

Model Potentials Suitable for Calculations with Slater-Type Basis for Sc through Zn

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Received March 18, 1985; in revised form June 27, 1985

Model potentials appropriate for molecular calculations with Slater-type (ST) basis sets have been generated for the first-row transition-metal atoms. Two sets of model potentials are presented. The first one has been optimized using standard 2ζ ST basis sets. The second is consistent with a reduced ST basis set. The reduced bases have been obtained by means of a new algorithm, whose results are compared to those found with the method of Y. Sakai and S. Huzinaga (*J. Chem. Phys.* **76**, 2537 (1982)). The comparison shows that the new approach leads to significant improvements in the overall results. Two different valence shells have been investigated, one formed by the $3s$, $3p$, $3d$, and $4s$ AOs (SPDS), and the other one formed by the $3d$ and $4s$ AOs (DS). The model potentials presented here describe these valence shells in good agreement with the all-electron calculations taken as reference, the SPDS calculations being uniformly more accurate. Special attention has been paid to the transferability of the model potentials to electronic states with different orbital occupation. It is shown that the reported potentials have a wide transferability of this sort, being thus suitable for calculating the electronic structure of transition-metal compounds with STO 2ζ quality. © 1986 Academic Press, Inc.

1. Introduction

Although very involved calculations can be performed today on transition-metal compounds, the large amounts of computer time required have been the stimulus for great progress in the development of approximate methods suitable for dealing accurately and still economically with these systems. Efficient schemes of core-valence separation (1-13), statistical treatment of the exchange interactions (14-20), and ionic-Hamiltonian formalisms (21-22) are significant contributions to this progress. Among these accurate and useful cluster methodologies, the frozen-core SCF MO method developed by Richardson *et al.* (23) has given very good results in the last years

(24-36). In certain applications of this method to the study of structural and electronic properties of transition-metal ions in ionic lattices we have found some theoretical difficulties, mainly related to an inadequate core-valence separation. We have observed, for instance, that incomplete core-valence orthogonality can seriously affect the prediction of the cluster nuclear potentials (36).

In an attempt to correct these difficulties we have considered the incorporation of a well-tested pseudopotential technique into Richardson's methodology. Further advantages of this work would be (a) the possibility of improving the atomic basis sets without greatly increasing the size of the calculation, (b) an easier treatment of sys-

tems with large number of electrons ($4d$ and $5d$ ions, for instance), and (c) a general reduction of computer time. Different pseudopotential schemes can be selected to accomplish this project. We have chosen the model potential (MP) approach of Huzinaga and collaborators (12, 13) because (a) it is a theoretically well-founded method (39, 40), (b) the core–valence repulsions are adequately represented by a flexible radial mono-electronic operator, and (c) the core–valence orthogonality and the correct nodal structure of the valence orbitals are enforced and guaranteed by appropriate core-projection operators, even if the valence basis is reduced. Furthermore, this method has been applied to a great number of cases with very satisfactory results (12, 13, 41–45).

Since our interest is in calculations over STO basis sets and, as far as we know, MPs of exponential form for $3d$ transition elements are not available, we have obtained them and their corresponding valence SCF solutions in this work. Molecular calculations with STO bases and exponential model potentials such as these reported here should become more appealing in the near future, in view of the renewed interest in accurate and efficient algorithms for computing multicenter integrals over exponential functions (46–51).

In this work we have analyzed in some detail the important problem of the basis reduction. We have used a new scheme, based on a simulation technique recently developed in our laboratory (52), and have compared it with the reduction method of Sakai and Huzinaga (13). The comparison shows that our scheme is simpler and more automatic. Furthermore, it gives better results.

As all-electron (AE) reference sets we have taken the 2ζ bases of Clementi and Roetti (53). Although larger STO basis sets are available (53), we think that the 2ζ basis has an overall quality appropriate for most

applications in systems of interest, can be accurately reproduced by economic MPs, and substantially improves the core description currently used within Richardson's methodology (37, 38).

In this paper we present two families of MPs, corresponding to the SPDS core–valence partition (valence shell = $3s$, $3p$, $3d$, and $4s$ AOs), and the DS partition (valence shell = $3d$ and $4s$ AOs). Results of SPDS and DS calculations are compared throughout the paper, but in the next section we present a brief examination of their respective merits and deficiencies. The rest of the paper is organized as follows. Section 3 is dedicated to the determination of the MPs for Sc to Zn corresponding to the high-spin state of the $3d^n 4s^2$ ($n = 1$ to 10) configurations. In Section 4 we give the MPs corresponding to the SPDS 2ζ calculation. In Section 5 we present and analyze the new method of basis reduction and give the MPs corresponding to the reduced bases. Results of a quality test on the MPs are presented in Section 6. They show that these MPs are widely transferable to states with a very different electronic occupation in the valence shell. In fact, the reported MPs are able to represent well the core–valence interactions even when the net charge of the element varies by several units. This is a very satisfactory result in connection with the use of the model potentials in molecular calculations where considerable charge transfer between different centers occurs.

2. Core–Valence Partition: SPDS or DS?

In obtaining the model potentials for the $3d$ elements, the first question to be solved is the definition of the core–valence partition. Since there is no doubt about either the core character of the $1s$, $2s$, and $2p$ AOs or the valence character of the $3d$ and $4s$ AOs, the question is simply to decide whether the $3s$ and/or the $3p$ AOs are in-

cluded in the core or not. We will call DS the partition with a valence formed by the $3d$ and $4s$ AOs, and SPDS the partition with the $3s$, $3p$, $3d$, and $4s$ AOs in the valence shell. Differences between these two partitions have been discussed several times in the literature. We will briefly comment on here some of these analyses.

Melius *et al.* (54) examined the deviations from the all electron (AE) values of the orbital and electronic transition energies of ab initio frozen-core (FC) and effective-potential (EP) calculations within the DS partition. Their work on different multiplets of Fe, Fe⁺, and Fe²⁺ shows that the FC assumption is an important source of error in the EP approximation. They remarked that "this error is particularly serious for the transition elements since the $3d$ orbitals are close enough to the $3s$ and $3p$ orbitals of the core that significant core relaxation effects occur as the occupation number of the $3d$ orbital changes" (54).

We have studied this error in comparing the DS and the SPDS partitions and verified that the presence of the $3s$ and $3p$ AOs in the valence is necessary to reproduce the AE results accurately. As an example, we present in Table I the $3d$ and $4s$ orbital energies obtained from AE, FC-SPDS, and FC-DS calculations on several states of Fe and Fe²⁺. We have used the 2ζ basis of Clementi and Roetti (53) in all these calculations. In this table we clearly see the worsening of the FC calculation in passing from the SPDS to the DS partition. Similar effects were found by Bonifacic and Huzinaga (12) in their MP calculations of the Fe/Fe²⁺ and Ni/Ni²⁺ systems. The MP-DS results tend to be worse when the MP optimized in a given state is used to compute properties of electronic states with different $3d$ occupation.

Deficiencies ascribable to the inclusion of the $3s$ and $3p$ AOs in the core have also been observed in several molecular calculations. Thus, Vincent and Murrell compared

TABLE I
RESULTS OF ALL ELECTRON CALCULATIONS (AE)
AND FROZEN-CORE CALCULATIONS (FC) USING
SPDS AND DS PARTITIONS IN SEVERAL ELECTRONIC
STATES OF Fe AND Fe²⁺

		AE	FC	
			SPDS	DS
Fe, $d^6s^2\ ^3D$	$\epsilon(3d)$	-0.61788	-0.61788	-0.61788
	$\epsilon(4s)$	-0.25129	-0.25129	-0.25129
Fe, $d^6s^2\ ^1S$	$\epsilon(3d)$	-0.50247	-0.50246	-0.50467
	$\epsilon(4s)$	-0.25180	-0.25180	-0.25186
Fe, $d^7s\ ^5F$	$\epsilon(3d)$	-0.25277	-0.25273	-0.22538
	$\epsilon(4s)$	-0.19825	-0.19825	-0.19802
Fe ²⁺ , $d^6\ ^3D$	$\epsilon(3d)$	-1.30858	-1.30858	-1.31139
Fe ²⁺ , $d^5s\ ^7S$	$\epsilon(3d)$	-1.67855	-1.67857	-1.71016
	$\epsilon(4s)$	-0.96776	-0.96775	-0.97338

Note. All numbers in a.u.

SPDSP (SPDS + $4p$) and DSP results of TiH₃F, obtained with a pseudopotential scheme (55), and found that the orbital energies deviate from the AE values by less than 0.02 a.u. in the SPDSP case, and by about 0.1 a.u. in the DSP calculation. So, they argue that their method requires the use of the extended-valence partition to give satisfactory results. In particular, their DSP predictions in species like MnO₄⁻ are rather poor. Furthermore, Sakai and Huzinaga (13) reported that the MP-AE discrepancies are larger in Cu₂ than in molecules without transition metals. They remarked that the promotion of the $3p$ AOs into the valence shell would be "an obvious remedy, but a rather unwelcome one" (13). Finally, we can also add that recent results of near ab initio, FC calculations in CrF₆³⁻, performed within the SPDDSP and the DDSP partitions, show a greater core-valence orthogonality in the SPDDSP calculations, giving rise to a better description of the cluster nuclear potential in this partition (32, 36).

From all this previous work it appears that the SPDS partition has clear advantages over the DS one. SPDS model potentials should work better and, also, they should be more transferable among differ-

ent electronic states. Accordingly, we have centered our attention on SPDS calculations. On the other hand, this partition gives a only moderate reduction in computer time with respect to the AE calculations. The DS partition, much more economic, could be an interesting option in some cases. For this reason we have also obtained the DS model potentials and their corresponding reduced basis sets, and have paid some attention to the results of the DS calculations. For instance, we will show in Section 6 that the DS MPs are less transferable than the SPDS ones.

3. Determination of the Model Potentials

According to the model potential method of Huzinaga *et al.* (12, 13), the effective valence Hamiltonian for the 3d elements is

$$\mathcal{H}_{\text{MP}} = \sum_{i=1}^{N_v} \left(-\frac{1}{2} \nabla_i^2 + V_{\text{mp}}(r_i) + \sum_{n=1}^{N_s} B_{ns} |\phi_{ns}\rangle \langle \phi_{ns}| + \sum_{n=1}^{N_p} B_{np} (|\phi_{npx}\rangle \langle \phi_{npx}| + |\phi_{npy}\rangle \langle \phi_{npy}| + |\phi_{npz}\rangle \langle \phi_{npz}|) \right) + \sum_{i>j}^{N_v} r_{ij}^{-1}. \quad (1)$$

In Eq. (1) N_v is the number of valence electrons. N_s and N_p are, respectively, the number of *s* and *p* core electrons. $V_{\text{mp}}(r_i)$ is the model potential operator that represents the effects of the nucleus as shielded by the core electrons. This operator, when combined with STO basis sets, is of the following form (12):

$$V_{\text{mp}}(r) = -\frac{Z - N_c}{r} \left\{ 1 + \sum_{k=1}^{\text{NT}} A_k r^{n_k} \exp(-\alpha_k r) \right\} \quad (2)$$

where N_c is the number of total core electrons ($N_c = N_s + N_p$), and NT, $\{n_k\}$, $\{A_k\}$, and $\{\alpha_k\}$ the effective potential parameters. The projection operators in Eq. (1) are con-

structed using the atomic solutions of the AE calculation chosen as the reference. The projection constants, B_c , are defined as $B_c = -2\varepsilon_c$, ε_c being the corresponding AE values of the core orbital energies.

The solution of the SCF equations derived from the MP valence Hamiltonian of Eq. (1), shall be referred to as the MP calculation.

The optimization of the parameters $\{A_k\}$ and $\{\alpha_k\}$ is achieved by an automatic iterative algorithm that minimizes the quantity

$$\Delta = \sum_{i=1}^{N_v} w_i |\varepsilon_i^{\text{AE}} - \varepsilon_i^{\text{MP}}| + \sum_{i=1}^{N_v} 2W_i (1 - |\langle \phi_i^{\text{AE}} | \phi_i^{\text{MP}} \rangle|). \quad (3)$$

This quantity has been proposed in a slightly different form by Sakai and Huzinaga (13). The sets $\{\phi_i^{\text{AE}}, \varepsilon_i^{\text{AE}}\}$ and $\{\phi_i^{\text{MP}}, \varepsilon_i^{\text{MP}}\}$ are the valence solutions of the reference AE and model potential (MP) calculations, respectively. w_i and W_i are appropriate weighting factors.

We have determined the parameters NT and $\{n_k\}$ by a process of trial and error and have found that a simple form of two terms is flexible enough when using a SPDS valence partition, but one with three terms is necessary when dealing with a DS one. Those forms are

$$\text{(SPDS):} \quad V_{\text{mp}}(r) = -\frac{Z - 10}{r} (1 + A_1 e^{-\alpha_1 r} + A_2 r^2 e^{-\alpha_2 r}) \quad (4a)$$

$$\text{(DS):} \quad V_{\text{mp}}(r) = -\frac{Z - 18}{r} (1 + A_1 e^{-\alpha_1 r} + A_2 r e^{-\alpha_2 r} + A_3 r e^{-\alpha_3 r}). \quad (4b)$$

4. Model Potential Results without Reduction of the Basis Set

To isolate possible sources of error in our MP calculations, we have started our work by analyzing the MP results without any reduction of the basis set. Thus, we have

TABLE II
SPDS MODEL POTENTIAL PARAMETERS FOR THE
ELEMENTS OF THE 3d TRANSITION SERIES^a

Atom	A_1	A_2	α_1	α_2
Sc $d^1 \text{ } ^2D$	0.929948	0.002096	6.429495	2.953665
Ti $d^2 \text{ } ^3F$	0.853003	0.001033	6.812561	3.066179
V $d^3 \text{ } ^4F$	0.787836	-0.000078	7.193537	3.880215
Cr $d^4 \text{ } ^5D$	0.731939	-0.003557	7.573653	4.677561
Mn $d^5 \text{ } ^6S$	0.683430	-0.022516	7.951935	6.270020
Fe $d^6 \text{ } ^5D$	0.640983	-0.017535	8.330677	5.792809
Co $d^7 \text{ } ^4F$	0.603376	-0.137216	8.699638	8.255674
Ni $d^8 \text{ } ^3F$	0.570135	-0.054337	9.085581	7.080356
Zn $d^9 \text{ } ^2D$	0.540153	-0.148110	9.455466	8.397742
Cu $d^{10} \text{ } ^1S$	0.513318	-0.094338	9.835593	7.882831

^a The optimization has been carried out in the highest-spin state of the $3d^n 4s^2$ configuration ($n = 1, 10$) using the 2ζ bases of Ref. (53).

optimized the $\{A_k\}$, $\{\alpha_k\}$ parameters in Eqs. (4), throughout the 3d series, in the SPDS case. Since the most useful calculations are those including basis reduction, we will not discuss the DS results until the next section.

We will name MP- 2ζ the model potentials obtained without basis reduction. In Table II we collect the optimum values of the SPDS MP- 2ζ parameters. In Fig. 1 we can see the evolution of the core shielding, $Z + rV_{mp}$, with the radial coordinate r and the nuclear charge Z . It can be observed that the asymptotic limits at $r \rightarrow 0$ and $r \rightarrow \infty$ are correct: the core shielding vanishes as $r \rightarrow 0$ a.u., and it is nearly complete at $r \approx 1$ a.u. Also, in the region $0 < r < 1$ a.u. this shielding increases with Z . All these properties of the V_{mp} 's are very satisfactory because they are not a consequence of any direct requirement upon the optimization process of the parameters.

Let us now to analyze the MP- 2ζ valence solution. In Table III we have collected the orbital and total electronic energies, the overlap integrals between MP and AE valence orbitals, $S(nl)$, and the (AE core|MP valence) overlaps, $S(nl, n'l')$ for the $d^6 s^2 \text{ } ^5D$ state of the Fe atom, taken as example. We have also included the corresponding AE values for comparison.

From this table we conclude that the results of the SPDS MP- 2ζ calculations are very satisfactory: the orbital energies of the $3s$, $3p$, and $3d$ AOs differ by less than 10^{-5} a.u. from the AE values ($\epsilon(4s)$ differs by 4×10^{-4} a.u.), the MP-AE overlap integrals are greater than 0.9999, and the core-valence orthogonality is better than 10^{-2} . This quality is uniformly obtained across the transition series. On the other hand, the DS MP- 2ζ calculation gives $4s$ and $3d$ orbital energies differing by less than 10^{-5} a.u. from the AE values. However, the MP-AE overlap integrals and the core-valence orthogonality turn out to be clearly worse in this short-valence partition, the larger differences appearing in those quantities involving the $4s$ AO.

5. Reduction of the Valence Basis Set: Method and Results

Method

One of the more promising characteris-

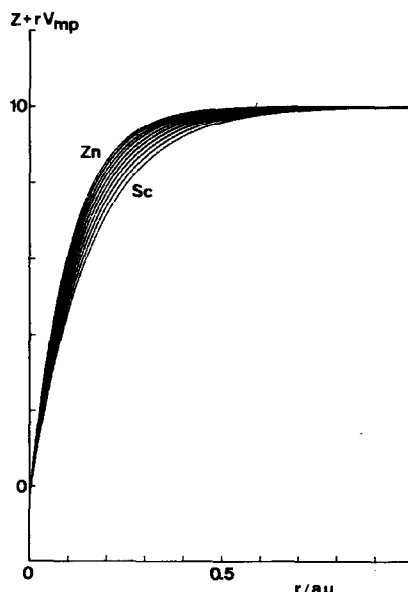


FIG. 1. Evolution of the core shielding, $Z + rV_{mp}(r)$, with the radial coordinate, r , and the nuclear charge, Z . The parameters of the V_{mp} 's appear in Table II.

TABLE III
MP-2 ζ RESULTS FOR Fe $d^6s^2\text{-}^5D$ USING SPDS AND DS PARTITIONS, AS COMPARED
WITH THE AE RESULTS^a

	(A) Orbital and total energies in a.u.					
	$\epsilon(3s)$	$\epsilon(4s)$	$\epsilon(3p)$	$\epsilon(3d)$	TE	
AE	-4.14242	-0.25129	-2.71718	-0.61788	-1262.372	
SPDS-MP-2 ζ	-4.14242	-0.25166	-2.71718	-0.61788	-1262.430	
DS-MP-2 ζ		-0.25129		-0.61788	-1262.208	
	(B) AE valence-MP valence overlap integrals					
	$S(3s)$	$S(4s)$	$S(3p)$	$S(3d)$		
SPDS-MP-2 ζ	0.99997	1.00000	1.00000	1.00000		
DS-MP-2 ζ		0.99963		0.99996		
	(C) Core-valence overlaps					
	$S(1s,3s)$	$S(2s,3s)$	$S(1s,4s)$	$S(2s,4s)$	$S(3s,4s)$	$S(2p,3p)$
SPDS-MP-2 ζ	0.00076	0.00760	0.00016	0.00152		0.00178
DS-MP-2 ζ			0.00125	0.00555	0.02102	

^a All energies in a.u. (hartrees).

tics of the MP method of Huzinaga *et al.* (12, 13) is the possibility of reducing the valence basis set without appreciable loss in the quality of the final results. Given the importance of this operation, Huzinaga and collaborators have analyzed it carefully. The most recent proposition for this reduction has been made by Sakai and Huzinaga (13, 41) and it can be summarized in the following four steps:

1. Definition of the reduced set (basis size and principal quantum numbers).
2. The reduction is made by elimination of basis functions (EBF) from the reference set.
3. The EBF should be "careful and judicious" (13a).
4. The reduction does not affect the definition of the projection operators constructed with the core solutions (AOs and $B_c = -2\epsilon_c$) of the reference AE calculation.

The aim of the reduction process is to make the MP calculation as economical as possible and still have MP valence orbitals that closely simulate the shapes of the ref-

erence AOs, including their inner nodes. This is the meaning of a "careful and judicious" EBF. In this context, Sakai and Huzinaga have remarked that the complete elimination of the inner members of the primitive basis gives rise to undesirable features, such as too deep model potentials, incorrect nodal structure of the pseudoorbitals, and basis dependence in the results.

We have studied in this work the process of reduction and have found that a method of generation of approximate functional sets, recently implemented in our laboratory (52), gives very good results. The new method is a simulation procedure requiring maximum overlap with the reference set. Our results show that this method can favorably substitute the EBF scheme of Sakai and Huzinaga. Accordingly, we have used a reduction procedure in which steps 2 and 3 above have been substituted by step 2':

- 2'. The reduction is made by application of the OFMO method (orthonormal functions with maximum overlap (52)) to the valence AOs of the AE reference set.

The completely automatic OFMO method (52) simulates the AE valence AOs by generating a new set whose components (a) are linear combinations of a new and shorter basis set, (b) give maximum overlap with their AE partners, and (c) are mutually orthonormal. Although the OFMO method gives the new orbital exponents and coefficients, in the present application we use only the exponents because the coefficients

are generated by the MP optimization. We notice that in this new reduction procedure only the first step (basis definition) is non-automatic.

We can now compare the MP-EBF and the MP-OFMO results. As an example of a wider numerical experimentation, we present the SPDS results corresponding to the $d^4s^2-^5D$ state of Cr. The reduction analyzed here transforms the 2ζ basis into the

TABLE IV
COMPARISON OF THE MP-EBF AND MP-OFMO RESULTS WITH THE MP- 2ζ AND AE CALCULATIONS FOR Cr ($d^4s^2-^5D$)

(A) Bases							
Orbital exponents				Orbital exponents			
STO	Ref.	EBF	OFMO	STO	Ref.	EBF	OFMO
1s	24.99790		6.13764	2p	15.50780		10.02993
1s	17.40750	17.40750		2p	9.02843	9.02843	
2s	12.66540		9.52063	3p	4.61536	4.61536	4.36337
2s	9.19252	9.19252		3p	2.86678	2.86678	2.75769
3s	4.64782	4.64782	3.99888				
3s	3.09125						
4s	1.77218	1.77218	1.86295	3d	5.40992	5.40992	5.40992
4s	1.01451	1.01451	1.03854	3d	2.34014	2.34014	2.34014
(B) Model potential parameters							
Basis	A_1	A_2	α_1	α_2			
2ζ	0.731939	-0.003557	7.573653	4.677561			
EBF	0.722838	4.510262	7.462980	8.020146			
OFMO	0.744164	-2.823967	7.463099	11.874363			
(C) Results of AE and MP calculations							
	AE	MP- 2ζ	MP-EBF	MP-OFMO			
$\epsilon(3s)$	-3.48316	-3.48316	-3.48316	-3.48316			
$\epsilon(4s)$	-0.23523	-0.23557	-0.23680	-0.23542			
$\epsilon(3p)$	-2.23420	-2.23420	-2.22588	-2.23421			
$\epsilon(3d)$	-0.55219	-0.55219	-0.55219	-0.55219			
TE	-1043.3271	-1043.3379	-1045.6103	-1043.2459			
S(3s)		0.99996	0.99417	0.99989			
S(4s)		0.99999	0.99982	0.99996			
S(3p)		1.00000	0.99890	0.99999			
S(3d)		1.00000	0.99897	1.00000			
S(1s,3s)		0.00083	0.00025	0.00013			
S(2s,3s)		0.00816	0.00189	0.00954			
S(1s,4s)		0.00018	0.00006	0.00002			
S(2s,4s)		0.00171	0.00053	0.00187			
S(2p,3p)		0.00194	0.00002	0.00221			

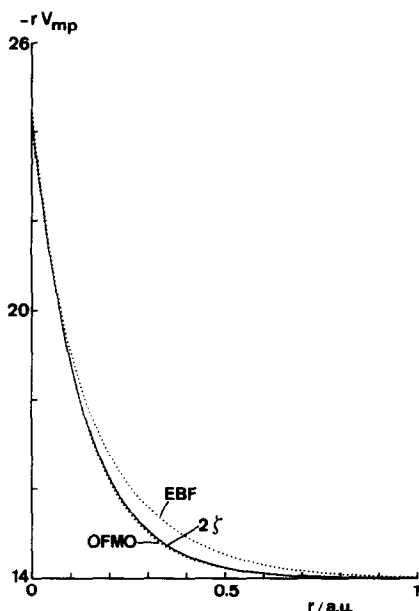


FIG. 2. Effective nuclear charge of Cr (d^6s^2-5D), $-rV_{mp}(r)$, as a function of r , calculated with the 2ζ (Table II), EBF, and OFMO (Table V) model potentials.

basis: $1s, 2s, 3s, 4s, 4s'; 2p, 3p, 3p'; 3d, 3d'$. In both calculations we first reduce the valence basis set and then optimize the MP parameters. Our results can be seen in Table IV and Figs. 2 and 3. We include the MP- 2ζ and the AE results for comparison.

We can first compare the MPs obtained in the three cases: 2ζ , EBF, and OFMO. The optimum parameters are collected in Table IVB. Equivalent degrees of optimization have been obtained in each case. In Fig. 2 we observe the evolution of the effective nuclear charge, $-rV_{mp}(r)$, as obtained in the MP- 2ζ , MP-EBF, and MP-OFMO calculations. The 2ζ and OFMO effective charges are very close. However, the EBF charge overestimates the 2ζ results for $0.1 \leq r \leq 1$ a.u. Consequently, the $3s, 3p$, and $3d$ EBF orbitals penetrate considerably into the inner regions whereas the OFMO densities remain very close to the AE ones (see Fig. 3). On the other hand, the $4s$ orbital, whose radial density at $r < 1$ a.u. is negli-

ble, is very well described in both reduced-basis calculations.

The better quality of the MP-OFMO densities is also shown by the values of the $\langle MP|AE \rangle$ overlap integrals, Table IVC. These integrals are larger than 0.9999 and almost identical in the MP-OFMO and MP- 2ζ calculations. The MP-EBF values are decidedly worse.

Also in Table IVC we can see that the effects of the basis reduction in the MP- 2ζ orbital and total energies are negligible when this operation is performed with the OFMO method. This is not the case when the EBF scheme is used.

According to this calculation, the only feature favorable to the MP-EBF procedure is the core-valence orthogonality attained (Table IVC), which is even greater than that found in the MP- 2ζ case. This is an unexpected result.

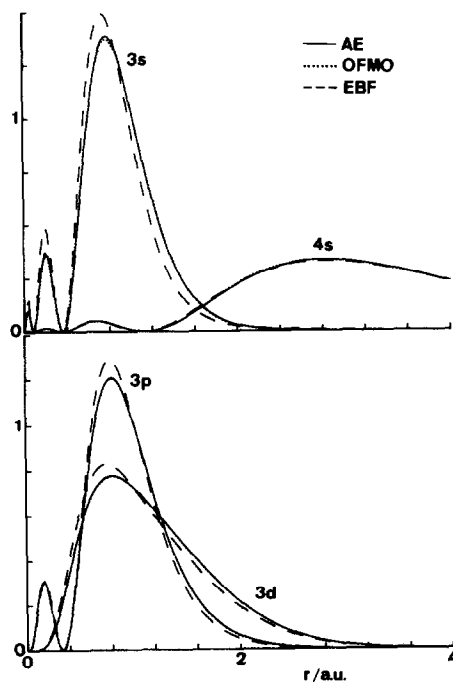


FIG. 3. Radial charge densities of the $3s, 4s$, and $3p, 3d$ orbitals corresponding to the AE (solid lines), MP-OFMO (dotted lines) and MP-EBF (dashed lines) calculations.

We have completed the analysis of the two methods by investigating the basis-set dependence of the valence results of both EBF and OFMO model potentials. The stability of the results of a given V_{mp} with different valence basis sets is a desirable property (13). With this idea in mind we have combined the 2ζ , EBF, and OFMO model potentials with the 2ζ , EBF, and OFMO basis sets in a single MP-SCF calculation per combination. Each combination is indicated by specifying the model potential and the valence basis set in this order, separated by a dash. In Table VA we present, first, the results of combining the three model potentials with the 2ζ basis, then the results of combining the 2ζ model potential with the reduced bases, and finally the AE values. We can see that the OFMO- 2ζ combination gives better results than the EBF- 2ζ one, showing that the OFMO potential is better. Also the combination of the 2ζ model potential with the two reduced bases shows that the OFMO basis is more efficient.

In Table VB we can observe the basis set dependence of the results generated by the OFMO and EBF potentials. The tabulated differences (absolute values) show the effects of changing the basis set on the results of each operator. The reference is in each

case the "natural" calculation in which the model potential is combined with its corresponding valence basis set. All quantities show the greater stability of the OFMO results.

Naturally, according to the EBF method of reduction there is not a unique way of eliminating the basis functions. In particular, one might think that a choice different from that shown in Table IVA would give better results. Nevertheless, the search for this improvement would lead to a tedious and nonautomatic process of trial and error. The OFMO method appears to be a faster and easier alternative.

We would like to point out that our results illustrate the two kinds of error appearing in the process of reduction of the valence basis set, one ascribable to the shortening of the basis set, and the other to the limited efficiency of the reduced set. The first error is unavoidable and demands equilibrium between economy and quality. The second one can be minimized, as we have just seen, by using the orbital exponents of the shorter set as free parameters. Obviously, the best orbital exponents would be produced by minimization of the quantity Δ in Eq. (3). We have substituted for this procedure the much more economical and easy OFMO method. The quality of

TABLE V
RESULTS OF MP-SCF CALCULATIONS WHERE THE 2ζ , OFMO, AND EBF MODEL POTENTIALS ARE COMBINED WITH THE 2ζ , OFMO, AND EBF BASIS SETS

V_{mp} -basis	TE	$\epsilon(3s)$	(A) Combined MP-SCF calculations							
			$\epsilon(4s)$	$\epsilon(3p)$	$\epsilon(3d)$	$S(3s)$	$S(4s)$	$S(3p)$	$S(3d)$	
2ζ - 2ζ	-1043.3377	-3.48316	-0.23557	-2.23420	-0.55219	0.99996	0.99999	1.00000	1.00000	
OFMO- 2ζ	-1043.3227	-3.50258	-0.23635	-2.23360	-0.54804	0.99995	0.99997	1.00000	0.99999	
EBF- 2ζ	-1045.9309	-3.51807	-0.23565	-2.28613	-0.57359	0.99958	0.99993	0.99911	0.99869	
2ζ -OFMO	-1043.2802	-3.46855	-0.23490	-2.23421	-0.55538	0.99988	0.99996	0.99998	1.00000	
2ζ -EBF	-1043.0348	-3.41427	-0.23689	-2.18112	-0.52826	0.99422	0.99983	0.99978	0.99996	
AE	-1043.3271	-3.48316	-0.23523	-2.23420	-0.55219					
(B) Basis set dependence										
			Δ TE	$\Delta\epsilon(3s)$	$\Delta\epsilon(4s)$	$\Delta\epsilon(3p)$	$\Delta\epsilon(3d)$			
(OFMO-OFMO)-(OFMO- 2ζ)			0.07680	0.01942	0.00093	0.00061	0.00415	(Absolute values)		
(EBF-EBF)-(EBF- 2ζ)			0.32060	0.03491	0.00115	0.06025	0.02140			

the OFMO results makes us feel that this reduced basis set is probably very close to the best solution that would be obtained by minimizing Δ .

Results

In Table VI we present the MP-OFMO parameters corresponding to the SPDS and DS calculations. The close resemblance between the OFMO and 2ζ model potentials discussed above for the Cr atom is found throughout the transition series. The OFMO model potentials show, in all cases, the correct asymptotic behavior at $r \rightarrow 0$ and $r \rightarrow \infty$. Moreover, the core shielding increases with Z in the range $0 < r < 1$ a.u., as observed within the MP- 2ζ calculations in Fig. 1.

In Tables VII and VIII we collect the OFMO basis sets for Sc–Zn corresponding to the SPDS and DS calculations, respectively. These pseudoorbitals, their corre-

sponding MP-OFMO operators (shown in Table VI), and the core-projection operators constructed with the AE 2ζ core AOs of Ref. (53), constitute the information required to perform molecular MP-SCF calculations on transition metal clusters.

Finally, in Table IX we present the results of the SPDS and DS MP-OFMO calculations for Sc–Zn corresponding to the highest-spin states of the $3d^n 4s^2$ configurations. The results for the Fe atom can be compared to the corresponding MP- 2ζ values appearing in Table III. This comparison reveals that the MP-OFMO scheme works very efficiently: the approximate representations of the valence shell found with and without basis reduction are nearly identical. In Table IX we also observe that the SPDS and DS MP-OFMO orbital energies reproduce the AE values within 10^{-4} a.u. for all the elements of the $3d$ series. Furthermore, the shape of the MP-OFMO or-

TABLE VI
MODEL POTENTIAL PARAMETERS FOR THE ELEMENTS OF $3d$ TRANSITION SERIES^a

Atom	Part.	A_1	A_2	A_3	α_1	α_2	α_3
Sc d^1 -2D	SPDS	0.951090	0.134534		6.603623	5.640197	
	DS	6.131269	11.299817	6.611602	7.364260	5.269040	2.514490
Ti d^2 -3F	SPDS	0.871485	0.053498		6.985352	5.036880	
	DS	4.748434	7.722201	5.888990	8.031507	5.592652	2.778723
V d^3 -4F	SPDS	0.804192	0.032587		7.372989	5.025068	
	DS	3.738188	6.064934	4.684884	7.960857	5.636509	2.918709
Cr d^4 -5D	SPDS	0.744164	-2.823967		7.463099	11.874363	
	DS	3.215495	3.653550	3.549836	8.159921	4.553626	3.072404
Mn d^5 -6S	SPDS	0.694189	-2.747250		7.842051	11.707725	
	DS	2.822279	5.462301	1.205623	9.053839	4.152701	2.933787
Fe d^6 -5D	SPDS	0.651023	-1.932285		8.317794	13.949235	
	DS	2.090378	4.840871	0.451412	7.478971	4.342367	2.148292
Co d^7 -4F	SPDS	0.613439	-0.068515		8.891388	7.979592	
	DS	1.964127	5.277421	0.127741	8.841077	4.374825	1.778116
Ni d^8 -3F	SPDS	0.579002	-0.054019		9.269925	7.144648	
	DS	1.755046	4.822788	0.094792	9.095943	4.506583	1.735900
Cu d^9 -2D	SPDS	0.548260	-0.035937		9.647781	6.366239	
	DS	1.665845	4.756398	0.058143	10.010288	4.673780	1.716317
Zn d^{10} -1S	SPDS	0.520397	-0.116238		10.018456	7.791328	
	DS	1.533803	4.616713	0.023256	10.511225	4.825718	1.378862

^a The optimization has been carried out in the highest-spin state of the $3d^n 4s^2$ configuration ($n = 1, 10$) using the OFMO basis sets. SPDS and DS partitions are included.

TABLE VII
OFMO BASIS SETS AND HFR COEFFICIENTS CORRESPONDING TO THE SPDS MP-OFMO CALCULATIONS FOR Sc-Zn

Orb.	STO	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.
		Sc		Ti		V		Cr		Mn	
3s	1s	5.60918	0.622281	5.77639	0.659151	5.94967	0.692833	6.13764	0.722258	6.32033	0.749527
	2s	8.27480	-0.977221	8.68521	-1.017766	9.09951	-1.053090	9.52063	-1.082617	9.94052	-1.108499
	3s	3.37213	1.030433	3.58730	1.026362	3.79539	1.021287	3.99888	1.016060	4.19582	1.009861
	4s	1.61155	0.028652	1.69943	0.028628	1.78364	0.028534	1.86295	0.028493	1.93730	0.028730
	4s	0.93699	-0.008003	0.97270	-0.008054	1.00679	-0.008060	1.03854	-0.008114	1.06767	-0.008328
4s	1s		-0.147080		-0.151605		-0.154868		-0.156850		-0.158003
	2s		0.232495		0.235626		0.236926		0.236611		0.235133
	3s		-0.282823		-0.274472		-0.265626		-0.256793		-0.247675
	4s		0.468096		0.471223		0.470856		0.470246		0.468464
	4s		0.642064		0.641488		0.643797		0.646017		0.649093
3p	2p	8.56584	-0.335162	9.05429	-0.343685	9.54238	-0.350797	10.02993	-0.356772	10.51730	-0.361390
	3p	3.56846	0.684519	3.83438	0.695732	4.09881	0.703508	4.36337	0.708033	4.62768	0.708372
	3p	2.32357	0.392356	2.46995	0.385669	2.61367	0.382056	2.75769	0.381339	2.90143	0.384456
3d	3d	4.22244	0.359534	4.67000	0.363345	5.05186	0.371746	5.40992	0.379983	5.76739	0.384936
	3d	1.74647	0.765761	1.98614	0.756636	2.17279	0.747313	2.34014	0.739234	2.50969	0.733755
		Fe		Co		Ni		Cu		Zn	
3s	1s	6.54432	0.771476	6.76976	0.789631	7.00105	0.806293	7.23717	0.821148	7.47480	0.834096
	2s	10.37332	-1.131738	10.80841	-1.149532	11.24623	-1.165746	11.68635	-1.180021	12.12798	-1.191857
	3s	4.40108	1.006513	4.60160	1.002543	4.80034	0.999006	4.99757	0.995762	5.19183	0.992532
	4s	2.01962	0.027770	2.09712	0.028357	2.17360	0.028340	2.24774	0.028279	2.31743	0.028432
	4s	1.10063	-0.007900	1.13115	-0.008175	1.16105	-0.008183	1.18967	-0.008176	1.21604	-0.008311
4s	1s		-0.158731		-0.159107		-0.158708		-0.157866		-0.156501
	2s		0.234295		0.233035		0.230835		0.228194		0.224915
	3s		-0.241061		-0.235067		-0.228737		-0.222554		-0.216289
	4s		0.467548		0.467110		0.464681		0.462248		0.459928
	4s		0.651865		0.653967		0.657773		0.661475		0.664892
3p	2p	11.00300	-0.367004	11.48854	-0.371635	11.97336	-0.375716	12.45746	-0.379475	12.93943	-0.382759
	3p	4.89117	0.707801	5.15576	0.715661	5.42273	0.715290	5.69213	0.713459	5.98922	0.696690
	3p	3.04805	0.386238	3.19588	0.383114	3.34700	0.386117	3.50151	0.390383	3.69392	0.409149
3d	3d	6.06828	0.402108	6.38612	0.410025	6.70551	0.418017	7.02531	0.425013	7.34928	0.429442
	3d	2.61836	0.721264	2.74495	0.715445	2.87381	0.709312	3.00372	0.703867	3.13941	0.700256

TABLE VIII
OFMO BASIS SETS AND HFR COEFFICIENTS CORRESPONDING TO THE DS MP-OFMO CALCULATIONS IN THE HIGHEST-SPIN STATE OF THE 3dⁿ4s² CONFIGURATION (n = 1,10) FOR Sc-Zn

Orb.	STO	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.	Exp.	Coef.
		Sc		Ti		V		Cr		Mn	
4s	1s	5.91914	-0.137437	6.22748	-0.143038	6.54627	-0.142784	6.87040	-0.143781	7.20124	-0.145016
	2s	8.59417	0.215671	9.05484	0.222556	9.52537	0.222240	10.00056	0.222195	10.48172	0.222078
	3s	3.42929	-0.257587	3.67997	-0.253599	3.92318	-0.246311	4.16309	-0.240038	4.39776	-0.234302
	4s	1.54564	0.504991	1.62661	0.510130	1.70518	0.507519	1.77961	0.505334	1.84963	0.502743
	4s	0.91747	0.596349	0.95236	0.592459	0.98607	0.595933	1.01754	0.598955	1.04648	0.602342
3d	3d	4.22244	0.359425	4.67000	0.367352	5.05186	0.382436	5.40992	0.383806	5.76739	0.397178
	3d	1.74647	0.765849	1.98614	0.753387	2.17279	0.738494	2.34014	0.736056	2.50969	0.723459
		Fe		Co		Ni		Cu		Zn	
4s	1s	7.52192	-0.113939	7.85030	-0.119262	8.18289	-0.116741	8.51802	-0.122787	8.85745	-0.121499
	2s	10.95344	0.180666	11.43207	0.187060	11.91440	0.183037	12.39886	0.190739	12.88701	0.188335
	3s	4.63536	-0.206931	4.86896	-0.205908	5.09950	-0.199901	5.32850	-0.200520	5.55522	-0.195294
	4s	1.92902	0.471899	2.00375	0.470107	2.07775	0.464711	2.14978	0.468066	2.21785	0.461711
	4s	1.07956	0.632658	1.11020	0.635851	1.14030	0.642399	1.16914	0.640945	1.19579	0.648164
3d	3d	6.06828	0.392799	6.38612	0.413293	6.70551	0.418048	7.02531	0.429371	7.34928	0.439147
	3d	2.61836	0.729112	2.74495	0.712656	2.87381	0.709285	3.00372	0.700098	3.13941	0.691805

TABLE IX
 SPDS AND DS MP-OFMO RESULTS FOR Sc–Zn ($d^n s^2$ -L STATES), AS COMPARED WITH THE AE RESULTS

		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\epsilon(3s)$	AE	-2.56216	-2.86513	-3.17131	-3.48316	-3.79670	-4.14242	-4.49019	-4.84609	-5.21057	-5.57917
	SPDS MP	-2.56216	-2.86512	-3.17131	-3.48316	-3.79670	-4.14242	-4.49019	-4.84609	-5.21057	-5.57917
$\epsilon(4s)$	AE	-0.20824	-0.21807	-0.22698	-0.23523	-0.24262	-0.25129	-0.25907	-0.26640	-0.27338	-0.27973
	SPDS MP	-0.20841	-0.21825	-0.22717	-0.23542	-0.24282	-0.25126	-0.25920	-0.26651	-0.27343	-0.27978
	DS MP	-0.20824	-0.21807	-0.22698	-0.23523	-0.24262	-0.25129	-0.25907	-0.26640	-0.27338	-0.27973
$\epsilon(3p)$	AE	-1.56990	-1.78759	-2.00839	-2.23420	-2.46116	-2.71718	-2.97456	-3.23877	-3.51016	-3.78452
	SPDS MP	-1.56990	-1.78765	-2.00839	-2.23421	-2.46116	-2.71718	-2.97456	-3.23880	-3.51016	-3.78452
$\epsilon(3d)$	AE	-0.33810	-0.43184	-0.49698	-0.55219	-0.61762	-0.61788	-0.63868	-0.66183	-0.68608	-0.71910
	SPDS MP	-0.33810	-0.43184	-0.49698	-0.55219	-0.61762	-0.61788	-0.63868	-0.66183	-0.68608	-0.71910
	DS MP	-0.33810	-0.43184	-0.49698	-0.55219	-0.61762	-0.61788	-0.63869	-0.66183	-0.68608	-0.71910
-TE ^a	AE	759.7264	848.3885	942.8573	1043.327	1149.814	1262.372	1381.320	1506.752	1638.803	1777.670
	SPDS MP	759.7723	848.4186	942.8674	1043.246	1149.694	1262.372	1381.177	1506.569	1638.595	1777.318
	DS MP	759.7267	848.3908	942.8724	1043.274	1149.869	1262.170	1381.229	1506.560	1638.752	1777.813
SPDS-MP-OFMO											
	$S(3s)^b$	0.99989	0.99989	0.99989	0.99990	0.99989	0.99990	0.99990	0.99990	0.99991	0.99991
	$S(4s)$	0.99998	0.99998	0.99997	0.99996	0.99997	0.99997	0.99997	0.99996	0.99996	0.99996
	$S(3p)$	0.99998	0.99996	0.99998	0.99999	0.99999	0.99998	0.99999	0.99999	0.99999	0.99999
	$S(3d)$	1.00000	1.00000	1.00000	1.00000	0.99999	1.00000	1.00000	1.00000	1.00000	0.99999
	$S(1s,3s)^c$	0.00030	0.00026	0.00027	0.00013	0.00011	0.00017	0.00022	0.00020	0.00018	0.00017
	$S(2s,3s)$	0.01012	0.00990	0.00958	0.00954	0.00952	0.00858	0.00838	0.00806	0.00772	0.00759
	$S(1s,4s)$	0.00003	0.00002	0.00002	0.00002	0.00002	0.00001	0.00001	0.00001	0.00002	0.00002
	$S(2s,4s)$	0.00219	0.00206	0.00194	0.00187	0.00181	0.00156	0.00148	0.00137	0.00127	0.00121
	$S(2p,3p)$	0.00239	0.00231	0.00222	0.00221	0.00220	0.00196	0.00190	0.00182	0.00173	0.00170
DS-MP-OFMO											
	$S(4s)^b$	0.99987	0.99991	0.99992	0.99992	0.99995	0.99956	0.99966	0.99964	0.99979	0.99978
	$S(3d)$	1.00000	1.00000	0.99997	1.00000	0.99998	0.99995	1.00000	1.00000	1.00000	0.99998
	$S(1s,4s)^c$	0.00006	0.00055	0.00035	0.00079	0.00107	0.00091	0.00039	0.00043	0.00000	0.00005
	$S(2s,4s)$	0.00343	0.00284	0.00225	0.00246	0.00207	0.00573	0.00486	0.00490	0.00378	0.00348
	$S(3s,4s)$	0.01518	0.01239	0.01175	0.01039	0.00840	0.02269	0.01853	0.01874	0.01486	0.01382

Note. All numbers in a.u.

^a The total electronic energy is calculated as $E_{\text{val}} + E_{\text{core}}$. E_{val} is the valence electronic energy evaluated with the Hamiltonian of (1) without the projection terms. $E_{\text{core}} = 2\sum_c(T_c + V_c) + \sum_{c,d}(2J_{cd} - K_{cd})$.

^b $S(nl) = \langle \phi_{nl}^{\text{AE}} | \phi_{nl}^{\text{MP}} \rangle$.

^c $S(nl, n'l) = \langle \phi_{nl}^{\text{AE}} | \phi_{n'l}^{\text{MP}} \rangle$; $n \in \text{core}$, $n' \in \text{valence}$.

bitals is very close to the shape of the AE orbitals, as the $\langle \phi_{nl}^{\text{AE}} | \phi_{nl}^{\text{MP}} \rangle$ integrals reveal. Thus, SPDS and DS partitions give essentially the same description of the MP orbitals, although the core–valence orthogonality is somewhat poorer in the DS calculation.

6. Transferability of the Model Potentials

It is well known that considerable charge transfer occurs upon molecular formation. This effect changes from state to state and with nuclear configuration. In transition-metal compounds many empirical arguments provide strong evidence for fractional charges most frequently being

between 1 and 2.3, even for $M(\text{III})$ and $M(\text{IV})$ compounds. Accordingly, it is desirable that the model potentials optimized for a given electronic state describe adequately the electronic characteristics of other states (57). To check on this property of the V_{mp} 's we have computed a collection of quantities corresponding to different multiplets and different oxidation states of $3d$ atoms. In this section we give some representative results.

An interesting property to be examined is the orbital energy. In Table X we have collected orbital energies of the $3s$, $3p$, $3d$, and $4s$ AOs corresponding to SPDS MP-OFMO calculations for different multiplets of Fe, Fe^+ , and Fe^{2+} . These calculations have

TABLE X
ORBITAL ENERGIES OF THE VALENCE AOs
CORRESPONDING TO THE SPDS- AND DS-MP
CALCULATIONS FOR DIFFERENT MULTIPLETS OF Fe,
Fe⁺, AND Fe²⁺^a

		$\epsilon(3s)$	$\epsilon(4s)$	$\epsilon(3p)$	$\epsilon(3d)$
Fe, $d^6s^2\text{-}^5D$	A	-4.14242	-0.25129	-2.71718	-0.61788
	B	-4.14242	-0.25166	-2.71718	-0.61788
	C	-4.14242	-0.25126	-2.71718	-0.61788
	D		-0.25129		-0.61788
Fe, $d^6s^2\text{-}^3H$	A	-4.14604	-0.25143	-2.72052	-0.58591
	B	-4.14602	-0.25180	-2.72051	-0.58592
	C	-4.14599	-0.25139	-2.72055	-0.58599
	D		-0.25141		-0.58676
Fe, $d^6s^2\text{-}^1S$	A	-4.15546	-0.25180	-2.72922	-0.50247
	B	-4.15541	-0.25216	-2.72918	-0.50248
	C	-4.15529	-0.25172	-2.72935	-0.50273
	D		-0.25173		-0.50554
Fe, $d^7s\text{-}^5F$	A	-3.76762	-0.19825	-2.36673	-0.25277
	B	-3.76703	-0.19858	-2.36711	-0.25345
	C	-3.76471	-0.19806	-2.36262	-0.24975
	D		-0.19920		-0.22187
Fe, $d^8\text{-}^3F$	A	-3.33484		-1.95870	0.15889
	B	-3.33556		-1.95936	0.15874
	C	-3.33628		-1.95692	0.15973
	D				0.21258
Fe ⁺ , $d^7\text{-}^4F$	A	-4.07534		-2.67729	-0.56074
	B	-4.07614		-2.67805	-0.56178
	C	-4.07614		-2.67577	-0.56026
	D				-0.52682
Fe ²⁺ , $d^6\text{-}^5D$	A	-4.83311		-3.41300	-1.30858
	B	-4.83405		-3.41394	-1.30945
	C	-4.83318		-3.41271	-1.30816
	D				-1.29837
Fe ²⁺ , $d^5s\text{-}^7S$	A	-5.17103	-0.96776	-3.72371	-1.67855
	B	-5.17140	-0.96925	-3.72415	-1.67860
	C	-5.16939	-0.96698	-3.72563	-1.67922
	D		-0.95670		-1.70400
Fe ²⁺ , $d^4s^2\text{-}^5D$	A	-5.51973	-1.00870	-4.04434	-1.97014
	B	-5.51947	-1.01002	-4.04425	-1.96922
	C	-5.51963	-1.00626	-4.05462	-1.97828
	D		-1.00012		-2.04374

^a A, B, C, and D stand for AE, SPDS MP-2 ζ , SPDS MP-OFMO, and DS MP-OFMO calculations, respectively. All numbers in a.u.

been performed with the basis sets, core orbitals, and V_{mp} 's of the $3d^64s^2\text{-}^5D$ ground state of the Fe atom. The orbital energies corresponding to states of the $3d^64s^2$ configuration differ by less than 10^{-4} a.u. from the AE 2 ζ values. The deviations are larger for states of other configurations although, in the worst case, they are smaller than 10^{-2} a.u. As expected, the discrepancies turn out to be of order 10^{-2} a.u. and, in some cases, 10^{-1} a.u. in the DS MP-OFMO calculations (see Table X).

To complete this analysis we present in Table XI several electronic transition energies involving different states of V, Mn, Fe, and Ni. Ionization potentials for V, Mn, and Ni are collected in Table XII. We recall that numbers in Tables X, XI, and XII should contain important relaxation effects since we have used a unique basis set for all these calculations. In Tables XI and XII we observe that these electronic transitions and IP's are very well computed with the SPDS 2 ζ and the SPDS-OFMO model potentials optimized in the ground states of the neutral atoms, even in cases of extensive ionizations ($V \rightarrow V^{5+}$ or $Ni \rightarrow Ni^{10+}$). We conclude that these V_{mp} 's reproduce

TABLE XI
ELECTRONIC TRANSITIONS OF V, Mn, Fe, Fe²⁺, AND Ni CORRESPONDING TO THE SPDS AND DS PARTITIONS^a

	SPDS-MP-		DS-MP- -OFMO	AE-2 ζ	Expt. ^b
	-2 ζ	-OFMO			
V $d^3s^2\text{-}^4F \rightarrow$					
4P	14500	14483	14596	14494	9343
2G	14584	14568	14674	14578	10635
$d^4s\text{-}^6D$	13590	13448	17263	13528	1924
V ⁺ $d^4\text{-}^3D$	54463	54302	58472	54309	54567
$d^3s\text{-}^3F$	45382	45496	45512	45330	57287
Mn $d^5s^2\text{-}^6S \rightarrow$					
6G	32236	32146	32427	32241	25279
4P	37205	37102	37423	37201	27230
$d^6s\text{-}^6D$	47615	47178	51524	47626	17301
4H	69233	68761	73142	69244	34268
4G	74738	74250	78640	74731	37611
$d^7\text{-}^4F$	151710	150568	165379	151811	45064
4P	167874	166698	181448	167986	51690
Fe $d^6s^2\text{-}^5D \rightarrow$					
3H	22389	22351	22213	22386	19173
1S	80876	80804	80253	80876	
$d^7s\text{-}^3F$	35829	35829	40201	35818	7057
$d^8\text{-}^3F$	141465	141458	155024	140617	32863
Fe ⁺ $d^7\text{-}^4F$	79402	79279	85033	79296	65714
Fe ²⁺ $d^6\text{-}^5D$	170519	170273	172428	170246	194244
Fe ²⁺ $d^6\text{-}^5D \rightarrow$					
$d^5s\text{-}^7S$	24807	25356	26383	25021	29666
$d^4s^2\text{-}^5D$	160936	162988	172483	161358	
Ni $d^8s^2\text{-}^3F \rightarrow$					
1D	16421	16395	16393	16417	12994
3P	19915	19882	19878	19906	15169
$d^9s\text{-}^3D$	35963	35827	41062	36016	204
1D	36774	36619	41869	36784	2882
$d^{10}s\text{-}^1S$	138276	137845	153950		14201

^a All numbers in a.u.

^b Ref. (56).

TABLE XII
 IONIZATION POTENTIALS OF V, Mn, AND Ni^a

		I	II	III	IV	V	VI	VII	VIII	IX	X
V	AE-2 ζ	6.734	12.331	28.84	46.27	63.73					
	SPDS-MP-2 ζ	6.753	13.344	28.86	46.30	63.77					
	SPDS-MP-OFMO	6.733	12.355	28.86	46.33	63.93					
	DS-MP-OFMO	7.250			59.32	72.93					
	Expt. ^b	6.74	14.65	29.310	46.707	65.23					
Mn	AE-2 ζ	5.853	14.531	33.40	51.70	72.31	94.31	116.51			
	SPDS-MP-2 ζ	5.865	14.562	33.42	51.73	72.33	94.34	116.53			
	SPDS-MP-OFMO	5.869	14.540	33.44	51.76	72.42	94.56	117.04			
	DS-MP-OFMO	5.873	14.608	33.98	53.64	76.21					
	Expt. ^b	7.453	15.640	33.667	51.2	72.4	95	119.27			
Ni	AE-2 ζ	10.014	12.365	33.83	55.92	77.12	108.48	132.51	160.03	189.74	219.68
	SPDS-MP-2 ζ	10.017	12.399	33.86	55.95	77.14	108.47	132.50	159.99	189.66	219.56
	SPDS-MP-OFMO	9.987	12.409	33.87	55.98	77.23	108.67	132.88	160.68	190.82	221.35
	DS-MP-OFMO	10.771	11.790	33.94	56.91	79.21	112.35	138.66	169.32	203.09	237.67
	Expt. ^b	7.635	18.168	35.17	54.9	75.5	108	133	162	193	224.5

^a All energies in eV.

^b Ref. (58).

faithfully the predictions of the reference AE calculation. Once again, the DS calculation is uniformly less accurate and even rather poor in some cases.

Some of the electronic transitions in Table XI deviate noticeably from the observed values, due to relaxation and correlation errors. The point here, however, is the simulation of the reference calculation. Deviation from the experiment is another problem that can be largely attenuated in molecular calculations by means of corrections such as those discussed in Ref. (29). Otherwise, they require sophisticated non-empirical methodologies. On the other hand, AE 2 ζ and MP-OFMO IPs show a very good agreement with the observed values (Table XII), mainly in highly ionized states. This remarkable result is probably due to a cancellation between correlation and relaxation energies.

The results presented in this paper show that the SPDS model potentials are widely transferable to states of different electronic configurations, within a given system, and

even to states of different ions of a given transition metal. Furthermore, the reduction of the basis set presented here has negligible effects on this transferability. Thus, we think that it is reasonable to expect that these V_{mp} 's will be able to reproduce closely the core-valence interactions in molecular and solid-state calculations involving 3d metals. They should be an appropriate tool for investigating many complicated features of the electronic structure of the 3d ions in crystal lattices with practically STO 2 ζ quality.

Acknowledgments

The authors are very grateful to Dr. Luis Seijo for his close collaboration in the design of a project directed to the incorporation of the model potential method of Huzinaga *et al.* (12) into the methodology of Richardson *et al.* (23), of which this work is a first step. This project comes naturally from the conclusions of his recent work on CrF₆³⁻ (32). Financial support from the Comisión Asesora para la Investigación Científica y Técnica is also gratefully acknowledged.

References

1. J. C. PHILLIPS AND L. KLEINMAN, *Phys. Rev.* **116**, 287 (1959).
2. J. D. WEEKS, A. HAZI, AND S. A. RICE, *Adv. Chem. Phys.* **16**, 283 (1969).
3. C. F. MELIUS AND W. A. GODDARD III, *Phys. Rev. A* **10**, 1528 (1974).
4. L. R. KAHN, P. BAYBUTT, AND D. G. TRUHLAR, *J. Chem. Phys.* **65**, 3826 (1976).
5. A. REDONDO, W. A. GODDARD III, AND T. C. MCGILL, *Phys. Rev. B* **15**, 5038 (1977).
6. P. A. CHRISTIANSEN, Y. S. LEE, AND K. S. PITZER, *J. Chem. Phys.* **71**, 4445 (1979).
7. R. N. DIXON AND I. L. ROBERTSON, *Mol. Phys.* **37**, 1223 (1979).
8. PH. DURAND AND J. C. BARTHELAT, in "Localization and Delocalisation in Quantum Chemistry" (O. Chalvet et al., Eds.), Vol. II, p. 91, Reidel, Dordrecht, 1976.
9. S. TOPIOL, J. MOSKOWITZ, AND C. F. MELIUS, *J. Chem. Phys.* **70**, 3008 (1979).
10. S. C. LEASURE, T. P. MARTIN, AND G. G. BALINT-KURTI, *J. Chem. Phys.* **80**, 1186 (1984).
11. M. KRAUSS AND W. J. STEVENS, *Annu. Rep. Phys. Chem.* **35**, 357 (1984).
12. (a) V. BONIFACIC AND S. HUZINAGA, *J. Chem. Phys.* **60**, 2779 (1974); (b) **62**, 1507 (1975); (c) **62**, 1509 (1975); (d) **64**, 956 (1976); (e) **65**, 2322 (1976).
13. (a) Y. SAKAI AND S. HUZINAGA, *J. Chem. Phys.* **76**, 2537 (1982); (b) **76**, 2552 (1982).
14. S. LARSSON AND J. W. D. CONNOLLY, *Chem. Phys. Lett.* **20**, 323 (1973).
15. S. LARSSON AND J. W. D. CONNOLLY, *J. Chem. Phys.* **60**, 1514 (1974).
16. H. ADACHI, S. SHIOKAWA, M. TSUKADA, C. SATOKO, AND S. SUGANO, *J. Phys. Soc. Jpn.* **47**, 1528 (1979).
17. B. E. BURNSTEIN AND F. A. COTTON, *Faraday Symp. R. Soc. Chem.* **14**, 180 (1980).
18. W. HEIJSER, E. J. BAERENDS, AND P. ROS, *Faraday Symp. R. Soc. Chem.* **14**, 211 (1980).
19. L. SCHEIRE, P. PHARISEAU, R. NUYS, A. E. FOTI, AND V. H. SMITH, *Physica (Utrecht)* **101**, 22 (1980).
20. D. A. CASE, *Annu. Rev. Phys. Chem.* **33**, 151 (1982).
21. J. EMERY AND J. C. FAYET, *Solid State Commun.* **33**, 801 (1980).
22. J. EMERY, A. LEBLE, AND J. C. FAYET, *J. Phys. Chem. Solids* **42**, 789 (1981).
23. J. W. RICHARDSON, T. F. SOULES, D. M. VAUGHT, AND R. R. POWELL, *Phys. Rev. B* **4**, 1721 (1971).
24. J. W. RICHARDSON, D. M. VAUGHT, T. F. SOULES, AND R. R. POWELL, *J. Chem. Phys.* **50**, 3633 (1969).
25. T. F. SOULES AND J. W. RICHARDSON, *Phys. Rev. Lett.* **25**, 110 (1970).
26. T. F. SOULES, J. W. RICHARDSON, AND D. M. VAUGHT, *Phys. Rev. B* **3**, 2186 (1971).
27. B. L. KALMAN AND J. W. RICHARDSON, *J. Chem. Phys.* **55**, 4443 (1971).
28. T. F. SOULES, E. J. KELLY, D. M. VAUGHT, AND J. W. RICHARDSON, *Phys. Rev. B* **6**, 1519 (1972).
29. (a) L. PUEYO AND J. W. RICHARDSON, *J. Chem. Phys.* **67**, 3577 (1977); (b) **67**, 3583 (1977).
30. L. SEJO, L. PUEYO, AND F. GÓMEZ BELTRÁN, *J. Solid State Chem.* **42**, 28 (1982).
31. Z. BARANDIARÁN, L. PUEYO, AND F. GÓMEZ BELTRÁN, *J. Chem. Phys.* **78**, 4612 (1983).
32. L. SEJO, Thesis Dissertation, Universidad de Oviedo, Spain, 1983.
33. (a) Z. BARANDIARÁN AND L. PUEYO, *J. Chem. Phys.* **79**, 1926 (1983); (b) **80**, 1597 (1984).
34. Z. BARANDIARÁN, L. SEJO, AND L. PUEYO, *J. Solid State Chem.* **55**, 236 (1984).
35. S. GUTIÉRREZ ORELLANA AND L. PUEYO, *J. Solid State Chem.* **55**, 30 (1984).
36. L. SEJO, Z. BARANDIARÁN, V. LUAÑA, AND L. PUEYO, *J. Solid State Chem.* **61**, 269 (1986).
37. J. W. RICHARDSON, W. C. NIEUWPOORT, R. R. POWELL, AND W. F. EDGELL, *J. Chem. Phys.* **36**, 1057 (1962).
38. J. W. RICHARDSON, R. R. POWELL, AND W. C. NIEUWPOORT, *J. Chem. Phys.* **38**, 796 (1963).
39. G. HÖJER AND J. CHUNG, *Int. J. Quantum Chem.* **14**, 623 (1978).
40. S. HUZINAGA AND A. A. CANTU, *J. Chem. Phys.* **38**, 796 (1963).
41. Y. SAKAI, *J. Chem. Phys.* **75**, 1303 (1981).
42. D. MCWILLIAMS AND S. HUZINAGA, *J. Chem. Phys.* **63**, 4678 (1975).
43. S. HUZINAGA AND M. YOSHIMINE, *J. Chem. Phys.* **68**, 4486 (1978).
44. O. GROFEN, S. HUZINAGA, AND A. D. MCLEAN, *J. Chem. Phys.* **73**, 402 (1980).
45. P. C. HARIHARAN, W. S. KOSKI, J. J. KAUFMAN, AND R. S. MILLER, *Int. J. Quantum Chem.* **23**, 1493 (1983), and references cited therein.
46. (a) E. O. STEINBORN AND E. J. WENINGER, *Int. J. Quantum Chem.* **11**, 509 (1977); (b) **12**, 103 (1978).
47. C. A. WEATHERFORD AND H. W. JONES, (Eds.), "ETO Multicenter Molecular Integrals," Reidel, Dordrecht (1982).
48. H. P. TRIVELDI AND E. O. STEINBORN, *Phys. Rev. A* **27**, 670 (1983).
49. E. J. WENINGER AND E. O. STEINBORN, *J. Chem. Phys.* **78**, 6121 (1983).

50. J. D. TALMAN, *J. Chem. Phys.* **82**, 2000 (1984).
51. J. O. HIRSCHFELDER, *Annu. Rev. Phys. Chem.* **34**, 1 (1984).
52. E. FRANCISCO, L. SEIJO, AND L. PUEYO, *J. Solid State Chem.*, in press.
53. E. CLEMENTI AND C. ROETTI, *Atom. Data Nucl. Data Tables* **14**, 177 (1974).
54. C. F. MELIUS, B. D. OLAFSON, AND W. A. GODDARD III, *Chem. Phys. Lett.* **28**, 457 (1974).
55. I. G. VINCENT AND J. N. MURRELL, *J. Chem. Soc. Faraday Trans. 2* **73**, 973 (1977).
56. C. E. MOORE, "Atomic Energy Levels," Vol. 2, NBS Circular No. 467, National Bureau of Standards, Washington, D.C., 1952.
57. We are indebted to a referee for illuminating comments on this point.
58. C. E. MOORE, "Analyses of Optical Spectra," NSRDS-NBS 34, National Bureau of Standards, Washington, D.C. 1979.