IV, we present results from different real-

izations of EXX in uncontracted ccPVTZ basis set.²⁴ When the projection space of type III is used, the shift constant is less negative for all three molecules, and for carbon monoxide and nitrogen it becomes even positive suggesting that $v_{x\sigma}(\mathbf{r})$ is too deep and/or it vanishes slower than $-1/|\mathbf{r}|$. It is worth mentioning that Partridge-3 and ccPVTZ basis sets do not contain very diffuse functions. As a result, these basis sets provide a better description of the occupied and lower lying states. The total ground-state and orbital energies from all EXX calculations are very close to one another. This suggests that the particular choice of projection basis and how to incorporate constraint (14) is of lesser importance than the size of the AO basis set, which in our implementations, determines the size of the projection space. As the AO basis set becomes larger and better balanced, it is expected that any deviations from the equality in Eq. (14) would be smaller. The choice of projection basis set I has a certain advantage, namely, this basis set is already orthonormal, so that it does not contain linear dependencies. Choice (III) effectively corresponds to a smaller projection basis set for the considered systems since there is a significant number of linear dependencies.

In Tables V–VII, we report results from all four different choices for the projection basis sets with or without including the HOMO condition via a Lagrange multiplier. We used Sadlej-type basis sets,²⁵ which are most commonly used in calculations for describing excited-state properties. These ba-

TABLE II. HF and EXX results for H₂O in an uncontracted ccPVTZ basis set.^a

Method Functions used for $v_{x\sigma}(\mathbf{r})^b$	HF	EXX- χ (81)	EXX- χ - L (81)	EXX- χ / r (61)	EXX- χ / r - L (61)
Total energy (a.u.)	-76.057 75	-76.055 45	-76.055 34	-76.055 32	-76.055 29
HOMO shift (a.u.)		-0.322	0.000	-0.231	0.000
$E_{\text{HOMO}-4}$ (eV)	-559.38	-517.06	-517.01	-516.78	-516.67
$E_{\text{HOMO}-3}$ (eV)	-36.64	-31.96	-31.96	-31.94	-31.93
$E_{\text{HOMO}-2}$ (eV)	-19.29	-19.28	-19.26	-19.21	-19.19
$E_{\text{HOMO}-1}$ (eV)	-15.77	-15.74	-15.74	-15.70	-15.69
E_{HOMO} (eV) ^c	-13.76	-13.71	-13.71	-13.73	-13.73
$E_{\text{HOMO}+1}$ (eV)	3.58	-5.35	-4.84	-5.51	-5.22
$E_{\text{HOMO}+2}$ (eV)	5.43	-3.31	-2.42	-3.30	-2.88

^aEquilibrium geometry: $R_{\text{OH}}=0.959 \text{ \AA}$, $A_{\text{HOH}}=103.9$.

^bIn parentheses, number of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$.

^cExperimental ionization potential, 12.62 (eV).

TABLE III. HF and EXX results for N₂ in an uncontracted ccPVTZ basis set.^a

Method Functions used for $v_{x\sigma}(\mathbf{r})^b$	HF	EXX- χ (94)	EXX- χ -L (94)	EXX- χ /r (65)	EXX- χ /r-L (65)
Total energy (a.u.)	-108.98468	-108.97948	-108.97926	-108.97941	-108.97939
HOMO shift (a.u.)		-0.392	0.000	0.178	0.000
$E_{\text{HOMO}-5}$ (eV)	-426.75	-390.65	-390.46	-390.16	-390.17
$E_{\text{HOMO}-4}$ (eV)	-426.65	-390.62	-390.43	-390.12	-390.13
$E_{\text{HOMO}-3}$ (eV)	-40.01	-35.58	-35.56	-35.62	-35.62
$E_{\text{HOMO}-2}$ (eV)	-21.18	-20.23	-20.21	-20.17	-20.17
$E_{\text{HOMO}-1}$ (eV)	-17.23	-18.12	-18.08	-18.00	-18.01
E_{HOMO} (eV)	-16.67	-17.16	-17.15	-17.19	-17.19
$E_{\text{HOMO}+1}$ (eV)	4.35	-7.91	-7.83	-7.85	-7.82
$E_{\text{HOMO}+2}$ (eV)	10.77	-0.26	-0.13	-0.19	-0.18

^aEquilibrium geometry, $R_{\text{NN}}=1.098 \text{ \AA}$.^bIn parentheses: number of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$.^cExperimental ionization potential: 15.58 (eV). HF approximation does not correctly predict the symmetry of the highest occupied state.

sis sets contain very diffuse functions. As a result, the correct asymptotic decay of $v_{x\sigma}(\mathbf{r})$ is essential for capturing the long-range shape of the KS orbitals built from these basis sets. It is interesting to note that when choice (II) is made, the ground-state energies from HF and EXX calculations are extremely close. Effectively, this choice corresponds to the *largest* projection space needed to describe the kernel of the OEP integral equation given the choice for AO basis set. This follows from the fact that each pair of $\varphi_i(\mathbf{r})$ and $\varphi_a(\mathbf{r})$ is actually a linear combination of products of two AO basis functions $\chi_p(\mathbf{r})\chi_q(\mathbf{r})$. However, our numerical results should not be used to infer that EXX and HF ground-states are identical. The HF energy is lower than the energy obtained from the OEP method as numerical results^{1,2,7-9} and very recent derivations²⁶ indicate. For two-electron diamagnetic systems, the HF and OEP ground-state energies are equal. We also note that, in general, the numerical grid-based ground-state energies are lower than the finite-basis-set ones, and it is possible that the numerical grid-based OEP ground-state energies are lower than certain finite-basis-set HF results.

We also present the number of functions used to expand $v_{x\sigma}(\mathbf{r})$. As the number of functions used in the representation of $v_{x\sigma}(\mathbf{r})$ within choices (I) and (II), or (III) and (IV),

becomes greater, the absolute value of the difference $\langle \varphi_{N\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{N\sigma} \rangle - \langle \varphi_{N\sigma} | v_{x\sigma} | \varphi_{N\sigma} \rangle$, in general, becomes smaller. The satisfaction of Eq. (14) is better when implementations (III) and (IV) are considered, namely, projection basis sets capable of describing the correct long range decay of $v_{x\sigma}(\mathbf{r})$. However, selecting a finite projection basis set that emphasizes the representation of the long range behavior is not enough since the projection basis set must describe well the product space built from all pairs $\varphi_{i\sigma}(\mathbf{r})\varphi_{a\sigma}(\mathbf{r})$. In other words, well-balanced projection basis sets are needed to minimize the magnitude of $\langle \varphi_{N\sigma} | v_{x\sigma}^{\text{NL}} | \varphi_{N\sigma} \rangle - \langle \varphi_{N\sigma} | v_{x\sigma} | \varphi_{N\sigma} \rangle$. Note the different signs of the shift constants when choices (I) and (II) are compared against (III) and (IV). This indicates that different projection basis sets capture different features of $v_{x\sigma}(\mathbf{r})$, and that the constant shift has its origin in the incompleteness of the projection basis sets. It should be stressed though that a complete projection basis set does not guarantee arriving at the exact $v_{x\sigma}(\mathbf{r})$ unless the AO basis is also complete.

We also note that when choices (I) and (III) with the Lagrange multiplier approach are compared, the ground-state energies corresponding to (III) are lower than the ones corresponding to (I). These findings ascertain the intimate con-

TABLE IV. HF and EXX results for CO molecule in an uncontracted ccPVTZ basis set.^a

Method Functions used for $v_{x\sigma}(\mathbf{r})^b$	HF	EXX- χ (94)	EXX- χ -L (94)	EXX- χ /r (63)	EXX- χ /r-L (63)
Total energy (a.u.)	-112.78160	-112.77652	-112.77643	-112.77628	-112.77615
HOMO shift (a.u.)		-0.234	0.000	0.575	0.000
$E_{\text{HOMO}-5}$ (eV)	-562.34	-519.63	-519.61	-519.43	-519.44
$E_{\text{HOMO}-4}$ (eV)	-309.11	-279.17	-278.98	-278.40	-278.62
$E_{\text{HOMO}-3}$ (eV)	-41.41	-36.23	-36.22	-36.27	-36.30
$E_{\text{HOMO}-2}$ (eV)	-21.88	-20.57	-20.57	-20.61	-20.64
$E_{\text{HOMO}-1}$ (eV)	-17.4	-17.99	-17.96	-17.94	-17.96
E_{HOMO} (eV) ^c	-15.07	-15.03	-15.02	-15.04	-15.04
$E_{\text{HOMO}+1}$ (eV)	3.72	-7.23	-7.19	-7.22	-7.34
$E_{\text{HOMO}+2}$ (eV)	7.02	-2.19	-1.82	-1.88	-2.13

^aEquilibrium geometry, $R_{\text{CO}}=1.128 \text{ \AA}$.^bIn parentheses, number of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$.^cExperimental ionization potential, 14.01 (eV).

TABLE V. HF and EXX results for H₂O in the Sadlej basis set.^a

Method	Total energy (a.u.)	EHOMO (eV)	Bound unoccupied states	HOMO shift (a.u.)	Functions used for $v_{x\sigma}(\mathbf{r})^b$
HF	-76.054 39	-13.87	0	0.000	
EXX- χ	-76.053 22	-13.98	8	-0.277	43(44)
EXX- χ -L	-76.052 70	-13.81	2	0.000	43(44)
EXX- χ^2	-76.054 38	-13.87	7	-0.122	154(280)
EXX- χ^2 -L	-76.054 13	-13.85	4	0.000	153(280)
EXX- χ/r	-76.053 19	-13.87	7	-0.231	40(41)
EXX- χ/r -L	-76.053 08	-13.86	3	0.000	40(41)
EXX- χ^2/r	-76.054 16	-13.86	8	-0.097	136(171)
EXX- χ^2/r -L	-76.054 14	-13.86	6	0.000	136(171)

^aEquilibrium geometry: $R_{\text{OH}}=0.959 \text{ \AA}$, $A_{\text{HOH}}=103.9$.

^bNumber of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$. In parentheses: number of linearly independent projection basis functions. Total number of projection basis functions: χ -space: 44; χ^2 -space: 990.

^cExperimental ionization potential, 12.62 (eV).

nection between Eq. (14) and the long range decay of $v_{x\sigma}(\mathbf{r})$ as represented in the projection basis set.

CLOSING REMARKS

In the present paper, a general finite-basis-set formulation of the OEP method has been presented. The current formulation can be viewed as a generalization of previous work.^{7,8,10} Different computational schemes have been discussed. Our consideration of EXX within only one basis set has certain advantages especially for routine calculations over other work that requires a projection basis different from the AO basis set. For a given AO basis, we propose four different projection basis sets for solving the OEP integral equation. We choose to enforce the HOMO condition by means of adding a constant to the exchange potential, or by means of a Lagrangian multiplier technique.

Taking into account the main objective of the EXX calculations and the choice of AO basis set, we will summarize the possible use of our proposed schemes as follows. Projection basis sets (I) and (II) are expected to be used for calcu-

TABLE VI. HF and EXX results for the nitrogen molecule in the Sadlej basis set.^a

Method	Total energy (a.u.)	EHOMO (eV)	Bound unoccupied states	HOMO shift (a.u.)	Functions used for $v_{x\sigma}(\mathbf{r})^b$
HF	-108.970 27	-16.74 ^c	0	0.000	
EXX- χ	-108.967 23	-17.23	9	0.284	52(52)
EXX- χ -L	-108.966 95	-17.23	13	0.000	52(52)
EXX- χ^2	-108.970 17	-17.29	11	-0.215	201(365)
EXX- χ^2 -L	-108.969 93	-17.29	5	0.000	198(365)
EXX- χ/r	-108.967 59	-17.26	13	-0.304	42(47)
EXX- χ/r -L	-108.967 25	-17.25	5	0.000	42(47)
EXX- χ^2/r	-108.969 63	-17.30	10	-0.169	158(206)
EXX- χ^2/r -L	-108.969 59	-17.30	10	0.000	156(206)

^aEquilibrium geometry, $R_{\text{NN}}=1.098 \text{ \AA}$.

^bNumber of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$. In parentheses, number of linearly independent projection basis functions. Total number of projection basis functions: χ -space, 52; χ^2 -space, 1378.

^cExperimental ionization potential, 15.58 (eV). HF approximation does not correctly predict the symmetry of the highest occupied state.

TABLE VII. HF and EXX results for the CO molecule in the Sadlej basis set.^a

Method	Total energy (a.u.)	EHOMO (eV)	Bound unoccupied states	HOMO shift (a.u.)	Functions used for $v_{x\sigma}(\mathbf{r})^b$
HF	-112.771 65	-15.10	0	0.000	
EXX- χ	-112.768 30	-15.06	9	1.052	52(52)
EXX- χ -L	-112.768 03	-15.06	12	0.000	52(52)
EXX- χ^2	-112.771 64	-15.11	11	-0.278	225(352)
EXX- χ^2 -L	-112.771 60	-15.12	9	0.000	223(352)
EXX- χ/r	-112.768 17	-15.09	10	-0.172	40(45)
EXX- χ/r -L	-112.768 13	-15.08	5	0.000	40(45)
EXX- χ^2/r	-112.770 91	-15.11	12	-0.194	151(206)
EXX- χ^2/r -L	-112.770 88	-15.11	9	0.000	149(206)

^aEquilibrium geometry: $R_{\text{CO}}=1.128 \text{ \AA}$.

^bNumber of projection basis functions used in the representation of $v_{x\sigma}(\mathbf{r})$. In parentheses: number of linearly independent projection basis functions. Total number of projection basis functions: χ -space: 52; χ^2 -space: 1378.

^cExperimental ionization potential: 14.01 (eV).

lations targeting ground-state properties. When the main objective is excited-state properties obtained by means of the time-dependent KS formalism, one should make use of choices (III) and (IV) as they incorporate projection basis sets capable of capturing the long range behavior of $v_{x\sigma}(\mathbf{r})$. The proper asymptotic decay of $v_{x\sigma}(\mathbf{r})$ is particularly important for arriving at the correct unoccupied KS orbitals. We note that choices (II) and (IV) can be computationally very demanding in large basis sets due to the size of the formed projection basis.

The options of adding a constant to $v_{x\sigma}(\mathbf{r})$ to satisfy constraint (14) or building the HOMO condition via Eq. (15) for a given projection basis set, lead to similar results for the total ground-state and orbital energies. Of course, the ground-state energies obtained from Eq. (9) are always lower than the ones from Eq. (15) for the same projection basis set. The very good agreement between numerical OEP and EXX results coming from Eq. (9) in even-tempered Gaussian basis sets for atoms. Table I, and Ref. 7, suggests that adding a constant to $v_{x\sigma}(\mathbf{r})$ in order to satisfy equality (14) is a reasonable way to compensate for the incompleteness of the AO and projection basis sets.

ACKNOWLEDGMENTS

This work has been supported by the U.S. Air Force Office of Scientific Research under Grant No. F49620-98-0116.

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