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New developments in the model potential method: ScO molecule

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An extension of Huzinaga's model potential method is presented and applied to the study of the equilibrium geometry of the ground electronic state of ScO. In the extended model potential method (EMP) the exchange interaction between the outer core and valence shells are handled more efficiently than in the standard MP method; furthermore, the long range behavior of the model potential is now independent on the reduction of the valence basis set. Using the new method, agreement with all electron results can be achieved in the difficult case of ScO molecule within 0.01 Å in R_e, 20 cm^{-1} in ω_e, 0.1–0.2 eV in the binding energy, and an order of 10^{-3} a.u. in the valence orbital energies.

I. INTRODUCTION

Valence electrons play a decisive role in the formation of molecules, while core electrons constitute a rather constant potential for the motion of the valence electrons. Assuming that the frozen-core approximation is valid, a number of different pseudopotential methods have been proposed in recent years (see, e.g., Refs. 1 and 2) and good molecular results have been obtained using them. The ultimate goal of the pseudopotential methods is to represent the valence orbitals using truncated basis sets and to replace operators of the core–valence interactions by simpler, preferably one electron, analytical potentials. The computational time can then be significantly reduced in comparison with all-electron (AE) calculations.

The one-electron model potentials are usually optimized in atomic calculations in order to account for the basis set truncation effects and for the nonlocal core–valence exchange interactions. Then, they usually lead to good molecular results. However, some problems remain when strong outer-core valence exchange interactions exist. This is the case of atoms whose outermost core orbitals are close in energy and shape to valence orbitals.[2–4]

A typical example of the problems is the ScO molecule. This molecule turned out to be a difficult test case since many effective core potential methods completely failed to reproduce the AE bond distance.[3] The difficulties seem to stem mainly from the wrong long-range behavior of the potentials[5] resulting from the accommodation of the strong nonlocal outer-core valence exchange interactions in the atomic optimization.

These problems were largely solved in ScO by using a frozen-core approach[3,6] in which the interactions between outer core and valence shells were exactly treated; however, in this approach the computation time is necessarily increased. The results may also be improved by explicitly considering the outermost core electrons as additional valence electrons in the model potential treatment.[2] In this case a

soft core projection was needed and, even then, the results for ScO did not match the AE ones as closely as for other molecules.

In this paper, we present an extension of the Sakai–Huzinaga model potential method[7] that approximates the core-valence exchange interactions more accurately, and prevents the deterioration of the model potential tails upon the basis set reduction. The present model potential consists of inner and outer core terms. Two important features of the outer-core potentials are: (i) They are determined so as to reproduce very accurately the reference all-electron interactions between outer-core and valence shells in the atom. In particular, the nonlocal representation used now for the exchange interactions assures the exact calculation of the one-center exchange integrals. (ii) The outer-core potentials that describe the tails of the effective core potential, remain unchanged as the valence basis set is reduced. In fact, only the inner Coulomb and exchange potentials are consequently relaxed and optimized in order to take proper account of the truncation effects that are known to occur in the inner regions. The details of the EMP method are given in Sec. II.

In Sec. III, the atomic model potentials and basis sets are described. In Sec. IV, we present the results of the new method as applied to the calculation of the equilibrium geometry and the binding energy of the ground state of ScO at the SCF level, and compare them with the reference AE and with previous frozen core (FC) and model potential (MP) calculations.

The new method, applied to the demanding $1s2s2p3s3p$ core of the scandium atom, leads to a considerable improvement of the results. The discrepancy between the scandium–oxygen equilibrium distance obtained in the AE calculations and the value calculated with the local approximation of Sakai–Huzinaga is reduced by 70%; the value of the fundamental vibrational frequency is also improved. Furthermore, when the $3p$ orbitals of the scandium atom are promoted to the molecular valence shell, the new method reaches the FC limit. It appears that the better representation of the outer exchange potential, in cases like ScO where some core orbitals are not unambiguously core orbitals, can correct nearly completely the deficiencies of the earlier MP

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approach. A remarkable feature is that in all our calculations the theoretically recommended hard projection $(2\epsilon_k)$ is used.[8]

II. METHOD

The MP Hamiltonian for the N valence electrons of an atom may be written in atomic units as[2]

$$H(1,2,...N) = \sum_{i=1}^{N} h_i + \sum_{i>j}^{N} r_{ij}^{-1} . \tag{1}$$

The one electron term h_i can be decomposed further into

$$h_i = -\frac{1}{2}\Delta_i - \frac{Z - Z_{\mathrm{core}}}{r_i} + V_{mp}(i) + P_{mp}(i) . \tag{2}$$

In Eq. (2), the first two terms represent the kinetic energy and the attraction of the nucleus whose charge Z is completely shielded by the Z_{core} electrons. The projection term $P_{mp}(i)$ prevents the valence orbitals from collapsing onto the core space, and the effective core potential $V_{mp}(i)$ includes the core–valence Coulomb and exchange interactions,

$$V_{mp}(i) = V_c(i) + V_{\mathrm{ex}}(i) , \tag{3}$$

and

$$V_c(i) = -\frac{Z_{\mathrm{core}}}{r_i} + 2\sum_{c}^{\mathrm{core}} J_c(i) , \tag{4}$$

$$V_{\mathrm{ex}}(i) = -\sum_{c}^{\mathrm{core}} K_c(i) , \tag{5}$$

where $J_c(i)$ and $K_c(i)$ are the Coulomb and exchange operators, and c runs over all core orbitals. The operator $V_{mp}(i)$ can be divided into inner (I) and outer (O) core potentials as follows:

$$V_c(i) = V_c^I(i) + V_c^O(i) \tag{6}$$

and

$$V_{\mathrm{ex}}(i) = V_{\mathrm{ex}}^I(i) + V_{\mathrm{ex}}^O(i) .$$

If we take the scandium atom as an example, the inner core can be composed of $1s$, $2s$, and $2p$ orbitals, and $3s$, $3p$ orbitals can constitute the outer core part. The plot of the inner and outer Coulomb potentials of Sc (Fig. 1) shows that the inner core potential is localized close to the nucleus within the inner part of the valence orbitals. Only the outer core potential enters the outermost region of valence orbitals. Although this kind of analysis is straightforward for Coulomb potential only, similar conclusions are expected to hold for the exchange operator, if one considers the kernel of that operator.[9]

The idea of division of the core potential into inner and outer core is not new[3] and was explored in the frozen core approach. There are several advantages in using the inner–outer concept. First, we can replace the outer-core potentials by very accurate representations of the outer-core valence reference AE interactions in the atom (see below). These representations are kept fixed as the valence basis set is reduced. Second, we can safely replace the inner-core potentials by approximate model potentials that are optimized upon the reduction of the basis set, so as to take proper account of the truncation effects.
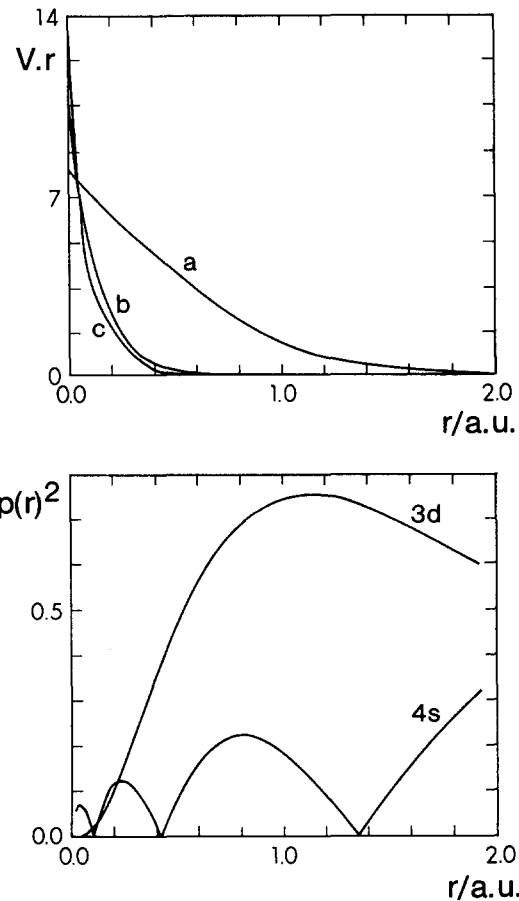

FIG. 1. The outer-core Coulomb potential (a) inner-core Coulomb potential (b) and inner-core Coulomb potential after optimization (c) are plotted in the upper figure. The square of the scandium $3d$ and $4s$ radial distributions are plotted below.

A. Outer core potentials

Provided that the core polarization effects are negligible (frozen-core approximation) we can approximate very accurately the outer-core Coulomb V_c^O and exchange,[9] V_{ex}^O, potentials as follows.

The local outer Coulomb potential is expressed as in Ref. 7:

$$V_c^O = \sum_{i=1}^{m} A_i r^{n_i} \exp\left(-\alpha_i r^2\right)/r , \tag{7}$$

where r is the radial coordinate and $\{A_i, \alpha_i\}$ are the parameters of the potential. Apart from the restriction

$$\Sigma_i A_i = Z_{\mathrm{core}}^O$$

imposed on the A_i's, the parameters $\{A_i, \alpha_i\}$ are unconstrained and are determined through a least-square fitting (LSF) to the reference AE outer Coulomb potential.

The nonlocal outer exchange potential is expanded in the form

$$V_{\mathrm{ex}}^O = \sum_{l} \sum_{m=-l}^{l} \sum_{a,b} |alm\rangle A\,(l;a,b)\langle alm| , \tag{8}$$

where the $\{|alm\rangle\}$ are products of primitive Gaussian-type functions (GTOs) and spherical harmonics. This form will yield the correct outer-core valence exchange integrals if all the valence primitives are contained in the $\{|alm\rangle\}$ set and

the elements $A (l;a,b)$ are given by

$$A = S^{-1}KS ,\qquad (9)$$

where

$$S_{ij} = \langle i|j\rangle, \quad K_{ij} = \langle i|K_c^O|j\rangle ,\qquad (10)$$

$|i\rangle$, $|j\rangle$ being any two functions of the set $\{|alm\rangle\}$.

Thus, for a chosen set $\{|alm\rangle\}$ (see next section) the evaluation of the overlap integrals and of the integrals of the reference AE outer exchange operator,

$$K_c^O = \sum_c^{\text{out}} K_c ,$$

leads through Eq. (9) to the parameters of the nonlocal form (8).

B. Inner core potentials

The inner core Coulomb potential is approximated by

$$V_c^I = \sum_i A_i r^{n_i} \exp(-\alpha_i r^2)/r .\qquad (11)$$

We use two kinds of approach for the inner core exchange potential (see Sec. III). One is the expansion of Eq. (8), and the other is as follows:

$$V_{\text{ex}}^I = \sum_i B_i r^{n_i-1} \exp(-\beta_i r^2) .\qquad (12)$$

The parameters of the potentials are respectively $\{A_i,\alpha_i\}$ and $\{B_i,\beta_i\}$. Initially, the set $\{A_i,\alpha_i\}$ is determined through a LSF using as the reference the AE inner core Coulomb potential, and the set $\{B_i,\beta_i\}$ is determined through a LSF with the reference AE inner core exchange potential calculated by means of the $X\alpha$ approach. It should be noted that this first step is unique in cases where the full valence basis set is not reduced. Then, as the valence basis set is reduced, the effects of the reduction are accomodated through the optimization of the sets $\{A_i,\alpha_i\}$ and $\{B_i,\beta_i\}$. The goal of the optimization is to restore the values of the orbital energies and the radial shapes of the valence orbitals. The pivotal quantity in the optimization procedure is

$$\Delta = \omega_1 \sum_v |\epsilon_v - \bar{\epsilon}_v|$$

$$+ \omega_2 \sum_v (P_v - \bar{P}_v)^2 + \omega_3 \sum_v \sum_c \langle v|c\rangle^2 ,\qquad (13)$$

where $\bar{\epsilon}$ and $\bar{P}$ are reference orbital energies and radial densities of the valence orbitals, and ω_i's are weighting factors. This expression is an extension of that used in Ref. 2 so as to introduce explicitly the core–valence orthogonality constraints which contribute to the reduction of the truncation errors.

The above procedure provides valence atomic solutions which are close to the reference ones at the cost of slight deformation of inner-core potential which occurs upon truncation of the basis set (see Sec. III). Since that deformation influences only the inner part of valence orbitals, its impact on molecular results is negligibly small (see Sec. IV).

The molecular model potential formalism used in this work is identical to that explained in Ref. 2 and therefore, will not be treated here.

III. MODEL POTENTIALS AND BASIS SETS

The explicit analytical form of the model potentials used in this work appears in Table I. The slash separates the description of the Coulomb and exchange potentials, respectively, and the dash separates the description of the inner and outer core potentials, respectively: inner Coulomb/inner exchange-outer Coulomb/outer exchange. Each couple of integers stands for the number of terms having a common n_i, and the value of n_i, respectively, as in Eqs. (7), (11), and (12). Finally, $A (ns,np,nd)$ refers to the outer-exchange representation of Eq. (8) with ns, np, and nd being the number of GTOs of type s, p, and d, respectively, used in the expansion.

Also in Table I we show the valence basis sets that we used together with the different MP. The reduced basis sets 2 and 3 were completely uncontracted when used in the atomic optimization and contracted as indicated in Table I during the molecular calculations.

In all cases, the atomic AE solutions used as reference were those corresponding to the (5333/53/5) basis set for $Sc(^2D)$ and to the (53/5) basis for $O(^3P)$ in Ref. 10.

First of all, we generated three model potentials for Sc and O, MP (3p, full), MP (3p, OEX) (OEX stands for outer exchange), and MP (3p, TEX) (TEX stands for total exchange), being $1s2s2p$ and $3s3p$ the inner and outer core orbitals in Sc, respectively, and $1s$ the core orbital in O (we indicate the outermost core orbital of Sc in our notation).

The parameters of MP (3p, full) potentials were generated as indicated in the previous section without optimizing the inner potentials since they are obtained using the full-length basis set (basis set 1 in Table I). All the GTOs of the full basis set of Ref. 10 were included in the expansion of the outer exchange in both Sc and O, plus a few diffuse GTOs in an attempt to better span the molecular valence space. Then, the MP (3p, OEX) and MP (3p, TEX) were obtained using the reduced basis sets number 2 in Table I. We also reduced considerably the number of terms in the MP of both atoms, as can be seen in Table I. MP (3p, OEX) and MP (3p, TEX) differ only in the representation of the exchange potentials. In the case of MP (3p, OEX), only the outer exchange potential is approximated by the nonlocal expansion of Eq. (8) and

TABLE I. Model potentials and basis sets definitions.

Model potential	Analytical form	
	Sc	O
MP (3p, full)	40/41-6021/A (15,11,7)	50/A (10,7)
MP (3p, OEX)	30/31-40 /A (7,2,5)	30/A (5,5)
MP (3p, TEX)	30/A -40 /A (7,2,5)	30/A (5,5)
MP (3s, OEX)	30/31-30 /A (7,6,5)	30/A (5,5)
MP (3s, TEX)	30/A -30 /A (7,6,5)	30/A (5,5)
	Valence basis sets	
Basis	Sc	O
1	(53321/1*1*/311)[a]	(521/41)[a]
2	(511/1*1*/311)[b]	(41/41)[b]
3	(511/311*1*/311)[c]	(41/41)

[a] Basis set from Ref. 10. Exponent of p-type polarization functions: 0.168, 0.053.

[b] The s primitive GTFs (7 in Sc and 5 in O) were obtained as in Ref. 4.

[c] The four p primitive GTFs were obtained as in Ref. 4.

TABLE II. Atomic valence orbital energies. All numbers in atomic units.

		Sc			O	
		3p	3d	4s	2s	2p
Reference AE		− 1.572 61	− 0.342 74	− 0.209 43	− 1.241 13	− 0.629 27
MP (3p, OEX)	a		− 0.363 68	− 0.207 40	− 1.237 91	− 0.629 48
	b		− 0.342 63	− 0.209 29	− 1.241 11	− 0.629 18
MP (3p, TEX)	a		− 0.344 37	− 0.207 83		
	b		− 0.342 74	− 0.208 96		
MP (3s, OEX)	a	− 1.560 83	− 0.365 82	− 0.208 22		
	b	− 1.572 68	− 0.342 91	− 0.210 55		
MP (3s, TEX)	a	− 1.558 52	− 0.352 45	− 0.208 83		
	b	− 1.572 41	− 0.342 53	− 0.209 89		

[a] Before optimization.
[b] After optimization.

the inner exchange is represented as in Eq. (12). In MP (3p, TEX), both the inner and outer exchange potentials are expanded as in Eq. (8). The basis set used in the expansion of the outer exchange in both atoms was the new reduced valence basis set. In these cases we optimized the parameters of the inner potentials. The effect of the optimization on the valence orbital energies is shown in Table II. In the MP (3p, TEX) only the parameters of the inner Coulomb potential were optimized. The effect of the optimization on the inner Coulomb potential can be seen in Fig. 1.

For Sc, two other model potentials including the 3p orbitals in the valence space: MP (3s, OEX) and MP (3s, TEX) were generated. Again, OEX and TEX indicate that the outer exchange or the total exchange is represented as in Eq. (8). In each case the coefficients A ($l;a,b$) of Eq. (8) were obtained using the valence basis set 3. The effects of the atomic optimization of the inner potential parameters in the orbital energies are shown in Table II. In the MP (3s, TEX) only the inner Coulomb potential parameters were optimized.

For reasons of space, only the reduced valence basis sets 2 and 3 are reported in the Appendix. The MP parameters may be obtained from the authors upon request.

IV. RESULTS

In this section we present the results of the model potential calculations for the ground state of ScO ($^2\Sigma^+$) obtained using the new approach presented in Sec. II. We analyze its performance by comparing our results with previous MP and frozen core (FC) calculations and with the reference all electron (AE) results. All calculations presented and quoted here are SCF calculations.

Our reference AE calculation of ScO (Table III) is the best among those found in the literature.[6,11] The total energy at $r(\text{Sc–O}) = 3.2$ a.u. is − 834.393 63 a.u.

In earlier MP calculations on the ScO molecule[2,3,5] the inclusion of the 3p orbitals of scandium into the valence space was necessary in order to get acceptable results. Furthermore, good results were obtained only after a soft core projection, resulting from the relaxation of the projection

constant values B_k, was allowed. Even then, the results were not as close to those from the AE calculations as in other molecules. Hence, the ScO molecule became a sensitive test case for effective core approximations. The inclusion of the 3p orbitals of Sc in the core space led to very poor results, in spite of the fact that the FC calculations of Petterson and Wahlgren[6] showed that the 3p orbitals of Sc could be treated as core orbitals. Therefore, (i) the incomplete 3p–valence orthogonality in the MP calculations and (ii) the incorrect long-range behavior of the potentials, resulting from the inability of the radial model potentials to accomodate for the nonlocal 3p–valence exchange interactions and for the truncation effects, appeared to be the responsible for the poor MP results when Sc-3p was included in the core.[5] In the EMP approach presented in this paper, firstly, the main part of the (Sc-3p)–(molecular valence) exchange interactions is correctly handled by nonlocal terms and, secondly, the tail of the local potential is not affected by the basis set reduction. Therefore, our results could clarify what were the causes for the poor results of earlier model potential approaches.

After a very brief description of our molecular calculations, we comment on the effects of the new representation of the core–valence exchange interactions, on the treatment of the Sc-3p as a core or as a valence orbital, and on the reduction of the valence basis set.

A. DS-valence results

In these calculations, the core of Sc is $1s2s2p$ (inner core) and $3s3p$ (outer core). Therefore, the difficult 3p–valence exchange interactions have to be accounted for properly by the model potential. We present three calculations that use this core–valence partitioning. We indicate next the MP and basis set used in each case:

Calculation	Model potential	Basis set
MP-1	MP (3p, full)	1
MP-2	MP (3p, OEX)	2
MP-3	MP (3p, TEX)	2

In Table III we present the spectroscopic constants of

TABLE III. Molecular results.[a]

		$R_e/\text{Å}$	ω_e/cm^{-1}	D_e/eV
	AE[b]	1.671	1062	2.62
DS	MP-1	1.626	868	
	MP-2	1.628	1027	2.46
	MP-3	1.620	1056	2.60
	HKS	1.52	750	
	FC[c]	0.007	16	−0.30
PDS	MP-4	1.668 (1.662)	1054 (1056)	2.42 (2.30)
	MP-5	1.660 (1.658)	1083 (1083)	2.60 (2.55)
	HKS	1.63	1047	
	FC[c]	0.011	23	−0.10

[a] Numbers in parenthesis correspond to nonoptimized MP's.
[b] Basis set from Ref. 10, Sc-(53321/531*1*/311), O-(521/41).
[c] Frozen core calculation from Ref. 6. All these numbers correspond to differences between FC results and their reference AE (Ref. 6).

ScO and in Table IV the orbital energies at four values of the Sc–O distance.

B. PDS-valence results

Now the $3p$ orbitals have been promoted to the valence shell. The calculations correspond to the reduced bases in all cases and are:

Calculation	Model potential	Basis set
MP-4	MP (3s, OEX)	3
MP-5	MP (3s, TEX)	3

The results are also collected in Tables III and IV.

C. Analysis of the results

We can start the analysis of the results by comparing ours with those obtained by Huzinaga *et al.*,[2] HKS. We have included their results in Table III. These authors calculated the equilibrium geometry of the ground state of ScO including the $3p$ orbitals in the core, DS–HKS, and also including them in the valence shell, PDS–HKS. We compare here only our results that have a basis set and core–valence partition similar to those in Ref. 2. The comparison is useful to determine the effects and performance of the new representation

TABLE IV. Absolute value of the valence molecular orbital energies. All numbers in atomic units.

Type[a]		R /a.u.			
		2.8	3.0	3.2	3.4
3s(Sc)	AE	1.695 26	1.673 30	1.666 77	1.670 88
	MP-4	1.704 80	1.678 40	1.670 73	1.674 62
	MP-5	1.703 41	1.676 97	1.669 01	1.672 67
3p(Sc)	AE	1.579 35	1.607 41	1.634 61	1.659 58
	MP-4	1.583 50	1.611 40	1.638 37	1.663 10
	MP-5	1.581 21	1.608 98	1.635 73	1.660 30
2s(O)	AE	1.101 78	1.115 15	1.116 07	1.108 25
	MP-1	1.132 19	1.125 97	1.114 76	1.101 03
	MP-2	1.154 51	1.145 00	1.129 87	1.111 56
	MP-3	1.154 46	1.144 74	1.129 43	1.109 97
	MP-4	1.101 77	1.114 71	1.115 59	1.107 92
	MP-5	1.099 54	1.113 02	1.114 35	1.107 12
2p(O)	AE	0.447 31	0.434 84	0.421 73	0.407 66
	MP-1	0.455 63	0.428 25	0.403 12	0.378 73
	MP-2	0.442 77	0.421 42	0.403 98	0.387 90
	MP-3	0.444 72	0.423 91	0.406 35	0.389 06
	MP-4	0.444 84	0.432 41	0.419 24	0.404 85
	MP-5	0.448 59	0.436 23	0.422 37	0.407 05
2p(O)	AE	0.487 66	0.446 51	0.412 77	0.384 81
	MP-1	0.464 33	0.430 56	0.401 72	0.377 62
	MP-2	0.464 23	0.426 37	0.394 65	0.367 77
	MP-3	0.462 51	0.424 86	0.393 44	0.366 14
	MP-4	0.482 31	0.442 09	0.409 29	0.382 08
	MP-5	0.480 80	0.441 31	0.409 05	0.382 24
4s(Sc)	AE	0.223 23	0.237 61	0.250 25	0.261 30
	MP-1	0.216 46	0.227 26	0.237 50	0.247 19
	MP-2	0.218 15	0.229 59	0.240 23	0.250 11
	MP-3	0.218 32	0.229 60	0.240 13	0.250 17
	MP-4	0.224 56	0.238 68	0.251 11	0.261 98
	MP-5	0.223 95	0.237 73	0.249 85	0.260 52

[a] Main component of the molecular orbital.

of the core–valence exchange interactions in those cases where all orbitals excluded from the valence have a clear core character as well as in those cases where their core character is doubtful.

Let us compare the results corresponding to the DS valence, MP-2 or MP-3 with DS–HKS (Table III). We can refer both calculations to the AE appearing in the same Table (this calculation is variationally better than the AE ones quoted in Ref. 2, GTO–RVV and STO). It can be seen that the new nonlocal approach to the outer core exchange potential ($3s,3p$ in MP-2) led to a considerable improvement of the results. In fact, the value of the Sc–O equilibrium distance R_e increased by about 0.1 Å, reducing the discrepancy with the AE results by 70%. The MP-2 value of ω_e is also closer to the AE result. It appears that the better representation of the outer core exchange potential, in cases like ScO where some of the core orbitals are not unambiguously core orbitals, can correct nearly completely the deficiencies of the earlier MP approach; in ScO, the curvature of the nuclear potential and the binding energy are calculated to be quite close to the AE results. The difference between the EMP and AE values of R_e is now smaller than 0.1 Å. The additional nonlocal representation of the inner core exchange potential (MP-3 in Table III) does not bring further corrections. Re and ω_e remain in the same range, and D_e is corrected by 7%.

We can now compare the results corresponding to the PDS valence. In this case, the PDS–HKS calculation takes proper account of the $3p$ exchange interactions, but the local potential has to account for the rest of the core–valence exchange interactions (the main contribution arising from the $3s$ orbitals of Sc) and the basis set reduction. It can be observed in Table III (MP-4, MP-5) that, again, our approach improves the results. Now the value of ω_e remains unchanged. This means that the incorrect representation of the $3p$ exchange interactions was responsible for the poor DS–HKS value of 750 cm^{-1}. However, the value of R_e is adequately corrected. The correction is now smaller than in the DS valence case (0.03 Å). Thus, the improvement of the value of R_e due to the nonlocal representation of $3s$-exchange interactions is almost one order of magnitude smaller than that due to the nonlocal representation of $3p$-exchange interactions. Once again, the additional nonlocal representation of the $1s,2s,2p$ exchange potential (MP-5) does not appreciably change the values of R_e and ω_e. The improvement of the binding energy is now very similar to that observed in the DS-valence case.

As can be seen in Table III, our PDS calculations reproduce the AE results within the same accuracy as the FC calculation does. Besides, the molecular orbital energies are quite close to the AE ones (Table IV). It seems that, at the PDS level, the present EMP, as proposed in Sec. II, reaches its limit of the frozen core approximation. However, if the DS-valence approximation is used, the R_e value is less accurate. The same happens with the molecular orbital energies. Two main factors could be responsible for that, namely, the incomplete core-valence orthogonality (mainly $3p$–valence) in the MP calculations and the still incomplete representation of the two center (frozen $3p$)–(molecular valence) exchange interactions. Nevertheless, our DS results are as

good as the PDS–HKS ones. This means that if the more economical DS valence is to be used in calculations with the $3d$ transition metals, then the core–valence exchange interactions, or at least the outer core–valence components, should be represented as in Eq. (8).

It is worth noting that the results of the new approach correspond to a hard projection, as commented in Sec. II. It has not been necessary to use the core projection constants as free parameters to be determined in the molecular calculations. Their value was kept fixed at the theoretical value $-2\epsilon_k$.[8]

Let us now comment on the effects of the basis set reduction and the MP optimization. In the earlier model of Sakai and Huzinaga[7] the optimization of the local model potential parameters became necessary at the atomic stage, not only to represent the deviations of the core Coulomb potential from the point charge model, but also to account for the nonlocal exchange and basis set reduction effects. As Petterson and Strømberg showed,[5] these last two effects were reponsible for the incorrect long-range behavior of the local potentials. These two problems were partly circumvented by treating the core projection constants as free parameters to be optimized in the molecular calculations.[2] As we showed in Sec. II, the local part of our potentials does not have to account for the outer exchange effects. We can show now how it accounts for the basis set reduction effects by comparing the results of MP-1 with those of MP-2 or MP-3. (We recall that MP-1 corresponds to the full basis and has not been optimized while MP-2 and MP-3 correspond to the reduced basis set and have been optimized as described in Sec. II.) The comparison shows that R_e is insensitive to the basis set reduction. On the other hand, the value of ω_e changes in the right direction. Furthermore, as the numbers in parentheses in Table III show, the optimization performed at the atomic stage does not lead to significant improvement of the molecular results. This means that the optimization could be avoided.

We want to stress the importance of including the valence basis set in the expansion of the core exchange [Eq. (8)]. This precaution ensures the correct calculation of all one-center core–valence exchange integrals. The results of a calculation in which the basis set does not coincide with that of the valence, but is built from the full basis set by picking up every second primitive, are: $R_e = 1.44$ Å, and $\omega_e = 760$ cm^{-1}. These values should be compared to those corresponding to MP-2 in Table III.

TABLE V. CPU time in seconds corresponding to calculations at R (Sc–O) = 3.2 a.u.

	Integral evaluation			SCF	Total
	1e	2e	total	time/iteration	
AE	1	199	200	3.7	330
MP-1	37	74	111	2.0	181
MP-2	15	47	62	1.5	116
MP-3	14	47	61	1.5	117
MP-4	21	85	106	2.5	197
MP-5	20	85	105	2.4	181

Finally, the timing of the MP molecular calculations are shown in Table V. The calculations were done in an AMDAHL 580/FF using a modified version of Almlöf's MOLECULE.[12]

V. CONCLUDING REMARKS

The modifications introduced to the model potential method of Saki and Huzinaga[7] have proven to lead to some conceptual and computational simplifications as well as to a considerable improvement of the results in the theoretical study of the ground state of the ScO molecule at the SCF level.

Partitioning of core into inner and outer parts gives more physical insight to the model potential terms and avoids deterioration of the representation of the outer regions of the local potentials upon the reduction of the valence basis set. Furthermore, the basis set used for the expansion of the outer exchange can be reduced together with the valence basis set without loss of accuracy.

The outer-core valence exchange interactions are now better represented as shown by the fact that the results obtained including the $3p$ orbitals of Sc into the outer core lead to the same accuracy as in the calculation of Huzinaga *et al.* in which the $3p$ orbitals were included into the valence shells.[2]

Using the new EMP method, agreement with AE results can be achieved in the ScO molecule within 0.01 Å in R_e, 20 cm^{-1} in ω_e, 0.1–0.2 eV in the binding energy, and an order of 10^{-3} a.u. in the valence orbital energies.

Finally, it should be mentioned that the new approach could account for relativistic effects if the method proposed by Klobukowski[4] is followed.

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APPENDIX

The following are the reduced basis sets used in the MP calculations. We present the valence atomic orbitals. The molecular basis sets were obtained from them using the splitting procedures described in Ref. 10.

Scandium

Exponents	Coef. MP-2	4s Coef. MP-3	Coef. MP-4	Coef. MP-5
928.376 94	− 0.005 917 14	− 0.004 723 70	− 0.005 057 00	− 0.004 772 02
107.162 69	− 0.030 639 74	− 0.030 838 63	− 0.031 834 69	− 0.031 719 36
6.44104 63	0.156 094 97	0.159 313 57	0.164 339 64	0.162 627 12
0.845100 28	− 0.301 833 07	− 0.300 829 03	− 0.321 098 09	− 0.308 466 83
0.375952 59	− 0.245 304 04	− 0.246 294 25	− 0.231 882 92	− 0.241 699 69
0.078617 54	0.610 585 69	0.611 261 89	0.619 019 49	0.617 125 00
0.030803 38	0.559 716 25	0.559 336 00	0.548 703 10	0.552 866 17

Exponents	Coef. MP-2	3d Coef. MP-3	Coef. MP-4	Coef. MP-5
19.137 456	0.022 854 55	0.028 514 95	0.028 036 57	0.029 319 26
5.104 739 8	0.136 312 51	0.138 179 14	0.141 140 95	0.138 858 10
1.661 303 3	0.348 915 03	0.347 291 38	0.350 219 92	0.347 202 00
0.543 774 72	0.485 620 87	0.485 771 60	0.483 445 18	0.485 387 11
0.163 315 97	0.344 809 82	0.344 015 76	0.341 895 49	0.344 010 01

Exponents	3p Coef. MP-4	Coef. MP-5
50.880 851	− 0.089 455 21	− 0.090 294 13
12.118 399	− 0.247 490 82	− 0.254 894 18
1.325 599 4	0.573 331 11	0.562 521 03
0.499 575 73	0.464 214 72	0.474 798 68
0.168	0.066 205 02	0.063 613 12
0.053	− 0.003 353 33	− 0.002 146 56

Oxygen

2s Exponents	Coef.	2p Exponents	Coef.
292.565 50	− 0.016 357 48	34.971 176	0.015 778 66
42.486 394	− 0.096 654 04	7.845 091 7	0.094 881 99
9.806 073 5	− 0.239 743 58	2.303 316 4	0.307 185 05
0.855 880 50	0.630 715 14	0.721 982 39	0.496 836 29
0.263 497 07	0.470 976 89	0.215 527 13	0.335 853 95

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