Core-Projection Effects in Near ab Initio Valence Calculations of the Electronic Ground State of the Octahedral CrF_6^{4-}

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Core-projection operators have been included in the one-electron effective Hamiltonian of the frozen-core formalism developed by Richardson *et al.* (J. W. Richardson, T. F. Soules, D. M. Vaught, and R. R. Powell, *Phys. Rev. B* **4**, 1721 (1971)) for transition-metal clusters. Projected and unprojected valence-only calculations have been carried out in CrF_6^{4-} to evaluate the projection effects of the cluster a_{1g} nuclear potential in the neighborhood of the equilibrium geometry. These calculations show that the dependence of the predicted geometry on the type of core–valence partition adopted in the unprojected description is due to insufficient core–valence orthogonality. Such dependence is practically removed by the action of the core-projection operators. The cluster geometry can be accurately computed with a metallic valence set formed by the $3d$ orbitals and the empty $4s$ and $4p$ AOs. © 1986 Academic Press, Inc.

Introduction

The open-shell SCF MO theory developed by Richardson and collaborators (*1*) has been an important contribution to the theoretical understanding of the structural, optical, and magnetic properties of transition-metal ions in ionic lattices. This theory, based upon the cluster model and the spin- and symmetry-restricted Hartree–Fock–Roothaan (HFR) SCF equations for open-shell systems, permits the calculation of MO wavefunctions and energies of any electronic state coming from the open-shell configurations of those systems. Combined with a useful, approximate HF basis set (*2*), the theory has given very good results in the interpretation of the *d–d* spectrum (*3, 4*), electronic delocalization and covalency (*3, 4*), transferred hyperfine interaction (*5,*

7c), and neutron magnetic form factors (*6*). The theory can also be a useful tool in the study of the cluster–lattice interaction in those systems (*4, 7*).

All these calculations have been carried out within the frozen-core approximation described as an economical version of the all-electron formulation (*1*). For most purposes, these valence-only SCF calculations turn out to be accurate enough to offer satisfactory descriptions of the experimental observations. In the calculation of the a_{1g} nuclear potentials of the octahedral ML_6 systems, necessary for predicting the equilibrium metal–ligand distance, we have found, however, that the curvature of these nuclear potentials can noticeably depend upon the type of core–valence partition used in the frozen-core calculation. In this paper we show that this dependence is a

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consequence of an insufficient core–valence orthogonality appearing in the valence-only calculations. We also show that this problem can be appropriately corrected by using adequate core-projection operators in the effective one-electron Hamiltonian.

This nonorthogonality appears because in Richardson's theory (1) the valence AOs are orthogonal to the core AOs of the same center but their nonorthogonality to the core AOs of all other centers is neglected. In consequence, this approximation works well when the atomic core and the valence shell give negligible two-center contributions to the core–valence overlap. Otherwise, it tends to break down. A clear example of insufficient orthogonality is found when the $3s$ and $3p$ metallic AOs are kept frozen in the core because their overlap with the ligand components of the valence shell is not at all negligible at ordinary metal–ligand separations.

In connection with this problem, Huzinaga and collaborators (8) have recently shown that the use of appropriate projection operators, constructed with core AOs found in all-electron calculations, enforces the necessary core-valence orthogonality in valence-only calculations. The theoretical justification of this fact is well known (9). Core-projection operators have also been used as preservers of orthogonality by Wahlgren, Gropen, and collaborators in their effective core potential calculations on small molecules containing transition metal atoms (10) and four period main group elements (11). Furthermore, Vincent and Murrell (12) have remarked that the collapse of the molecular valence into the cores, produced by the core-valence nonorthogonality, can be considerably avoided by means of suitable pseudopotentials that repel the valence densities.

Accordingly, it seems natural to incorporate the ideas of these authors into the theory of Richardson et al. (1), in order to remove, or at least to attenuate, the difficulties commented above. We have organized such a program in two steps. On the one hand, we have performed "projected" calculations in which the frozen-core Hamiltonian of Richardson et al. (1) is augmented with core-projection operators. In this way the effects of such operators can be easily obtained and evaluated. Such study is reported in this paper. On the other hand, we plan to introduce the model potential technique of Huzinaga and collaborators (8) into Richardson's theory, in order to deal with the core–valence separation. In connection with this second step, model potentials of the exponential form for the first-row transition metals are reported elsewhere (13).

We have separated the study of the projected frozen-core calculations from the model potential calculations because we understand these two schemes as appropriate for different types of transition-metal compounds. The results of this paper suggest that the projected frozen-core formalism would be a useful theoretical scheme to investigate, *in 3d transition metal fluorides and oxides*, not only the optical spectroscopy and electronic charge distributions but also such interesting problems as the effects of the external pressure on the electronic spectra and the cluster–lattice interaction in terms of geometry-relaxed lattice models. The latter studies become problematic in the unprojected frozen-core scheme. On the other hand, inclusion of one-particle model potentials into Richardson's methodology would make this type of studies feasible for systems such as $4d$ transition-metal fluorides and oxides and $3d$ transition-metal *chlorides*. This research is now in progress in our laboratory.

We describe in the next section the details of the projected calculations and the quantities considered for the evaluation of the projection effects on the unprojected description. In the rest of the paper we

present the results of projected and unprojected calculations of the nuclear potential of the CrF_6^{4-}, taken as example, performed with three different core–valence partitions. The two main conclusions of this work are (a) the partition dependence of the equilibrium geometry, found in the unprojected results, is essentially due to insufficient core–valence orthogonality; and (b) this dependence is practically eliminated by the action of appropriate core-projection operators. In this way, the octahedral value of R_e for CrF_6^{4-} can be satisfactorily predicted by a valence-only calculation in which the metallic valence contains only the $3d$ orbitals and the empty $4s$ and $4p$ AOs.

Core-Projection Operators in the Frozen-Core Approximation

Following Ref. (8), we can define the one-particle core-projection operator:

$$\hat{\Omega}(\psi) = \sum_a \sum_c B(a,c)|\psi(a,c)\rangle\langle\psi(a,c)| \quad (1)$$

where the indices, a, c run over centers and core orbitals, respectively. We will use $B(a,c) = -2\varepsilon(a,c)$, $\varepsilon(a,c)$ being the orbital energy of the atomic core orbital $\psi(a,c)$, following the theoretical analysis of Höjer and Chung (9), and recent work of Sakai and Huzinaga (8d). Both $\psi(a,c)$ and $\varepsilon(a,c)$ are usually taken from all-electron calculations (8).

In molecular calculations it is more convenient to define the core-projection operators in terms of symmetry adapted core orbitals $\chi(i\Gamma\gamma)$, transforming as the γ subspecies of the Γ irreducible representation of the group of interest, namely

$$\hat{\Omega}(\Gamma\gamma) = \sum_{i\Gamma\gamma}^{core} B(i\Gamma)|\chi(i\Gamma\gamma)\rangle\langle\chi(i\Gamma\gamma)|. \quad (2)$$

In dealing with octahedral ML_6 clusters, the $\chi(i\Gamma\gamma)$ are immediately found by means

of the well-known unitary transformations of the multicenter atomic set (1). The $B(i\Gamma)$ are evidently the $B(a,c)$ of Eq. (1).

The frozen-core approximation is performed by introducing the effective one-electron Hamiltonian matrix $\mathcal{H}^{core}$ (Eq. (40) of Ref. (1)). In this paper we will refer to this matrix as the unprojected Hamiltonian matrix and will designate it by $\mathcal{H}^U$. Its matrix element connecting symmetry-adapted valence functions $\lambda(k\Gamma\gamma)$ and $\lambda(l\Gamma\gamma)$ is

$$\mathcal{H}^U(\Gamma;k,l) = \mathcal{H}(\Gamma;k,l)$$
$$+ 2\sum_{i\Gamma}^{core} d_\Gamma, P(\Gamma';i,i|\Gamma;k,l). \quad (3)$$

In this equation, $\mathcal{H}(\Gamma;k,l)$ contains the kinetic energy, the nuclear attractions energy, and the interaction energy with the external lattice potentials of the k,l distribution. The second term collects the (frozen) core–valence electron repulsions.

Now we incorporate the $\hat{\Omega}$ projection operator into the effective Hamiltonian and obtain the projected matrix $\mathcal{H}^P$, with elements

$$\mathcal{H}^P(\Gamma;k,l) = \mathcal{H}^U(\Gamma;k,l) + \Omega(\Gamma;k,l) \quad (4)$$

where

$$\Omega(\Gamma;k,l) = \langle\lambda(k\Gamma\gamma)|\hat{\Omega}(\Gamma\gamma)|\lambda(l\Gamma\gamma)\rangle. \quad (5)$$

At this point we recall that the atomic basis functions used in molecular calculations are not always the solutions of an all-electron atomic calculation. In some cases, for instance, the basis set is formed by approximate HF orbitals that satisfy some convenient conditions, such as the simulation of high-quality HF AOs (2). In those cases, the approximate atomic functions used for the calculation of the core–valence repulsions in the second term of Eq. (3) should also be used in Eq. (5). Furthermore, the projection constants $B(i\Gamma)$ in Eq. (2), should be, in any case, high enough to effectively prevent the collapse of the valence orbitals into the core (8d, 9, 14).

In this paper we will analyze the effects of the core projection on the a_{1g} nuclear potential of an octahedral cluster, the CrF_6^{4-}. To do that, we will use the quantity $E^{ortho}(R) = E^P(R) - E^U(R)$ as a direct measure of these effects. $E^P(R)$ and $E^U(R)$ are the *total* valence energy of the cluster in the projected and unprojected calculations, respectively.

A second index for evaluating the effects of the projection can be the energy associated with the projection operators themselves. We will define such energy as a weighted sum of the expectation values of the core projectors over the set of occupied MOs, $\phi(i\Gamma\gamma)$, namely

$$E^{\Omega}(R) = \sum_{\Gamma} \sum_{i} n(i\Gamma\gamma)$$

$$\langle \phi(i\Gamma\gamma)|\hat{\Omega}(\Gamma\gamma)|\phi(i\Gamma\gamma)\rangle. \quad (6)$$

In Eq. (6) the first sum runs over all the symmetry blocks having occupied MOs; $n(i\Gamma\gamma)$ is the electron occupation number of $\phi(i\Gamma\gamma)$.

Inserting the definition of $\hat{\Omega}(\Gamma\gamma)$, Eq. (2), into Eq. (6) we have

$$E^{\Omega}(R) = \sum_{\Gamma} \sum_{i} \sum_{j\Gamma\gamma}^{core} n(i\Gamma\gamma)B(j\Gamma)$$

$$\langle \chi(j\Gamma\gamma)|\phi(i\Gamma\gamma)\rangle^2. \quad (7)$$

Equation (7) clearly shows that if the core–valence orthogonality is complete, $E^{\Omega}(R)$ vanishes. For that reason this energy is a measure of the core–valence orthogonality reached after the core projected, valence calculation.

Results and Discussion

We present here our different calculations of the a_{1g} nuclear potential of the $t_{2g}^3 e_g^{-5}E_g$ electronic ground state of the CrF_6^{4-} ion. We will limit ourselves to the study of the effects of the core projection on the valence electronic energy of the

cluster *in vacuo*, without considering the cluster–lattice interaction.

Since we want to know the influence of the core-valence partition in the predicted equilibrium geometry of the cluster, we have considered in this work three different partitions. Their definitions are as follows:

Partition	Metallic core AOs	Metallic valence AOs
SPDD	$1s, 2s, 2p$	$3s, 3p, 3d, 3d'$
SPDDSP	$1s, 2s, 2p$	$3s, 3p, 3d, 3d', 4s, 4p$
DDSP	$1s, 2s, 2p, 3s, 3p$	$3d, 3d', 4s, 4p$

In all these cases, the $1s$ AOs of the fluorides are core orbitals and the $2s$ and $2p$ fluoride AOs are valence orbitals.

We will add a U or P to the name of the partition to designate unprojected or projected calculations, respectively.

We have used the STO basis set of Richardson *et al.* (2) for the chromium orbitals, except for the $4s$ AO that has been taken from Ref. (4). The fluoride basis has also been taken from Ref. (4). In the partitions above, the $3d'$ function is the inner STO of the regular 2-ζ $3d$ AO (2). SPDD and DDSP partitions have been used in pre-

TABLE I

VALUES OF THE PROJECTION CONSTANTS USED IN THE PROJECTED CALCULATIONS

Ion	AO	-2ε (a.u.)
Cr^{2+a}	$1s$	442.4898
	$2s$	54.17370
	$3s$	8.273619
	$2p$	46.03194
	$3p$	5.783535
F^{-b}	$1s$	51.65904

^{a} From the HFR calculations of Watson in the average of configurations state of d^4-Cr^{2+}, Ref. (18).

^{b} From the extended basis HFR calculation of Clementi and Roetti, Ref. (16).

TABLE II

RESULTS OF THE UNPROJECTED AND PROJECTED CALCULATIONS ON THE GROUND-STATE VALENCE
ENERGY OF CrF$_6^{4-}$, AT DIFFERENT Cr^{2+}–F$^-$ DISTANCES, USING SPDD, SPDDSP, AND DDSP BASES

Basis		R (a.u.)						
		3.26	3.425	3.59	3.772	3.99	4.19	4.39
SPDD	$E^{U a}$	−0.57937	−0.68548	−0.73519	−0.74766	−0.72689	−0.68809	−0.63896
	E^{P}	−0.46452	−0.62105	−0.69847	−0.72764	−0.71710	−0.68297	−0.63628
	E^{ortho}	0.11485	0.06443	0.03672	0.02002	0.00979	0.00512	0.00268
	E^{Ω}	0.10983	0.06253	0.03599	0.01976	0.00972	0.00509	0.00267
SPDDSP	E^{U}	−1.38682	−1.39874	−1.38581	−1.35071	−1.28891	−1.21961	−1.14247
	E^{P}	−1.03021	−1.14690	−1.20358	−1.22045	−1.20018	−1.15674	−1.09789
	E^{ortho}	0.35661	0.25184	0.18223	0.13026	0.08873	0.06287	0.04458
	E^{Ω}	0.27852	0.20242	0.15096	0.11147	0.07862	0.05723	0.04148
DDSP^{b}	E^{U}	−1.84949	−1.67430	−1.54727	−1.43711	−1.32565	−1.23210	−1.14166
	E^{P}	−0.80255	−1.01248	−1.12636	−1.17790	−1.17657	−1.13968	−1.08285
	E^{ortho}	1.04694	0.66182	0.42091	0.25921	0.14908	0.09242	0.05881
	E^{Ω}	0.99308	0.63367	0.40306	0.24716	0.14154	0.08774	0.05606

[a] The tabulated values correspond to the valence total energy plus 224. a.u.

[b] The core energy corresponding to the 3s and 3p atomic orbitals has been included in the calculation of E^{U} and E^{P}.

vious unprojected calculations (3–7). An extension of the original programs developed by Richardson and collaborators has been necessary to allow for the inclusion of the 4s and 4p AOs into the SPDDSP partition (15).

The projection constants $B(i\Gamma)$ needed in this calculation have been taken, for the Cr^{2+} ion, from the atomic HF results of Watson (18), because Richardson's basis (2) is a simulation of Watson's. For the fluoride ion we have used the orbital energies of Clementi and Roetti (16). These projection constants are collected in Table I. Their values are large enough to prevent the collapse of the valence orbitals into the core (14).

Results of the Unprojected Calculations

We will give the results of these calculations, performed at seven different Cr^{2+}–F$^-$ distances, from 3.26 a.u. (1.73 Å) to 4.39

a.u. (2.32 Å). This range of R covers most values of R_e observed in chromium fluorides and hexafluorochromates.

The unprojected nuclear potentials $E^{U}(R)$ corresponding to the three partitions quoted above have been collected in Table II. To display the "partition effect" in the value of R_e, we have plotted these $E^{U}(R)$ in Fig. 1. The information in this figure is quite disturbing. In passing from the U-SPDD potential to the U-SPDDSP one, we find the expected variational gain in valence electronic energy but the predicted value of R_e is shifted from 3.755 to 3.414 a.u. (values deduced from a cubic interpolation). As we discuss below, this shift is *not* a physical effect produced by the presence of the 4s and 4p empty AOs, but a consequence of the insufficient core–valence orthogonality in the SPDDSP partition. Still more shocking is the result of the U-DDSP calculation: a nuclear potential continuously attractive,
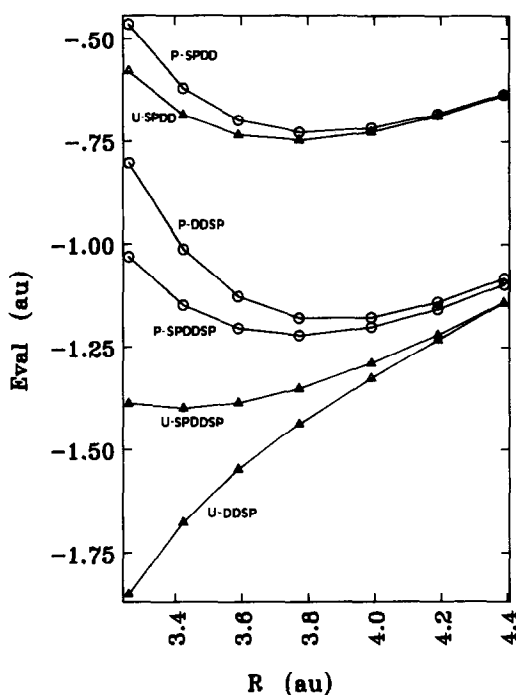
FIG. 1. Projected (O) and unprojected (△) SPDD, SPDDSP, and DDSP nuclear potentials (plus 224 a.u.) corresponding to the ground state $t_{2g}^3 e_g$-^5E_g of the CrF_6^{4-} ion.

down to the lower value of R explored here. From this result one could conclude that the DDSP partition is unable to give a bonding image of the CrF_6^{4-} ion. However, the results we present below show that this partition can give such a bonding image *if* the core projection is included in the calculation.

The large variations of R_e with the core-valence partition were the reason that motivated the research reported in this work.

Effects of the Core Projection in the $t_{2g}^3 e_g$-^5E_g Nuclear Potential

The values of $E^P(R)$, $E^{ortho}(R)$, and $E^{\Omega}(R)$ computed in the three partitions at seven different Cr^{2+}–F^- distances are collected in Table II. The $E^P(R)$ functions are also plotted in Fig. 1.

We first notice, from Table II, that E^{ortho} is always positive, i.e., the projection raises the nuclear potential energy. This effect increases when R decreases, as the two-center overlap integrals do. In the SPDD partition E^{ortho} is rather small, indicating a comparatively minor effect of the core projection on the U-SPDD potential. As a consequence, the P-SPDD and U-SPDD nuclear potentials are quite similar in the equilibrium region: R_e = 3.755 (U-SPDD) vs 3.813 a.u. (P-SPDD); $\bar{\nu}(a_{1g})$ = 486 (U-SPDD) vs 520 cm^{-1} (P-SPDD).

The effects of the projection are greater in the SPDDSP basis. E^{ortho}(SPDDSP) is uniformly larger than E^{ortho}(SPDD), and the projected and unprojected potentials are noticeably different (see Fig. 1), giving R_e(U-SPDDSP) = 3.414 vs R_e(P-SPDDSP) = 3.770 a.u. and $\bar{\nu}(a_{1g})$ = 438 cm^{-1} (U-SPDDSP) vs 505 cm^{-1} (P-SPDDSP).

A most interesting result is that the P-SPDDSP and P-SPDD nuclear potentials are almost parallel in the range of R investigated here and give practically the same R_e (3.79 ± 0.02 a.u.). Furthermore, this theoretical R_e agrees with the equatorial Cr^{2+}–F^- distances observed in the Jahn–Teller distorted $KCrF_3$, R_e = 3.78 a.u. (17). In comparing these two partitions, we finally remark that the nuclear potentials obtained after the core projection do agree with the variational effect intuitively expected when the valence segment is extended with the $4s$ and $4p$ *empty* orbitals, a rather uniform energy stabilization around the equilibrium value of R_e.

Let us now comment on the projection effects in the DDSP partition. Our results show that inclusion of the $3s$ and $3p$ AOs into the core gives rise to a significant collapse of the ligand valence into these AOs, particularly at small distances. On the other hand, the appropriate core projectors create a barrier that efficiently prevent such a collapse, restore the bonding image found within the other two partitions, and give

comparable values of R_e (3.858 a.u.) and $\bar{\nu}(a_{1g})$ (569 cm^{-1}).

We finalize this discussion by remarking that the promotion of the $3s$ and $3p$ AOs into the valence segment (DDSP $\rightarrow$ SPDDSP) implies two different effects. First, there is the variational improvement produced by the increase of the valence set. Such effect would result in a SPDDSP nuclear potential more stable than the DDSP one. The second effect refers to the orthogonality of the $3s$ and $3p$ AOs with the valence MOs. In the DDSP partition this orthogonality is forced through the action of the core-projection operators, although, as we have seen, it is not fully accomplished ($E^{\Omega}(R) \neq 0$). In the SPDDSP partition this orthogonality is secured by means of the SCF procedure in the valence segment. Insufficient core–valence orthogonality in the DDSP partition would make the P-DDSP potential more stable than the P-SPDDSP one. Our results show that in CrF_6^{4-} the variational effect is dominant.

As a consequence of these two effects the promotion of the $3s$ and $3p$ AOs into the valence set *does* change the curvature of the nuclear potential. However, this change is rather small and we can conclude that the three partitions considered here predict an a_{1g} nuclear potential for CrF_6^{4-} at equilibrium quite consistently ($R_e = 3.81 \pm 0.05$ a.u., $\bar{\nu}(a_{1g}) = 536 \pm 34$ cm^{-1}).

From this work we have learned that the core projection tends to make the calculation of the equilibrium geometry partition independent, a situation rather different from that found in the unprojected description. We could expect that an improvement in the quality of the core orbitals would improve the efficiency of the whole projection procedure, through the definition of $\hat{\Omega}$ and the evaluation of the core-valence repulsions. We are presently working in this question (13), as well as in the study of the effects of the projection in other properties and in other systems. Preliminary results

indicate that the electronic excited states of these octahedral systems suffer projection effects analogous to those described here for the ground state. Consequently, the theoretical values of the vertical electronic transition energies would be slightly altered by the projection. This is a rather welcome result because the optical spectra of such systems can be very accurately described by means of unprojected calculations (3). On the other hand, the variation with R of different properties like transition energies (19), covalency parameters, and transferred hyperfine interactions (7c), could be seriously affected by the projection. Results for several systems will be reported soon.

Acknowledgments

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