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BRIEF COMMUNICATIONS

On the Importance of an Accurate Representation of the Ewald Potential throughout the Cluster Volume in the Calculation of the Cluster–Lattice Interaction

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In most theoretical studies on the cluster–lattice interaction the lattice ions are represented by point charges. The electrostatic potential generated by these charges—external potential or V_{ext}—has usually been analyzed along the metal–ligand direction of the reference cluster (*1*). However, we have found that an inaccurate representation of the external potential in other regions of the cluster could produce artificial and not negligible distortions in the nuclear potential, the electronic charge distribution of the ground state, and other properties of the cluster.

In fact, a recent study of the cluster–lattice interactions in the $\mathrm{KMgF_3:Cr^{2+}}$ system shows that the $\mathrm{CrF_6^{4-}}$ octahedral ground state, $t_{2g}^3e_g - {}^5E_g$, can transform into an unstable state by the action of a V_{ext} accurate only along the metal-ligand directions.

In our study of the $\mathrm{KMgF_3:Cr^{2+}}$ system we represented the Ewald potential energy (EPE) of the $\mathrm{KMgF_3}$ lattice (*2*) by means of two monoelectronic operators called 6*P* (see Ref. (*3*) for definition and fitting procedure) and 7*P*. The 7*P* is the 6*P* plus a term in $x^2y^2z^2$ (cluster coordinates). This term makes the 7*P* representation uniformly accurate throughout the cluster volume. Moreover, both operators describe with similar accuracy the EPE values along the M–L directions as stated by their appropriate rms deviations δ_{100}: $\delta_{100}(6P) = 0.0005$, $\delta_{100}(7P) = 0.0003$ a.u. This is also true in the neighborhood of the metal and ligands positions.

The comparison of the 6*P* and 7*P* representations in regions other than the M–L axes (Figs. 1 and 2) makes clear that the 6*P* operator produces an erroneous stabilization of the electronic densities located around the 110 directions that increases with the value of the metal–ligand distance, *R*. This stabilization is erroneous because it is not shown by the Ewald results. Its effects can be observed in Table IA, where the difference in valence–lattice interaction energy calculated in the ground state of $\mathrm{CrF_6^{4-}}$, $\Delta I_{\mathrm{VAL}}(0;R) = I_{\mathrm{VAL}}^{6P}(0;R) - I_{\mathrm{VAL}}^{7P}(0;R)$, is tabulated at seven metal–ligand distances. The corresponding difference in core–lattice interaction energy is comparatively smaller (see Table IA) at all values of *R*, since the core densities ($1s_{\mathrm{M}}$, $2s_{\mathrm{M}}$, $2p_{\mathrm{M}}$, $1s_{\mathrm{L}}$) are very concentrated on the metal and the ligands sites. Thus, the net distortion of the nuclear potential of the $t_{2g}^3e_g - {}^5E_g$ state is dominated by $\Delta I_{\mathrm{VAL}}(R)$. Consequently,

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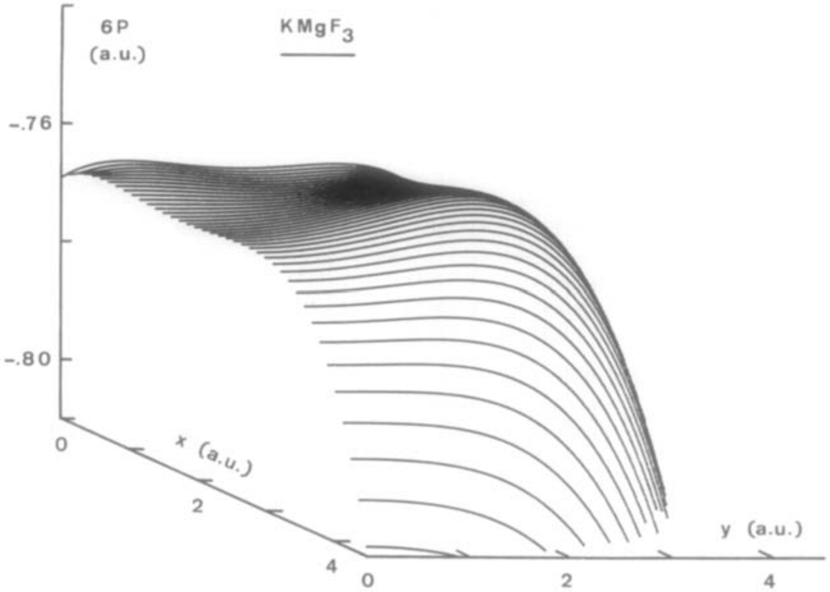

FIG. 1. Representation of the $6P$ potential energy through the $z = 0$ plane of the CrF_6^{4-} cluster.

the minimum obtained in the $7P$ calculations disappears in the $6P$ results (see Table IB).

An analogous effect has been found in the CrF_6^{3-} : K_2NaCrF_6 system (3). The considerable reduction of the metal–ligand equilibrium distance, R_e, and the metallization of the ground state $t_{2g}^3 - {}^4A_{2g}$, detected

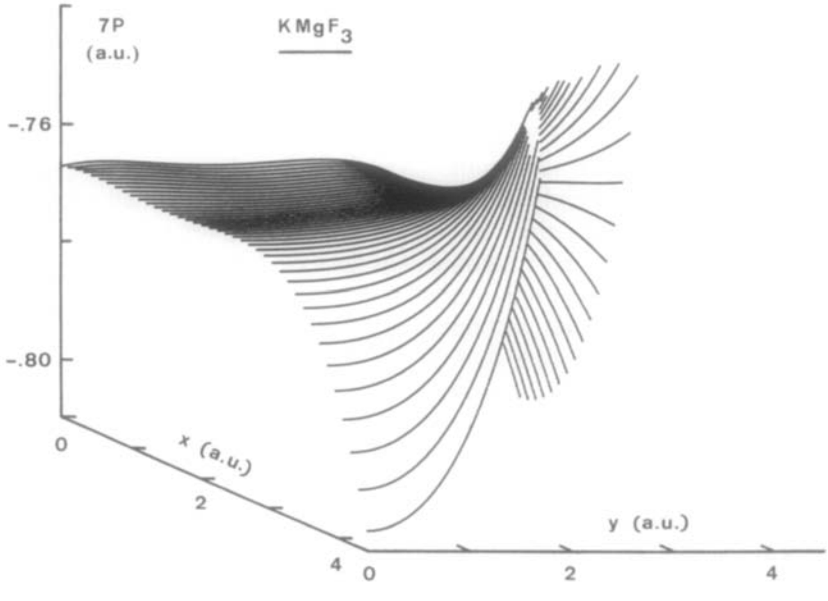

FIG. 2. Representation of the $7P$ potential energy through the $z = 0$ plane of the CrF_6^{4-} cluster.

TABLE I

DIFFERENCES IN VALENCE, CORE, AND TOTAL CLUSTER–LATTICE INTERACTION ENERGIES AND IN TOTAL VALENCE ENERGY OF THE GROUND STATE $|0\rangle = t_{2g}^3 e_g - {}^5E_g$, OF THE CrF_6^{4-} : $KMgF_3$, DEDUCED FROM THE 6*P* AND 7*P* CALCULATIONS

(A) $\Delta I(0;R) = I^{6P}(0;R) - I^{7P}(0;R)$, all numbers in a.u.

	R						
	3.26	3.425	3.59	3.772	3.99	4.19	4.39
$\Delta I_{VAL}(0;R)$	−0.12661	−0.18744	−0.27055	−0.39323	−0.59237	−0.83617	−1.15102
$\Delta I_{CORE}(R)$	0.01718	0.01052	0.00636	0.00630	0.01551	0.03624	0.07238
$\Delta I_{TOTAL}(0;R)$	−0.10943	−0.17692	−0.26419	−0.38683	−0.57686	−0.79993	−1.07864
(B) Total valence electronic energy of the $t_{2g}^3 e_g - {}^5E_g$ state + 228 (a.u.)							
$E_T^{7P}(t^3e - {}^5E_g;R)$	−0.42234	−0.48484	−0.49814	−0.46910	−0.38570	−0.26768	−0.11006
$E_T^{6P}(t^3e - {}^5E_g;R)$	−0.53177	−0.66176	−0.76233	−0.85603	−0.96256	−1.06761	−1.18870

in the PAR representation (*3*) (R_e(PAR) = 3.346, R_e(6*P*) = 3.475 a.u., q_{Cr}(PAR) = 2.007, q_{Cr}(6*P*) = 2.025) can be interpreted as a consequence of the inaccurate description of V_{ext} by the PAR operator along directions other than the M–L ones. In fact, due to the spherical symmetry of the PAR operator, the electronic densities located around the 100, 110, and 111 directions become increasingly unstable as *R* increases, whereas according to the Ewald results, only the densities along the 100 direction should show this behavior (see Fig. 1 in Ref. 3).

All these results show that the valence electronic densities seem to be very sensitive to the accuracy of the EPE representation in the inner regions of the cluster volume and not only along the M–L directions. Consequently, the EPE should be represented by a $\hat{V}_{ext}$ operator uniformly accurate *throughout* the cluster volume. Although the 6*P* model introduced in Ref. 3 should be in general reasonably accurate, these new results show that it could need improvements in certain cases. We have tried to systematize these improvements by considering those potential forms and numerical procedures that give uniform good representations of the Ewald results in octahedral clusters. From our studies we can suggest a double modification to the 6*P* model. First, we replace the term $(x^2y^2 + x^2z^2 + y^2z^2)$ by $r^m(x^2y^2 + x^2z^2 + y^2z^2)$ and add a new term of the form $r^lx^2y^2z^2$. In these new terms *m* and *l* are integers. Second, we use a sequential fit of the $\hat{V}_{ext}$ parameters to the Ewald values: the *r* polynomial is fitted to the 100 points, then *m* and the linear coefficient of $r^m(x^2y^2 + x^2z^2 + y^2z^2)$ are fitted to the 110 points and, finally, the remaining parameters are fitted to the rest of the Ewald points, including those along the 111 direction. We have found that this technique works uniformly well in all the octahedral cases examined. Although we cannot claim a wider generality, we think that this modified procedure should be appropriate for most octahedral clusters in fluoride lattices.

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