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# The Maximum Overlap Method: A General and Efficient Scheme for Reducing Basis Sets. Application to the Generation of Approximate AO's for the 3*d* Transition Metal Atoms and Ions

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The method of maximum overlap, often applied to the problem of basis set reduction, is formulated in terms of weighted least squares with orthogonality restrictions. An analytical solution for the linear parameters of the reduced set is given. In this form, the method is a general and efficient scheme for reducing basis sets. As an application, orthogonal radial wavefunctions of the STO type have been obtained for the 3*d* transition metal atoms and ions by simulation of the high-quality sets of Clementi and Roetti. The performance of the reduction has been evaluated by examining several one- and two-electron interactions. Results of these tests reveal that the new functions are highly accurate simulations of the reference AO's. They appear to be appropriate for molecular and solid state calculations.

## Introduction

Most quantum-mechanical calculations on atoms and molecules are usually carried out within the framework of an expansion method. The one-electron orbitals are expressed in terms of a basis set and the expansion coefficients are chosen by minimization of the total energy (*1*). Several high-quality Slater-type (*2*) and Gaussian-type (*3*) bases are available. However, in problems with a large number of electrons or in processes demanding repetitive calculations, smaller basis sets are needed.

On the other hand, many molecular and solid state calculations are carried out by using a basis set of atomic orbitals instead of one of primitive STOs or GTOs. This choice has several advantages, including the automatic one-center orthogonality of the AO's and an easy correlation between the molecular results and the separated-atoms description.

Atomic orbitals useful for molecular and solid state calculations, i.e., expanded over practical, small bases of STOs or GTOs, can be prepared by minimizing the atomic total energy (*4*) but they produce molecular results notably separated from those obtained with better bases (*5*). An interesting alternative approach is to prepare practical AO's (expanded over a small basis set) that accurately reproduce the desired characteristics of a given set of high-quality AO's (expanded over a large basis set). This idea was fruitfully applied by Richardson *et al.* (*6*) to obtaining practical (STO 2$\zeta$) 3*d* AO's for the first transition series, by maximizing their overlap with the high-quality 4$\zeta$ AO's of Watson (*2a*). Later, Kalman discussed

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some algebraic properties of this approach (*7*).

Recently, obtaining practical orbitals has been considered again by Adamowicz (*8*), who proposed a different reduction scheme based on the minimization of the sum of differences of the orbital energies in the two bases. It is clear that for a given basis set, taken as reference, different sets of practical bases can be generated by selecting different requirements.

We are interested in practical AO's that reproduce in a satisfactory manner the characteristics of the high-quality basis sets presently available. For some applications, such as molecular calculations within the valence shell, we want an *optimum* reproduction of the valence segment of the reference basis. In other cases, one might be more interested in the inner part of the wavefunction. A useful reduction method should be able to deal with such different situations easily. In this context, we have found that the methods of Kalman (*7*) and Adamowicz (*8*) are particular cases of the more general and well-known procedure of maximizing the overlap between the reference set and the reduced one by means of weighted least squares with constraining conditions. The arbitrary weighting factors control the characteristics of the new set.

In this paper we present a general formulation of the maximum-overlap method and give the analytical solution for the linear parameters. Using this formulation we have obtained approximate AO's for the $3d$ atoms and ions. The multi-$\zeta$ bases of Clementi and Roetti (*2b*) have been taken as reference. Furthermore, we present numerical results that show the high performance of the reduction method and the accuracy of the approximate radial functions.

## The Method

Let $\{\psi_i^o\}$ be a known orthonormal set of orbitals. Although it is not required in the present method, the $\psi_i^o$'s can be an accurate approximation of the Hartree-Fock solution of an atomic or molecular system and can be expressed in terms of a known basis set $\{\chi_i^o\}$:

$$\psi_i^o = \sum_k^{P_o} \chi_k^o C_{ki}^o \tag{1}$$

or in matrix form:

$$\boldsymbol{\psi}^o = \boldsymbol{\chi}^o \mathbf{C}^o.$$

We want to find another orthonormal set $\{\psi_i\}$ that maximizes the overlap integrals $O_{ii} = \langle \psi_i | \psi_i^o \rangle$. These $\psi_i$'s can also be expanded in terms of a smaller basis set $\{\chi_i\}$:

$$\psi_i = \sum_k^{P} \chi_k C_{ki} \qquad (P < P_o) \quad \text{or}$$

$$\boldsymbol{\psi} = {}_{\chi}\mathbf{C}. \tag{2}$$

The problem is then to find the basis functions $\chi_i$ and the matrix $\mathbf{C}$ that maximize the diagonal elements of the matrix $\mathbf{O}$ with the condition $\boldsymbol{\psi}^\dagger\boldsymbol{\psi} = \mathbf{I}$, the unit matrix. The constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ operate only when $\psi_i$ and $\psi_j$ have the same total symmetry. Therefore, if $\boldsymbol{\psi}$ can be divided in blocks of different symmetry the problem can be solved within each block.

First, we will show that the $\mathbf{C}$ matrix can be found analytically, provided the $\boldsymbol{\chi}$ vector is known. Later on, we shall discuss the obtention of $\boldsymbol{\chi}$. To find $\mathbf{C}$ we use Lagrange's method of undetermined multipliers. The $i$th Lagrangian function to be maximized will be

$$L_i = w_i O_{ii} + \sum_{s=1}^{N} \lambda_{si}(\langle \psi_i | \psi_s \rangle - \delta_{is}) \tag{3}$$

where $w_i$ are weighting factors, $N$ the number of $\psi_i$ orbitals, $\lambda_{si}$ the Lagrange multipliers, and $\delta_{is}$ the Kronecker symbol. From $(\partial L_i/\partial \lambda_{si}) = 0$ we obtain $\langle \psi_i | \psi_s \rangle = \delta_{is}$ or, in matrix form

$$\mathbf{C}^\dagger\mathbf{S}\mathbf{C} = \mathbf{I} \tag{4}$$

where $\mathbf{S} = \chi^\dagger\chi$. Furthermore, we have

$$\frac{\partial L_i}{\partial C_{ki}} = w_i \frac{\partial O_{ii}}{\partial C_{ki}} + \sum_{s=1}^{N} \lambda_{si} \frac{\partial \langle\psi_i|\psi_s\rangle}{\partial C_{ki}} = 0. \quad (5)$$

If we define the overlap matrix

$$\mathbf{B} = \chi^\dagger \boldsymbol{\psi}^{\mathrm{o}} \quad (6)$$

Eq. (5) transforms to

$$w_i B_{ki} + 2\lambda_{ii} \sum_{l=1}^{P} C_{li} S_{kl} + \sum_{s\neq i}^{N} \lambda_{si} \sum_{r=1}^{P} C_{rs} S_{kr} = 0. \quad (7)$$

This equation can be written in the form

$$w_i B_{ki} = \sum_{s=1}^{N} \eta_{si} \sum_{r=1}^{P} C_{rs} S_{kr} \quad (8)$$

where the new set of multipliers $\eta_{si} = -(1 + \delta_{si})\lambda_{si}$ has been introduced. Considering all values of $k$ we can write $w_i\mathbf{B}_i = \mathbf{S}\mathbf{C}\boldsymbol{\eta}_i$, where $\mathbf{B}_i$ and $\boldsymbol{\eta}_i$ are column vectors: $(\mathbf{B}_i)_k = B_{ki}$, $(\boldsymbol{\eta}_i)_k = \eta_{ki}$. The result of maximizing all the $L_j$ functions can be written in the form

$$\mathbf{S}\mathbf{C}\boldsymbol{\eta} = \mathbf{B}\mathbf{w} \quad (9)$$

where $(\boldsymbol{\eta})_{ij} = \eta_{ij}$ and $(\mathbf{B})_{ij} = B_{ij}$.

Equations (9) and (4) must be simultaneously satisfied. Note that $\boldsymbol{\eta}$ is a symmetric matrix because the condition $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ is equivalent to $\langle\psi_j|\psi_i\rangle = \delta_{ji}$. Since the multipliers are real numbers, $\boldsymbol{\eta}$ is Hermitian.

From Eqs. (4) and (9) we find that $\boldsymbol{\eta} = \mathbf{C}^\dagger\mathbf{B}\mathbf{w}$ and after left-multiplying Eq. (9) by $\mathbf{w}^\dagger\mathbf{B}^\dagger\mathbf{S}^{-1}$ we have

$$\boldsymbol{\eta}^2 = \boldsymbol{\eta}\boldsymbol{\eta} = \mathbf{w}^\dagger\mathbf{B}^\dagger\mathbf{S}^{-1}\mathbf{B}\mathbf{w}. \quad (10)$$

Diagonalization of $\boldsymbol{\eta}^2$ gives (*9*)

$$\mathbf{U}^\dagger\boldsymbol{\eta}^2\mathbf{U} = \mathbf{d} = \mathbf{d}^{1/2}\mathbf{d}^{1/2}. \quad (11)$$

From this equation we obtain $\boldsymbol{\eta}$ as

$$\boldsymbol{\eta} = \mathbf{U}\mathbf{d}^{1/2}\mathbf{U}^\dagger. \quad (12)$$

Finally, left-multiplying Eq. (9) by $\mathbf{S}^{-1}$ and right-multiplying by $\boldsymbol{\eta}^{-1}$ we have

$$\mathbf{C} = \mathbf{S}^{-1}\mathbf{B}\mathbf{w}\boldsymbol{\eta}^{-1}. \quad (13)$$

Equation (13) is the wanted analytical solution for the linear coefficients.

The orbital exponents of the basis $\chi$, $\zeta_k$, must be found by minimizing the functional

$$F(\zeta_k) = \sum_{i=1}^{N} W_i(1 - \langle\psi_i|\psi_i^{\mathrm{o}}\rangle) \quad (14)$$

where $W_i$ are weighting factors. Numerical procedures are required for the obtention of the $\zeta_k$'s, since $F(\zeta_k)$ is a non-linear and too involved function of these parameters. In the applications quoted in the next Section, the simple method of Roothaan and Bagus (*10*) has given satisfactory results, in complete agreement with other, generally more efficient, schemes (*11*).

Let us now summarize the main steps of the present method:

1. Selection of a trial set of $\zeta_k$'s.
2. Calculation of $\mathbf{S} = \chi^\dagger\chi$, $\mathbf{B} = \chi^\dagger\boldsymbol{\psi}^{\mathrm{o}}$ and $\mathbf{S}^{-1}$.
3. Calculation of $\boldsymbol{\eta}^2$, Eq. (10), and diagonalization, having $\mathbf{U}$ and $\mathbf{d}$, Eq. (11).
4. Obtention of $\boldsymbol{\eta}$, Eq. (12), and $\boldsymbol{\eta}^{-1}$.
5. Calculation of $\mathbf{C}$, Eq. (13).

Steps 1–5 are repeated until the $\zeta_k$'s minimize $F(\zeta_k)$ in Eq. (14). The $\chi$ and $\mathbf{C}$ matrices define the final orbitals.

If the basis set $\chi$ is fixed, steps 1–5 must be executed only once, and the matrix $\mathbf{C}$ is the wanted result. In this sense, the present scheme could also be applied as an orthogonalization procedure, the initial and final functions having maximum overlap.

## Practical Atomic Wave Functions for the 3*d* Elements

Following the method described in the previous section we have found the approximate AO's for the 3*d* atoms, in their ground state, collected in Table I. Multi-$\zeta$ basis sets of Clementi and Roetti (*2b*) have been used as reference. All calculations have been performed with weighting fac-

## TABLE I

APPROXIMATE AO'S FOR THE 3*d* TRANSITION METAL ATOMS IN THE GROUND STATE

Sc(I) 4s(2) 3d(1)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 20.25135 | .9995821 | -.3553464 | .1351133 | -.0319247 | 2p | 8.45936 | .9692898 | -.3455277 | 3d | 3.49640 | .5217980 |
| 2s | 7.57916 | .0012352 | 1.0640957 | -.4689656 | .1127677 | 3p | 3.86183 | .0912865 | .5202415 | 3d | 1.46828 | .6210154 |
| 3s | 3.47789 | .0003048 | -.0085454 | 1.0807737 | -.2934964 | 3p | 2.49266 | -.0388370 | .5658785 | | | |
| 4s | 1.57703 | -.0002487 | .0050808 | .0477761 | .4917817 | | | | | | | |
| 4s | .92719 | .0001587 | -.0027048 | -.0168758 | .6130821 | | | | | | | |

Ti(I) 4s(2) 3d(2)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 21.22433 | .9997931 | -.3593120 | .1387856 | -.0318112 | 2p | 8.95980 | .9700410 | -.3534851 | 3d | 3.93614 | .5194337 |
| 2s | 8.00480 | .0005833 | 1.0660508 | -.4786483 | .1116790 | 3p | 4.11453 | .0880974 | .5442180 | 3d | 1.69765 | .6160065 |
| 3s | 3.70969 | .0005079 | -.0095213 | 1.0856067 | -.2855499 | 3p | 2.65182 | -.0369697 | .5449747 | | | |
| 4s | 1.64017 | -.0003269 | .0051023 | .0469499 | .5168417 | | | | | | | |
| 4s | .95258 | .0001982 | -.0026818 | -.0168601 | .5900293 | | | | | | | |

V(I) 4s(2) 3d(3)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 22.19826 | .9999918 | -.3628605 | .1418508 | -.0318241 | 2p | 9.45669 | .9710012 | -.3599484 | 3d | 4.28259 | .5285397 |
| 2s | 8.42940 | -.0000199 | 1.0678664 | -.4864590 | .1110991 | 3p | 4.35398 | .0846087 | .5722680 | 3d | 1.85968 | .6054484 |
| 3s | 3.93871 | .0007043 | -.0105256 | 1.0885422 | -.2802616 | 3p | 2.79301 | -.0349819 | .5200450 | | | |
| 4s | 1.74011 | -.0004045 | .0053069 | .0474818 | .5025338 | | | | | | | |
| 4s | .99516 | .0002453 | -.0027339 | -.0166455 | .6067734 | | | | | | | |

Cr(I) 4s(1) 3d(5)-$^{7}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 23.17292 | 1.0001804 | -.3665639 | .1427496 | -.0294802 | 2p | 9.94327 | .9731054 | -.3608374 | 3d | 4.25230 | .5805679 |
| 2s | 8.86415 | -.0005804 | 1.0691151 | -.4853917 | .1020439 | 3p | 4.55151 | .0772856 | .6177829 | 3d | 1.68001 | .5809623 |
| 3s | 4.13446 | .0008705 | -.0100839 | 1.0861240 | -.2564492 | 3p | 2.82529 | -.0303269 | .4811284 | | | |
| 4s | 1.79681 | -.0004408 | .0048492 | .0534357 | .4607289 | | | | | | | |
| 4s | .99223 | .0002407 | -.0022226 | -.0181074 | .6507192 | | | | | | | |

Mn(I) 4s(2) 3d(5)-$^{6}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 24.14714 | 1.0003564 | -.3691776 | .1466178 | -.0310885 | 2p | 10.45069 | .9722877 | -.3698462 | 3d | 4.93752 | .5421265 |
| 2s | 9.28162 | -.0011000 | 1.0708098 | -.4973308 | .1073847 | 3p | 4.84957 | .0790901 | .6070901 | 3d | 2.15253 | .5912117 |
| 3s | 4.38084 | .0010407 | -.0114997 | 1.0935376 | -.2653683 | 3p | 3.07671 | -.0315097 | .4905962 | | | |
| 4s | 1.88093 | -.0005018 | .0051805 | .0475602 | .5104822 | | | | | | | |
| 4s | 1.05182 | .0002798 | -.0026067 | -.0168250 | .6019573 | | | | | | | |

Fe(I) 4s(2) 3d(6)-$^{5}$D

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 25.12190 | 1.0005313 | -.3718948 | .1488512 | -.0310822 | 2p | 10.94715 | .9728355 | -.3744856 | 3d | 5.20238 | .5565098 |
| 2s | 9.70648 | -.0016084 | 1.0721634 | -.5026893 | .1068989 | 3p | 5.09505 | .0769124 | .6234226 | 3d | 2.22946 | .5818387 |
| 3s | 4.60471 | .0012008 | -.0120591 | 1.0958626 | -.2618205 | 3p | 3.22020 | -.0302014 | .4764066 | | | |
| 4s | 1.96575 | -.0005495 | .0052060 | .0474162 | .5105677 | | | | | | | |
| 4s | 1.08746 | .0003042 | -.0025811 | -.0165644 | .6041016 | | | | | | | |

Co(I) 4s(2) 3d(7)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 26.09709 | 1.0006921 | -.3744194 | .1507361 | -.0308612 | 2p | 11.44553 | .9730581 | -.3784978 | 3d | 5.47142 | .5682698 |
| 2s | 10.13171 | -.0020707 | 1.0733603 | -.5069385 | .1056816 | 3p | 5.35768 | .0753343 | .6288716 | 3d | 2.32233 | .5728601 |
| 3s | 4.82462 | .0013567 | -.0124304 | 1.0978002 | -.2568793 | 3p | 3.37543 | -.0290515 | .4729500 | | | |
| 4s | 2.03875 | -.0005789 | .0051578 | .0474283 | .5137749 | | | | | | | |
| 4s | 1.11741 | .0003177 | -.0025258 | -.0165835 | .6025909 | | | | | | | |

Ni(I) 4s(2) 3d(8)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 27.07259 | 1.0008460 | -.3767298 | .1524309 | -.0306320 | 2p | 11.93863 | .9737635 | -.3817178 | 3d | 5.75944 | .5749325 |
| 2s | 10.55674 | -.0025069 | 1.0744575 | -.5105875 | .1044461 | 3p | 5.58584 | .0730729 | .6492790 | 3d | 2.42640 | .5682986 |
| 3s | 5.04312 | .0014801 | -.0127452 | 1.0993620 | -.2521739 | 3p | 3.49597 | -.0277894 | .4545620 | | | |
| 4s | 2.11426 | -.0006181 | .0050980 | .0476677 | .5132650 | | | | | | | |
| 4s | 1.14835 | .0003491 | -.0024724 | -.0166652 | .6047041 | | | | | | | |

Cu(I) 4s(1) 3d(10)-$^{2}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 28.04513 | 1.0010099 | -.3798148 | .1522305 | -.0242754 | 2p | 12.42936 | .9747036 | -.3816597 | 3d | 5.71833 | .6167744 |
| 2s | 11.00585 | -.0029511 | 1.0747036 | -.5052684 | .0818631 | 3p | 5.81158 | .0693572 | .6665595 | 3d | 2.22308 | .5486696 |
| 3s | 5.20749 | .0015310 | -.0104072 | 1.0998687 | -.1968064 | 3p | 3.55085 | -.0252158 | .4417443 | | | |
| 4s | 1.95118 | -.0004895 | .0034598 | .0441861 | .5285045 | | | | | | | |
| 4s | 1.01897 | .0002593 | -.0016307 | -.0163023 | .5925486 | | | | | | | |

Zn(I) 4s(2) 3d(10)-$^{1}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 29.02366 | 1.0011288 | -.3809914 | .1551579 | -.0299002 | 2p | 12.93236 | .9741369 | -.3873900 | 3d | 6.32474 | .5870337 |
| 2s | 11.40952 | -.0032969 | 1.0763234 | -.5157297 | .1012067 | 3p | 6.10285 | .0706414 | .6561700 | 3d | 2.63772 | .5589574 |
| 3s | 5.47091 | .0017210 | -.0129568 | 1.1019163 | -.2419127 | 3p | 3.79737 | -.0260188 | .4508108 | | | |
| 4s | 2.24755 | -.0006676 | .0048649 | .0470905 | .5181990 | | | | | | | |
| 4s | 1.20037 | .0003538 | -.0023189 | -.0163957 | .6028833 | | | | | | | |

## TABLE Ia

### APPROXIMATE AO'S FOR THE MONOPOSITIVE 3*d* IONS IN THE GROUND STATE

Sc(II) 4s(1)3d(1)-$^{3}$D

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 20.25465 | .9995570 | -.3545677 | .1353333 | -.0386548 | 2p | 8.47374 | .9673698 | -.3460895 | 3d | 3.69085 | .4737211 |
| 2s | 7.56340 | .0013126 | 1.0650924 | -.4718055 | .1373791 | 3p | 3.93749 | .0943274 | .4725249 | 3d | 1.57758 | .6608578 |
| 3s | 3.50323 | .0003365 | -.0120466 | 1.0727220 | -.3561030 | 3p | 2.55304 | -.0394728 | .6119473 | | | |
| 4s | 1.78386 | -.0004193 | .0095697 | .0660940 | .3207686 | | | | | | | |
| 4s | 1.18358 | .0002777 | -.0055845 | -.0224501 | .7596836 | | | | | | | |

Ti(II) 4s(1)3d(2)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 21.22745 | .9997733 | -.3584809 | .1390272 | -.0392983 | 2p | 8.96825 | .9689687 | -.3538712 | 3d | 4.04060 | .4937553 |
| 2s | 7.98682 | .0006388 | 1.0671718 | -.4818260 | .1389015 | 3p | 4.15875 | .0900637 | .5156183 | 3d | 1.76316 | .6370456 |
| 3s | 3.73872 | .0005890 | -.0133277 | 1.0772522 | -.3544943 | 3p | 2.69436 | -.0376005 | .5724053 | | | |
| 4s | 1.88264 | -.0005679 | .0097379 | .0656824 | .3486408 | | | | | | | |
| 4s | 1.23108 | .0003702 | -.0055191 | -.0220476 | .7356622 | | | | | | | |

V(II) 4s(1)3d(3)-$^{5}$F

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 22.20236 | .9999676 | -.3620263 | .1420941 | -.0395348 | 2p | 9.46630 | .9698768 | -.3602118 | 3d | 4.37977 | .5056438 |
| 2s | 8.41090 | .0000451 | 1.0689337 | -.4896349 | .1390015 | 3p | 4.40091 | .0868681 | .5418743 | 3d | 1.91866 | .6248758 |
| 3s | 3.96748 | .0007934 | -.0141281 | 1.0813586 | -.3502201 | 3p | 2.84228 | -.0358447 | .5491370 | | | |
| 4s | 1.95536 | -.0006705 | .0096899 | .0655514 | .3826248 | | | | | | | |
| 4s | 1.27004 | .0004235 | -.0054277 | -.0223175 | .7037476 | | | | | | | |

Cr(II) 4s(0)3d(5)-$^{6}$S

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 23.20663 | .9999921 | -.3616727 | .1446131 | 2p | 9.94849 | .9724792 | -.3603961 | 3d | 4.44657 | .5395503 |
| 2s | 8.72816 | -.0001123 | 1.0807512 | -.5094661 | 3p | 4.58254 | .0784189 | .5972150 | 3d | 1.82522 | .6103503 |
| 3s | 4.53650 | .0021464 | -.0514760 | .8440391 | 3p | 2.85640 | -.0306498 | .5010369 | | | |
| 3s | 3.01955 | -.0015816 | .0287665 | .3035838 | | | | | | | |

Mn(II) 4s(1)3d(5)-$^{7}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 24.15151 | 1.0003385 | -.3681926 | .1469492 | -.0399475 | 2p | 10.45755 | .9715133 | -.3701827 | 3d | 5.01856 | .5249347 |
| 2s | 9.25771 | -.0010627 | 1.0721060 | -.5012886 | .1391170 | 3p | 4.88859 | .0806023 | .5847597 | 3d | 2.19945 | .6064101 |
| 3s | 4.41928 | .0011825 | -.0157231 | 1.0852892 | -.3438153 | 3p | 3.11926 | -.0320684 | .5121269 | | | |
| 4s | 2.16345 | -.0008609 | .0097348 | .0670001 | .3929039 | | | | | | | |
| 4s | 1.35867 | .0005276 | -.0051184 | -.0209946 | .6986773 | | | | | | | |

Fe(II) 4s(0)3d(7)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 25.16345 | 1.0003472 | -.3664919 | .1495562 | 2p | 10.94394 | .9732287 | -.3707305 | 3d | 5.01093 | .5672051 |
| 2s | 9.53501 | -.0012406 | 1.0869270 | -.5258144 | 3p | 5.09536 | .0745999 | .6207801 | 3d | 2.02383 | .5879564 |
| 3s | 5.10268 | .0031172 | -.0616870 | .8107006 | 3p | 3.15646 | -.0282142 | .4819982 | | | |
| 3s | 3.42891 | -.0021862 | .0335532 | .3463447 | | | | | | | |

Co(II) 4s(0)3d(8)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 26.14151 | 1.0005120 | -.3687090 | .1516801 | 2p | 11.43963 | .9738113 | -.3749113 | 3d | 5.26852 | .5813642 |
| 2s | 9.94186 | -.0017573 | 1.0892595 | -.5323432 | 3p | 5.33061 | .0726928 | .6392519 | 3d | 2.10270 | .5772596 |
| 3s | 5.36702 | .0035416 | -.0648798 | .8070806 | 3p | 3.29093 | -.0271680 | .4652874 | | | |
| 3s | 3.60808 | -.0024414 | .0348882 | .3535486 | | | | | | | |

Ni(II) 4s(0)3d(9)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 27.12053 | 1.0008101 | -.3704995 | .1535130 | 2p | 11.94061 | .9736474 | -.3788862 | 3d | 5.55889 | .5880140 |
| 2s | 10.35196 | -.0026595 | 1.0913118 | -.5376071 | 3p | 5.61418 | .0719787 | .6345057 | 3d | 2.20920 | .5717878 |
| 3s | 5.63008 | .0039411 | -.0673173 | .8029559 | 3p | 3.46224 | -.0264130 | .4718336 | | | |
| 3s | 3.78046 | -.0026690 | .0358501 | .3608330 | | | | | | | |

Cu(II) 4s(0)3d(10)-$^{1}$S

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 28.08829 | 1.0008219 | -.3739796 | .1550592 | 2p | 12.43275 | .9743814 | -.3814575 | 3d | 5.83709 | .5956689 |
| 2s | 10.82224 | -.0026077 | 1.0859330 | -.5349431 | 3p | 5.83173 | .0699950 | .6555346 | 3d | 2.31356 | .5647968 |
| 3s | 5.64437 | .0032259 | -.0476396 | .9437858 | 3p | 3.57586 | -.0254377 | .4523569 | | | |
| 3s | 3.45447 | -.0020157 | .0237173 | .2183469 | | | | | | | |

Zn(II) 4s(1)3d(10)-$^{2}$S

| STO | Expn. | 1s | 2s | 3s | 4s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 29.02896 | 1.0011078 | -.3801716 | .1553628 | -.0355999 | 2p | 12.94168 | .9732665 | -.3876015 | 3d | 6.42013 | .5706462 |
| 2s | 11.38684 | -.0032579 | 1.0772018 | -.5186497 | .1212039 | 3p | 6.15888 | .0723212 | .6302690 | 3d | 2.70716 | .5723383 |
| 3s | 5.50446 | .0018508 | -.0158684 | 1.0965211 | -.2890584 | 3p | 3.85944 | -.0266395 | .4760219 | | | |
| 4s | 2.50374 | -.0009978 | .0078289 | .0619972 | .4096293 | | | | | | | |
| 4s | 1.49277 | .0005712 | -.0041604 | -.0212596 | .6834154 | | | | | | | |

TABLE Ib

APPROXIMATE AO'S FOR THE DIPOSITIVE 3*d* IONS IN THE GROUND STATE

Sc(III) 3d(1)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 20.27847 | .9993787 | -.3514448 | .1362421 | 2p | 8.50212 | .9634774 | -.3468956 | 3d | 3.93039 | .4257783 |
| 2s | 7.48046 | .0018555 | 1.0745049 | -.4868996 | 3p | 4.09370 | .0990353 | .3884056 | 3d | 1.74692 | .6937778 |
| 3s | 3.80254 | .0009323 | -.0511446 | .7927932 | 3p | 2.65106 | -.0393351 | .6931347 | | | |
| 3s | 2.70730 | -.0009196 | .0320320 | .3372957 | | | | | | | |

Ti(III) 3d(2)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 21.25754 | .9995753 | -.3545878 | .1399105 | 2p | 8.99792 | .9650299 | -.3546261 | 3d | 4.26344 | .4466764 |
| 2s | 7.87358 | .0012003 | 1.0802428 | -.5006001 | 3p | 4.33327 | .0950282 | .4205817 | 3d | 1.91802 | .6722521 |
| 3s | 4.15159 | .0016520 | -.0634415 | .7178701 | 3p | 2.81239 | -.0376467 | .6646025 | | | |
| 3s | 2.98801 | -.0014226 | .0386370 | .4203779 | | | | | | | |

V(III) 3d(3)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 22.23513 | .9997798 | -.3576670 | .1430421 | 2p | 9.48934 | .9668585 | -.3609749 | 3d | 4.57328 | .4649071 |
| 2s | 8.27526 | .0005267 | 1.0842872 | -.5111203 | 3p | 4.55102 | .0906804 | .4611621 | 3d | 2.05853 | .6555985 |
| 3s | 4.45040 | .0022849 | -.0697609 | .6975754 | 3p | 2.95097 | -.0358772 | .6278169 | | | |
| 3s | 3.19162 | -.0018350 | .0413191 | .4470924 | | | | | | | |

Cr(III) 3d(4)-$^{5}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 23.21374 | .9999646 | -.3605154 | .1457388 | 2p | 9.98103 | .9687686 | -.3653014 | 3d | 4.87331 | .4807584 |
| 2s | 8.68063 | -.0000730 | 1.0872802 | -.5195754 | 3p | 4.72510 | .0877190 | .5117448 | 3d | 2.18688 | .6418006 |
| 3s | 4.71971 | .0027702 | -.0733294 | .7015268 | 3p | 3.07239 | -.0355337 | .5793565 | | | |
| 3s | 3.36058 | -.0021247 | .0424202 | .4484696 | | | | | | | |

Mn(III) 3d(5)-$^{6}$S

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 24.19582 | 1.0001379 | -.3625815 | .1480312 | 2p | 10.47213 | .9698194 | -.3704478 | 3d | 5.18183 | .4918734 |
| 2s | 9.05791 | -.0006683 | 1.0943468 | -.5302621 | 3p | 4.97773 | .0834444 | .5351121 | 3d | 2.32361 | .6316458 |
| 3s | 5.13342 | .0034792 | -.0860335 | .6109423 | 3p | 3.20362 | -.0327904 | .5600939 | | | |
| 3s | 3.65270 | -.0025745 | .0476416 | .5468531 | | | | | | | |

Fe(III) 3d(6)-$^{5}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 25.17144 | 1.0003243 | -.3652802 | .1503885 | 2p | 10.96561 | .9708123 | -.3749026 | 3d | 5.43793 | .5099828 |
| 2s | 9.47752 | -.0012474 | 1.0946099 | -.5357521 | 3p | 5.20454 | .0806727 | .5627340 | 3d | 2.39908 | .6188933 |
| 3s | 5.32616 | .0038367 | -.0838093 | .6648961 | 3p | 3.33644 | -.0314396 | .5349621 | | | |
| 3s | 3.75962 | -.0027711 | .0461409 | .4959891 | | | | | | | |

Co(III) 3d(7)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 26.14799 | 1.0005011 | -.3677610 | .1522803 | 2p | 11.45646 | .9719916 | -.3780709 | 3d | 5.74378 | .5171936 |
| 2s | 9.89541 | -.0017937 | 1.0952228 | -.5398994 | 3p | 5.41009 | .0777311 | .5955011 | 3d | 2.51863 | .6136718 |
| 3s | 5.53954 | .0041923 | -.0823765 | .6970310 | 3p | 3.44749 | -.0300822 | .5044024 | | | |
| 3s | 3.88333 | -.0029594 | .0449915 | .4661719 | | | | | | | |

Ni(III) 3d(8)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 27.12882 | 1.0006502 | -.3695249 | .1541782 | 2p | 11.95456 | .9721735 | -.3820283 | 3d | 5.99611 | .5319372 |
| 2s | 10.28700 | -.0022824 | 1.0990546 | -.5473537 | 3p | 5.68088 | .0761302 | .6001358 | 3d | 2.59660 | .6029275 |
| 3s | 5.85838 | .0046320 | -.0881950 | .6748267 | 3p | 3.60412 | -.0288599 | .5020410 | | | |
| 3s | 4.09136 | -.0032051 | .0470205 | .4937795 | | | | | | | |

Cu(III) 3d(9)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 28.10956 | 1.0008187 | -.3710419 | .1557653 | 2p | 12.44599 | .9729974 | -.3846236 | 3d | 6.25146 | .5444223 |
| 2s | 10.66651 | -.0028618 | 1.1046500 | -.5550828 | 3p | 5.89977 | .0739163 | .6223219 | 3d | 2.68766 | .5928065 |
| 3s | 6.24700 | .0052573 | -.0970499 | .6194815 | 4p | 3.72444 | -.0277773 | .4815242 | | | |
| 3s | 4.35458 | -.0035567 | .0500141 | .5549657 | | | | | | | |

Zn(III) 3d(10)-$^{1}$S

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 29.08590 | 1.0009708 | -.3730768 | .1572408 | 2p | 12.94786 | .9726636 | -.3876630 | 3d | 6.52815 | .5523358 |
| 2s | 11.08774 | -.0033114 | 1.1041980 | -.5575389 | 3p | 6.20008 | .0734295 | .6102452 | 3d | 2.79240 | .5864676 |
| 3s | 6.44329 | .0055026 | -.0941057 | .6550059 | 3p | 3.90869 | -.0269779 | .4952094 | | | |
| 3s | 4.46549 | -.0036847 | .0484329 | .5278991 | | | | | | | |

tors $w_i$ and $W_i$ (Eqs. (3) and (14), respectively) equal to unity. Results for mono-, di-, and tripositive ions appear in Tables Ia, Ib, and Ic, respectively.

The simulation process has been accomplished satisfactorily, as the overlap integrals between practical and reference AO's show. Such integrals, averaged over the pe-

## TABLE Ic

### APPROXIMATE AO'S FOR THE TRIPOSITIVE 3*d* IONS IN THE GROUND STATE

Ti(IV) 3d(1)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 21.29816 | .9994494 | -.3484158 | .1398549 | 2p | 9.06436 | .9559140 | -.3628708 | 3d | 4.65052 | .3958511 |
| 2s | 7.09961 | .0013681 | 1.3317721 | -.6376917 | 3p | 4.69006 | .1066758 | .2695608 | 3d | 2.23093 | .7021611 |
| 3s | 6.52868 | .0022397 | -.3472749 | .2431719 | 3p | 3.06799 | -.0384884 | .8069423 | | | |
| 3s | 3.60779 | -.0014955 | .0403922 | 1.0317121 | | | | | | | |

V(IV) 3d(2)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 22.27629 | .9996965 | -.3514667 | .1429556 | 2p | 9.54471 | .9598533 | -.3683596 | 3d | 4.97775 | .4091435 |
| 2s | 7.53319 | .0002498 | 1.3057829 | -.6364580 | 3p | 4.83326 | .1020188 | .3270968 | 3d | 2.39278 | .6899188 |
| 3s | 6.77303 | .0031511 | -.3205948 | .2489416 | 3p | 3.20482 | -.0389392 | .7537329 | | | |
| 3s | 3.80312 | -.0017530 | .0430023 | 1.0206282 | | | | | | | |

Cr(IV) 3d(3)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 23.25443 | .9999322 | -.3543205 | .1456458 | 2p | 10.03486 | .9619049 | -.3731742 | 3d | 5.25519 | .4291013 |
| 2s | 7.95549 | -.0007564 | 1.2881384 | -.6368166 | 3p | 5.05463 | .0976371 | .3632478 | 3d | 2.51797 | .6727652 |
| 3s | 7.02477 | .0039723 | -.3024486 | .2563688 | 3p | 3.34933 | -.0373051 | .7215592 | | | |
| 3s | 3.99622 | -.0020136 | .0450286 | 1.0102955 | | | | | | | |

Mn(IV) 3d(4)-$^{5}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 24.23190 | 1.0001725 | -.3569916 | .1480034 | 2p | 10.50131 | .9664889 | -.3770515 | 3d | 5.53912 | .4448968 |
| 2s | 8.36638 | -.0017482 | 1.2772502 | -.6387339 | 3p | 5.11997 | .0915050 | .4590619 | 3d | 2.63851 | .6598134 |
| 3s | 7.29099 | .0047831 | -.2912043 | .2647743 | 3p | 3.41669 | -.0370073 | .6300538 | | | |
| 3s | 4.18816 | -.0022829 | .0465788 | 1.0011947 | | | | | | | |

Fe(IV) 3d(5)-$^{6}$S

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 25.20836 | 1.0002808 | -.3600925 | .1505984 | 2p | 10.98963 | .9681220 | -.3802833 | 3d | 5.82192 | .4589048 |
| 2s | 9.01949 | -.0017784 | 1.1918348 | -.6011897 | 3p | 5.32372 | .0875960 | .4982234 | 3d | 2.76346 | .6478077 |
| 3s | 7.05850 | .0047045 | -.2009599 | .2698181 | 3p | 3.53388 | -.0352620 | .5939614 | | | |
| 3s | 4.32618 | -.0025578 | .0515126 | .9532687 | | | | | | | |

Co(IV) 3d(6)-$^{5}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 26.16863 | 1.0010271 | -.3653950 | .1535535 | 2p | 11.48863 | .9684676 | -.3840827 | 3d | 6.08328 | .4749462 |
| 2s | 9.83360 | -.0034736 | 1.1064013 | -.5523766 | 3p | 5.59726 | .0853088 | .5063943 | 3d | 2.84268 | .6368411 |
| 3s | 5.87257 | .0047560 | -.1073985 | .5173584 | 3p | 3.69374 | -.0335382 | .5883650 | | | |
| 3s | 4.21101 | -.0033601 | .0570240 | .6514832 | | | | | | | |

Ni(IV) 3d(7)-$^{4}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 27.26292 | .9995054 | -.3575752 | .1491187 | 2p | 11.97923 | .9696310 | -.3866962 | 3d | 6.36348 | .4862318 |
| 2s | 5.87318 | .0045767 | 4.0609734 | -2.0467428 | 3p | 5.80925 | .0824396 | .5366987 | 3d | 2.95033 | .6282883 |
| 3s | 7.41504 | -.0015752 | -3.0536939 | 1.7085933 | 3p | 3.81292 | -.0322166 | .5604461 | | | |
| 3s | 4.74249 | -.0016523 | -.2508602 | 1.1003663 | | | | | | | |

Cu(IV) 3d(8)-$^{3}$F

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 28.14181 | 1.0008701 | -.3665128 | .1559048 | 2p | 12.46602 | .9709445 | -.3893185 | 3d | 6.61363 | .5007835 |
| 2s | 10.21183 | -.0039241 | 1.1909394 | -.6144631 | 3p | 6.00813 | .0793243 | .5713512 | 3d | 3.02887 | .6177405 |
| 3s | 7.87544 | .0064884 | -.2003642 | .3048632 | 3p | 3.92103 | -.0308297 | .5280324 | | | |
| 3s | 4.88526 | -.0033139 | .0541868 | .9265212 | | | | | | | |

Zn(IV) 3d(9)-$^{2}$D

| STO | Expn. | 1s | 2s | 3s | STO | Expn. | 2p | 3p | STO | Expn. | 3d |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1s | 29.11751 | 1.0010423 | -.3686301 | .1574377 | 2p | 12.96612 | .9709315 | -.3918893 | 3d | 6.89745 | .5085404 |
| 2s | 10.65435 | -.0044367 | 1.1807361 | -.6119986 | 3p | 6.28943 | .0781804 | .5694913 | 3d | 3.13403 | .6124385 |
| 3s | 8.03447 | .0069120 | -.1892613 | .3204438 | 3p | 4.08629 | -.0297734 | .5317125 | | | |
| 3s | 5.05203 | -.0035975 | .0552372 | .9068658 | | | | | | | |

riod, appear in Table II. They are always greater than 0.999. Valence AO's 3*p* and 4*s* are particularly well reproduced, with overlaps larger than 0.99995 and 0.9998, respectively. As observed by Richardson *et al.* (*6*), the quality of this simulation increases with the oxidation state.

The optimum orbital exponents show a linear correlation with the nuclear charge *Z*. This correlation, particularly good for exponents of the inner STOs, indicates that the regularity of the Hartree-Fock AO's with *Z* is maintained in the reduced bases.

TABLE II

VALUES OF THE OVERLAP INTEGRALS, AVERAGED OVER THE PERIOD, BETWEEN THE APPROXIMATE AND REFERENCE AO'S

| AO | $M$(I) | $M$(II) | $M$(III) | $M$(IV) |
|---|---|---|---|---|
| 1$s$ | 0.99994 | 0.99995 | 0.99995 | 0.99996 |
| 2$s$ | 0.99954 | 0.99955 | 0.99957 | 0.99963 |
| 3$s$ | 0.99964 | 0.99975 | 0.99978 | 0.99973 |
| 4$s$ | 0.99990 | 0.99995 | — | — |
| 2$p$ | 0.99972 | 0.99972 | 0.99974 | 0.99978 |
| 3$p$ | 0.99997 | 0.99997 | 0.99997 | 0.99996 |
| 3$d$ | 0.99922 | 0.99923 | 0.99959 | 0.99979 |

## Evaluation of the Reduced Bases

### 3d Functions

Besides the overlap integrals in Table II, we will present the results of two different tests on the quality of the simulation process for the 3$d$ AO's. The first one refers to the one-electron integrals $\langle r^n \rangle$ ($n = -2, 1, 2,$ and 3). In Fig. 1 we plot the relative error $(\langle r^n \rangle_x - \langle r^n \rangle_o)/\langle r^n \rangle_o$, where subscripts x,o refer to practical and reference AO's, respectively.

The errors associated with the operators $r^{-2}$ and $r^3$ measure the discrepancies between reduced and reference AO's in the regions near to the nucleus and far apart from it, respectively. When the criterion of maximum overlap is followed, these regions are less accurately reproduced than the segment around the maximum of the radial distribution. Accordingly, the relative error of $\langle r \rangle$ is noticeably smaller. Peaks at the positions of Cr and Cu in Fig. 1 correspond to changes in electronic configuration ($4s^2 3d^n \rightarrow 4s^1 3d^{n+1}$). Apart from these peaks, the relative errors tend to increase

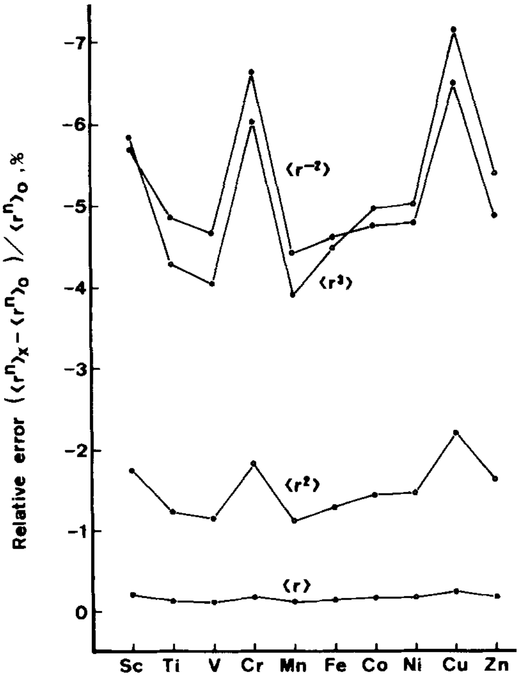

FIG. 1. Relative errors in the calculation of the expectation values $\langle 3d|r^n|3d\rangle$, $n = -2, 1, 2, 3$. *Note*: Subscripts x and o stand for reduced and reference AO's, respectively.

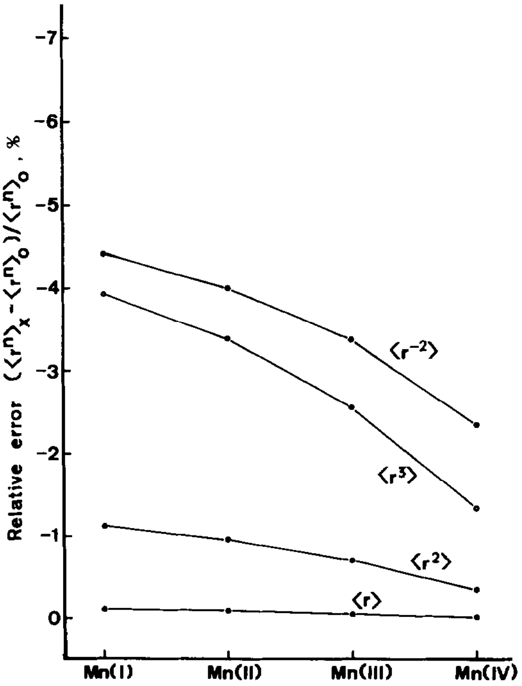

FIG. 2. Relative errors in $\langle 3d|r^n|3d\rangle$ versus the oxidation state of the manganese ions.

TABLE III

LOWER *d*–*d* ELECTRONIC TRANSITIONS ($\text{cm}^{-1}$) OF V(IV), Cr(IV), AND Fe(IV), AS COMPARED WITH THE REFERENCE BASIS (FIRST ROW) AND THE REDUCED BASIS (SECOND ROW)

| V(IV) $3d^2$–$^3$F | | Cr(IV) $3d^3$–$^4$F | | Fe(IV) $3d^5$–$^6$S | |
|---|---|---|---|---|---|
| Transition | $\Delta E$ | Transition | $\Delta E$ | Transition | $\Delta E$ |
| $^3\text{F} \rightarrow {}^1\text{D}$ | 13,782 | $^4\text{F} \rightarrow {}^4\text{P}$ | 17,653 | $^6\text{S} \rightarrow {}^4\text{G}$ | 37,934 |
| | 13,812 | | 17,702 | | 38,078 |
| | 10,536 | | 13,758 | | 32,281 |
| $\rightarrow {}^1\text{G}$ | 21,498 | $\rightarrow {}^2\text{P}$ | 23,824 | $\rightarrow {}^4\text{P}$ | 43,856 |
| | 21,546 | | 23,889 | | 44,025 |
| | 17,968 | | 18,919 | | 35,297 |
| $\rightarrow {}^3\text{P}$ | 16,534 | $\rightarrow {}^2\text{G}$ | 17,940 | $\rightarrow {}^4\text{D}$ | 47,186 |
| | 16,573 | | 17,988 | | 47,363 |
| | 12,776 | | 14,699 | | 38,865 |
| $\rightarrow {}^1\text{S}$ | 53,198 | $\rightarrow {}^2\text{H}$ | 23,824 | $\rightarrow {}^4\text{F}$ | 63,681 |
| | 53,313 | | 23,889 | | 63,921 |
| | 42,039 | | 20,658 | | 52,715 |
| | | $\rightarrow {}^2\text{D}$ | 25,928 | $\rightarrow {}^2\text{I}$ | 54,086 |
| | | | 25,998 | | 54,294 |
| | | | 20,112 | | 47,085 |
| | | $\rightarrow {}^2\text{F}$ | 41,478 | $\rightarrow {}^2\text{H}$ | 66,617 |
| | | | 41,591 | | 66,873 |
| | | | 33,899 | | 56,229 |

*Note*. Third-row entries are experimental values, Ref. (*12a*) for V(IV) and Cr(IV), and Ref. (*12b*) for Fe(IV).

slowly from left to right in the period. Furthermore, these relative errors clearly decrease when the oxidation number increases. This effect is depicted in Fig. 2.

The second test refers to the behavior of the *d*–*d* repulsion integrals. As examples, we present in Table III the lower *d*–*d* transition energies of the V(IV), Cr(IV), and Fe(IV) ions, computed with the AO's reported in this work as well as with the corresponding sets of Clementi and Roetti. The differences are always very small: smaller than 120 $\text{cm}^{-1}$ for V(IV) and Cr(IV), and 260 $\text{cm}^{-1}$ for Fe(IV). These discrepancies are negligible when compared with the separation between the theoretical spectrum (reference basis) and the observed one (*12*). Accordingly, we can say that the reduced basis sets reproduce the theoretical spectrum faithfully.

### *s and p Functions*

In Table IV we present the values of $T + V$ (kinetic plus nuclear attraction energy), computed with the reduced and reference bases, for the AO's of the Fe atom in the ground state. The worse cases correspond to the 2*s* and 2*p* AO's. Valence 3*p* and 4*s* AO's are very well reproduced.

In Table V we collect a set of interaction energies of pairs of electrons, as defined by Slater (*13*). They correspond to valence–valence electronic repulsions for the Fe atom in the ground state. The performance of the reduced set is very good, particularly in the case of the 4*s*–4*s* repulsion. Analogous results are found for other elements. The performance is still better for ions.

All these results show that the reduced basis sets presented in this paper are very good approximations to the high-quality ba-

TABLE IV

KINETIC PLUS NUCLEAR ATTRACTION ENERGY OF THE AO'S OF THE Fe ATOM ($4s^23d^6$–$^5$D STATE (ATOMIC UNITS)

| Atomic orbital | This work | Clementi-Roetti[a] | Difference |
|---|---|---|---|
| 1*s* | −337.62635 | −337.58483 | 0.04152 |
| 2*s* | −82.54069 | −82.69238 | −0.15169 |
| 3*s* | −31.81308 | −31.85502 | 0.05194 |
| 4*s* | −9.33421 | −9.35900 | 0.02479 |
| 2*p* | −81.81697 | −82.01925 | 0.20228 |
| 3*p* | −29.96868 | −29.95723 | −0.01145 |
| 3*d* | −24.76088 | −24.86904 | 0.10816 |

[a] Ref. (*2b*).

TABLE V

SPHERICALLY AVERAGED INTERELECTRONIC INTERACTIONS FOR THE Fe ATOM ($4s^23d^6$–$^5$D STATE) (ATOMIC UNITS)

| Interaction | This work | Clementi-Roetti | Difference |
|---|---|---|---|
| (3*s*,3*s*) | 1.10037 | 1.09979 | 0.00058 |
| (4*s*,4*s*) | 0.27816 | 0.27814 | 0.00002 |
| (3*p*,3*p*) | 1.00265 | 1.00252 | 0.00013 |
| (3*d*,3*d*) | 0.84689 | 0.84568 | 0.00121 |
| (3*p*,4*s*) | 0.36113 | 0.36164 | −0.00051 |
| (3*d*,4*s*) | 0.35503 | 0.35538 | −0.00035 |
| (3*p*,3*d*) | 0.89341 | 0.89379 | −0.00038 |

ses of Clementi and Roetti. They have a size appropriate for molecular and solid state calculations involving 3*d* atoms and ions. Moreover, the reduction method presented here seems to work very well. It could be a useful tool in the problem of reducing atomic or molecular basis sets.

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