

Energetics of transition-metal ions in low-coordination environments

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The energetics of the interaction of transition-metal ions with low-coordination, non-close-packed neighbor shells are studied by *ab initio* total-energy calculations using plane-wave and other basis sets. Total energies are calculated for small clusters containing 3*d* transition-metal ions in simple, low-coordination environments. The clusters are obtained by placing four molecules of NH₃, H₂O, or H₂S at the vertices of a square or tetrahedron, with the N, O, or S facing the ion. The energy differences between square and tetrahedral structures are found to be ≈ 1 eV in several cases. Such a large magnitude is expected for open *d*-shell systems because of ligand-field-splitting effects, but similar energy differences are also found in closed-shell systems. We use the results to show that the main factors determining the structural energetics of the ions, in addition to direct ligand-ligand interactions, are the ligand-field splitting of the transition-metal *d* shell, and a contribution from the interaction of the ligand orbitals with the transition metal charge and *sp* orbitals. The results are used to parametrize a classical force field for Cu²⁺ and evaluate its accuracy.

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I. INTRODUCTION

Transition-metal ions are often found in bonding environments in which their coordination number is less than those of close-packed structures. A common type of low-coordination environment is one in which the ion has four neighbors, arranged in a square or tetrahedral configuration, or a distorted version of one of these. Transition-metal ions in such low-coordination environments are found in several types of materials and molecules. Our main interest is in proteins, which often have low-coordination transition-metal binding sites. For example, the enzyme superoxide dismutase contains both a Cu²⁺ and a Zn²⁺ ion.¹ The Cu²⁺ ion is coordinated by four nitrogen atoms from histidine residues, in a distorted square geometry. A more distant water also interacts with the Cu²⁺ ion, but much less strongly. The Zn²⁺ ion is coordinated by three nitrogen atoms from histidine residues and one oxygen atom from an aspartic acid group, in a distorted tetrahedral structure. Low-coordination transition-metal environments often occur in inorganic materials as well. In high-*T_c* superconductors, for example, a typical Cu²⁺ ion is coordinated² by four near oxygen neighbors in a nearly square arrangement at a distance of 1.9 Å, and has a pair of farther oxygen neighbors at 2.4 Å; similar local packing is seen in other copper oxide materials. The main types of transition metal neighbors that are found in low-coordination environments are N, O, and S.

When the transition metal ion is part of a large molecule or a complex material, either crystalline or amorphous, modeling with *ab initio* methods has a limited range of applicability because of both length scale and time scale problems. Thus it is desirable to perform simulations of such systems with classical force fields, which are faster than *ab initio* methods by several orders of magnitude. However, the low-coordination environments are particularly difficult to model with classical force fields because the importance of electronic effects relative to steric and electrostatic ligand-ligand interactions is greater than in close-packed environments. Most classical force fields treat electronic effects inaccurately.

Recently, results have been presented for the functional form of classical force fields for transition-metal ions which include some electronic effects.³⁻⁵ However, the relative importance of the factors considered in these works, and other potentially important effects, have not been firmly established either from experimental data or *ab initio* calculations.

The aim of this work is to establish the nature and magnitude of the key energetic factors determining the structural energies of transition metals in low-coordination environments. For ions with filled *d* shells (or filled magnetic subshells), the main energetic factors have generally been taken to be electrostatic and steric ligand-ligand interactions.⁶ These favor tetrahedral coordination, consistent with observed coordination geometries. For ions with partly occupied *d* shells, the best studied factor in determining structural energetics is the ligand-field stabilization energy (LFSE). In the presence of ligands, the degeneracy of the *d* orbitals is lost and an energy splitting (the “ligand-field splitting”) results. The splitting depends on both the arrangement and type of the ligands. The LFSE contribution to the structural energy causes, for example, Cu²⁺ complexes to generally form in square or tetragonal coordination. It does not contribute to the total energy for metal ions that have completely occupied magnetic subshells, such as Zn²⁺ and Mn²⁺. In these cases, the splitting does not affect the total energy because when a subband is full, its contribution to the total energy is determined only by the average energy of the subshell, not its width. However, additional terms can be important for the energetics. For example, there are quantum-mechanical electronic effects not involving the *d* shell. In II-VI semiconductors such as ZnS, the bonding is partly ionic and partly covalent,⁷ and the covalent part favors formation of a tetrahedral structure. Such covalency effects should also be important in the energetics of transition metals in other low-coordination structures. In addition, the charge on the transition-metal ion can polarize the ligands. This would generally enhance the charges and dipoles on the neighboring atoms and thus favor tetrahedral coordination. The rela-

tive importance of these contributions to the energy and the other two mentioned above has not yet been established.

In order to achieve a better understanding of the magnitudes of the various energy terms, we perform structural-energy calculations for transition metal ions interacting with square and tetrahedral neighbor configurations. The calculations use the VASP (Vienna *ab initio* simulation package)⁸⁻¹⁰ method, and other methods to check the results. We focus on the 3*d* transition metals because their narrow *d* bands render the perturbative approaches necessary for developing our classical force fields^{4,5} more applicable. Of the 3*d* transition metals, we treat the range Mn through Zn, since of the 3*d* transition metals they are the most prone to form low-coordination structures. The neighbors of the transition metals in our calculations include N, O, and S, since these are the most common neighbors in the low-coordination environments. We passivate the neighbors by attaching appropriate numbers of hydrogen atoms. By comparing the energies of the square and tetrahedral coordination geometries for a large range of transition metals, we are able to determine the most important physical factors determining the structural energetics. We also obtain the spatial decay rate of the various energy contributions by varying the radius of the cluster,

The organization of the remainder of the paper is as follows. Section II describes the clusters used and the calculational methods. Section III presents the *ab initio* results. Section IV describes our method for decomposing the energy differences into simple physical factors, and presents results for a classical force field for Cu²⁺. Section V summarizes our main conclusions.

II. MODEL CLUSTERS AND CALCULATIONAL APPROACH

In order to study the energetics of transition metal ions in low-coordination environments, we have chosen the simplest transition metal-centered square and tetrahedral clusters that have four neighbors at the same distance from the central ion. Most observed bonding configurations are in some way intermediate between square and tetrahedral geometries, so our calculations treat mainly these two geometries. The tetrahedral clusters are obtained by a distortion of the square clusters in which one pair of trans neighbors is moved up and the other moved down. We use as neighbors N, O, and S, with the aim of reproducing the most basic aspects of the transition metal environments described above. In the case of nitrogen, four ammonia molecules (NH₃) are placed as neighbors, so that the nitrogens are effectively terminated by hydrogens. In order to minimize contact between the ammonia molecules in the tetrahedral structure, their orientation in the square structure is chosen so that upwards-pointing triangles alternate with downwards-pointing ones. The orientations of the molecules are preserved as they are rotated to form the tetrahedral structure. We have experimented with other orientations, and find that the energy changes by only a few hundredths of an eV. The resulting tetrahedral and square clusters are shown in Fig. 1. In the clusters where transition metals interact with oxygen, four molecules of water were used in the clusters. The waters were placed in a

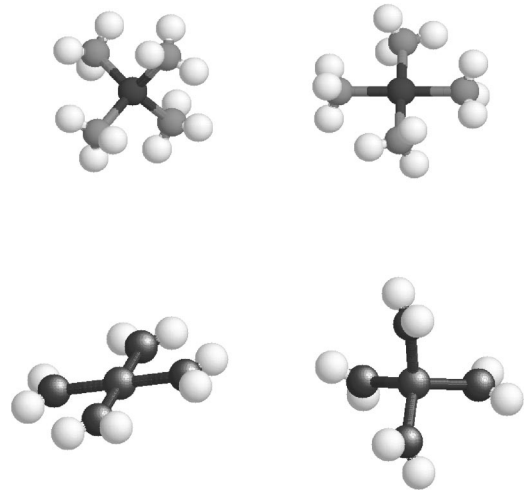


FIG. 1. Clusters used with N-surrounded (top) and O-surrounded (bottom) transition metals.

planar orientation for the square geometry, because in most observed cluster structures of this type in the Cambridge Structural Database¹¹ the waters are within about 20° of being planar. The same type of structures are used for S neighbors, with H₂S replacing water. We note that some calculations similar in spirit to these have been performed for transition metals surrounded by water molecules and several types of amino acids.¹² These calculations were aimed at understanding site specificity in metal binding to proteins, and thus treat considerably more complex environments than those treated here. Our purpose is to extract the basic physical mechanisms rather than to understand specific cases in detail.

In low-coordination environments, although the nearest neighbors to the transition metal are usually those (N, O, S) considered here, the ligand molecules are often different from those that we treat. The results obtained here thus cannot be expected to have quantitative accuracy in general. However, examination of the spectrochemical series of ligands,¹³ a tabulation of the strengths of ligand-field interactions, reveals that the most important factor in determining the strength of the ligand-transition metal interaction is the nearest neighbor to the transition metal. In fact, to a good approximation, all of the nitrogen ligands are stronger than all of the oxygen ligands, which in turn are stronger than all of the sulfur ligands. The basic physical mechanisms and rough energy magnitudes that we derive here for our chosen simple ligands should therefore hold for other ligands having the same neighbor to the transition metal. In classical force field calculations, we feel that using parameters derived from the present results would be more accurate than most calculations based on existing force fields, in which electronic effects are often ignored entirely.

Most of the calculations were performed within the framework of density functional theory (DFT). The DFT calculations used a plane-wave basis set as implemented in the VASP method,⁸⁻¹⁰ as well as a local-orbital basis set for comparison. We employ the VASP code for most of the calculations because it eliminates ambiguities resulting from the

choice of basis set. It performs an iterative solution of the Kohn-Sham equations of density functional theory, by using residual minimization techniques. The electron-ion interaction is described using an ultrasoft pseudopotential and the generalized gradient approximation^{14,15} is used for the exchange-correlation functional. In order to check the reliability of these calculations, we have made some comparisons with non-DFT methods, as well as other basis sets within DFT methods. These comparisons used the GAUSSIAN 98 package.¹⁶ The non-DFT calculations were performed with the Hartree-Fock and Møller-Plesset (MP2, MP4) methods, using the LANL2DZ basis set.^{17,18} The GAUSSIAN 98 density-functional calculations also utilized the LANL2DZ basis set, together with the “PW91” gradient-corrected exchange and correlation functional.¹⁹

III. TOTAL-ENERGY RESULTS

Before stating our *ab initio* results, we briefly summarize our expectations for the energy differences on the basis of simpler considerations. The general assumption in the literature has been that the structural energetics are dominated by the ligand-field stabilization energy E_{LFSE} and direct ligand-ligand interactions. E_{LFSE} is defined as the sum of the one-electron energies of the d orbitals relative to the average energies of their subbands. The magnitude²⁰ of E_{LFSE} for Cu^{2+} in water is about 1 eV. The ligand-field stabilization energy of the square structure is much greater than that in the tetrahedral structure,¹³ so we can expect the ligand-field contribution to the square-tetrahedral energy difference

$$\Delta E = E_{\text{square}} - E_{\text{tetrahedral}} \quad (1)$$

for Cu^{2+} surrounded by O to be roughly 1 eV as well. Because N has stronger ligand-field effects than O, we expect the ligand-field contribution to ΔE for Cu^{2+} surrounded by N to be greater than 1 eV; that for S ligands should be less than 1 eV because S has weaker ligand-field splitting effects than O. A straightforward calculation gives the following estimate of the contribution of ligand-ligand electrostatic interactions to ΔE :

$$\Delta E_{\text{elec}} = \frac{Z^2 e^2}{d} [2\sqrt{2} + 1 - 3\sqrt{6}/2] = 1.1Z^2 \text{ eV}, \quad (2)$$

where Ze is the magnitude of the charge on the neighbors and d is their distance from the central ion, which we have taken to be 2 Å in the second equality. For a doubly charged central ion, taking an actual charge transfer from the ion's formal charge would give $Z=0.5$. This would give $\Delta E_{\text{elec}} = 0.3 \text{ eV}$, much smaller than the ligand-field contribution.

Figure 2(a) shows our results for ΔE for 3d transition metal ions and other types of centers in the NH_3 -surrounded geometry shown above. The center-to-ligand distance is 2.06 Å, which is typical for transition metal-N complexes. The spin states are chosen to be those which minimize the energy in the lowest-energy structure (either square or tetrahedral); the same spin state is used for the higher-energy structure as well. This procedure simplifies the analysis of the energetics for structures relatively near the lowest-energy structure. The

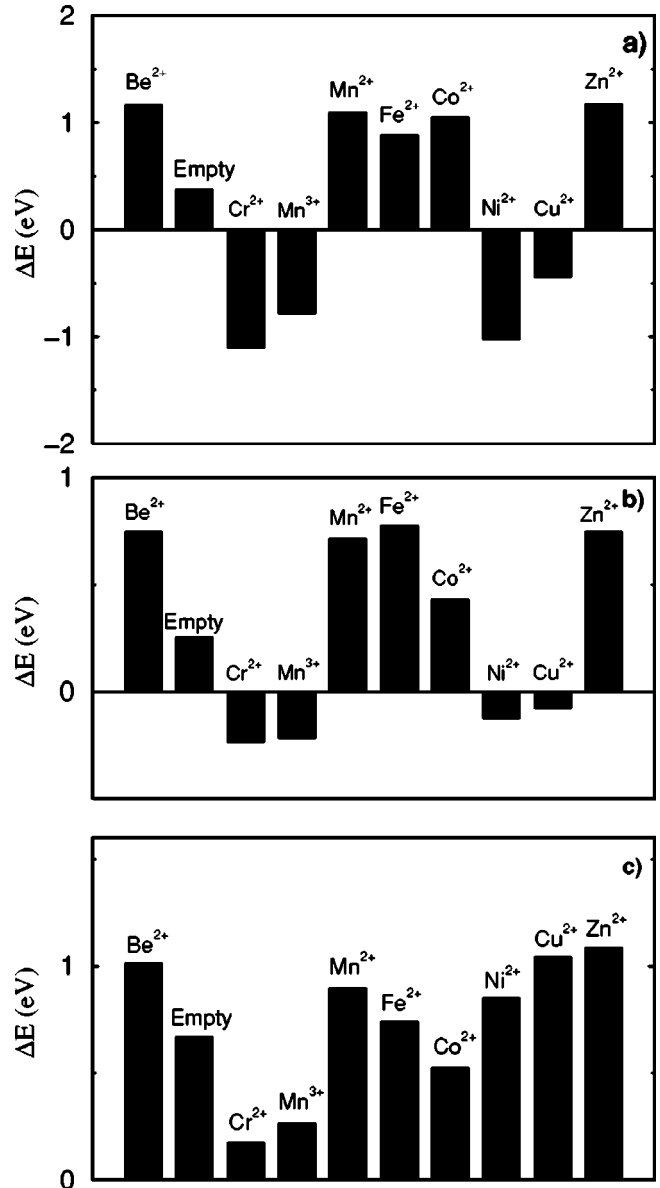


FIG. 2. ΔE for N-coordinated (a), O-coordinated (b), and S-coordinated (c) transition metal ions.

spin states are given in Table I. The structural preferences seen in Fig. 2(a) for the ions Mn^{2+} - Zn^{2+} are consistent with the observed structures of a large number of complexes of these ions. These have been summarized in recent analyses^{6,21} of the Cambridge Structural Database.¹¹ Both studies found that for fourfold-coordinated Ni^{2+} and Cu^{2+} , square coordination dominates, well-defined tetrahedral coordination is almost never observed, and that the nonsquare structures are distorted intermediates. This is consistent with the calculated negative values of ΔE for these ions. For Mn^{2+} , Fe^{2+} , and Zn^{2+} both square and tetrahedral coordi-

TABLE I. Metal Ions and Spin States Used

Ion	Be^{2+}	Cr^{2+}	Mn^{3+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Spin	0	2	2	5/2	2	3/2	0	1/2	0

nation are observed. However, a restriction of the analysis to monodentate ligands²¹ showed that the formation of square structures around these ions is due to chelation, i.e., a preformed ligand shell, and does not reflect the inherent structural preferences of the ions. Thus the observed geometries are consistent with our calculated positive values of ΔE for these three metals. For Co^{2+} , both square and tetrahedral coordination were observed,⁶ but no distinction was made between monodentate ligands and others. However, the preference of Co^{2+} with monodentate ligands is known to be for tetrahedral coordination.²⁰

From the theoretical point of view, the cases of Zn^{2+} and Mn^{2+} should be the simplest because in both cases the ligand-field energy vanishes, as discussed above. This would lead us to expect values of ΔE in line with the electrostatic estimate above for ligand-ligand interactions. However, we see from Fig. 2(a) that the tetrahedral structure is favored over the square one by 1.18 eV for Zn^{2+} and 1.10 eV for Mn^{2+} . Thus, although the d shell or subshell is filled, the magnitude of ΔE substantially exceeds that expected for direct electrostatic ligand-ligand interactions. Accordingly we have considered the case of Be^{2+} to see if the d shell is important for ΔE in these cases despite *a priori* expectations to the contrary. The energy difference that we find for Be^{2+} , 1.10 eV, is very close to those for Zn^{2+} and Mn^{2+} . Thus the d shell does not seem to be an important factor in producing the large energy differences. To shed further light on this issue we have performed calculations for the NH_3 cluster with an empty center (no ion). In this case, the energy difference is 0.38 eV, much smaller than for the metal centered case, and consistent with the electrostatic estimate above. This suggests that the large energy values found favoring the tetrahedral structure are due to an interaction between the ligands that is induced by the transition-metal ion but does not involve the d orbitals. Two possibilities for such interactions come to mind. The first is hybridization interactions between formally occupied sp orbitals on the ligands and the formally empty $s-p$ states of the metal ion. Such interactions would lead to a partial covalency in the interactions between the ion and the ligands, above and beyond that causing the ligand-field splittings of the d shell. The second type of induced interaction would result from polarization of the ligands by the ion's charge. A classical description of these types of interactions will be described below. We note that the similarity of the ΔE values of Mn^{2+} and Zn^{2+} suggests that the non- d -band effects are fairly constant across this part of the $3d$ series.

We now turn to the ions with partly filled d shells. For Cu^{2+} and Ni^{2+} , the energies favoring the square structure are 0.46 and 1.03 eV, respectively. The larger energy difference for Ni^{2+} results from the presence of two holes in the d shell; one of the holes is in each magnetic subshell in the low-spin configuration obtained here. The energy differences are not precisely measurable, but some comparison with experiment can be made on the basis of ligand-field parameters, as discussed below. The values of ΔE for Fe^{2+} and Co^{2+} are similar to those for Mn^{2+} and Zn^{2+} . This is expected, since ligand-field theory predicts that the lowest two levels in the partly filled d complex have nearly the same

energies in the square and tetrahedral structures.¹³ The calculations for Cr^{2+} and Mn^{3+} are not directly comparable to observed structures, but are included here with the purpose of evaluating the general picture of the energetics that we develop. The large energy favoring the square structure for these two ions suggests that similar ligand-field effects operate as in Cu^{2+} , and that the effects are enhanced by the greater spatial extent of the d orbitals relative to the later transition metals.

As a check on the accuracy of our treatment of exchange and correlation, we have performed calculations with other treatments based on Hartree-Fock theory and its extensions, using the LANL2DZ basis set.^{17,18} These were performed using the GAUSSIAN 98 package,¹⁶ for the Cu^{2+} ion surrounded by NH_3 . For the unrestricted Hartree-Fock, and second- and fourth-order Møller-Plesset perturbation theories (MP2 and MP4), the values of ΔE are -0.02 , -0.27 , and -0.35 eV, respectively, in comparison with the VASP value of -0.46 eV. It is not possible to say what the limiting value of the Hartree-Fock based methods is, but the calculated numbers are consistent with a value between -0.35 and -0.46 eV. We have also performed calculations with the PW91 approximation¹⁹ for exchange and correlation using the LANL2DZ basis set, and we obtain a ΔE value of -0.61 eV. In order to check the convergence of the calculations with respect to lattice constant, we have performed calculations at a smaller lattice constant of 10 Å. We find that the ΔE values change by 0.1–0.2 eV. Considering all of these results, an uncertainty of 0.1–0.2 eV seems to be a reasonable estimate.

Figure 2(b) shows similar results for clusters with oxygen neighboring the transition-metal ions, with a center-to-ligand distance of 1.95 Å. We see that for Ni^{2+} and Cu^{2+} the square structure is favored, again consistent with observed structures. A plausible explanation of the calculated energy differences for Ni^{2+} and Cu^{2+} is that the LFSE favors the square structure for these ions, and is almost canceled by the contributions favoring the tetrahedral structure. This would imply a LFSE energy scale of about half that corresponding to N-coordinated ions, which is consistent with the observed greater strength of N in generating ligand-field splittings.¹³ For the metals without ligand-field splitting effects, the magnitude of the energy favoring the tetrahedral structure is about 75% of that in the clusters with N neighbors, and several times greater than the value for the empty clusters.

Figure 2(c) shows similar results for clusters with sulfur neighbors to the transition-metal ions, at a center-to-ligand distance of 2.10 Å. Here the tetrahedral structure is found to be preferred in all cases. Although we are not aware of published structures of complexes in which Cu^{2+} or Ni^{2+} are surrounded by four monodentate sulfur ligands, the results for Cu^{2+} are consistent with the observations in the spectrochemical series¹³ that S ligands have weaker ligand-field interactions with transition-metal ions than N or O ligands. To the extent that ligand-field effects are present in our results for S neighbors, they do not follow the typical pattern of being largest for Ni^{2+} and Cu^{2+} , but rather maximize at Co^{2+} . We believe that this effect is partly due to a reduction of electron transfer from the transition-metal ions to the S;

this causes a filling of the d shell and thus shifts the maximum of the ligand-field energy difference to lower atomic numbers. In addition, it is believed that π interactions are more important for S ligands.²² These can reverse the sign of the ligand-field effects.⁵ Because the case of S neighbors does not seem to be described well by simple implementation of ligand-field theory, we do not pursue these results further.

Although application of the above results to specific molecular geometries will likely occur via the parametrization of classical force fields, as described below, we note that the large scales of the energy differences that are obtained here have important implications regarding the extent of structural site selectivity for different ions. Consider, for example, the attachment of a Cu^{2+} and a Zn^{2+} ion to preorganized square and tetrahedral sites with N neighbors. We define configuration A as that in which the Cu^{2+} is in the square site and the Zn^{2+} is in the tetrahedral site, and configuration B as that in which the occupancies are reversed. One readily shows that the energy difference favoring A is $E(A) - E(B) = \Delta E(\text{Cu}) - \Delta E(\text{Zn}) = -1.63$ eV. This means that at room temperature, the likelihood of configuration B being observed is 10^{-27} . Thus the extent of selectivity is very high. This is consistent with numerous examples²³ of metal-binding sites in proteins which bind Cu^{2+} despite the much larger ambient concentration of Zn^{2+} . Such effects are difficult to model with existing force fields.

IV. INTERPRETATION OF *ab initio* RESULTS

A. Partitioning of ΔE into physical factors

The results in the preceding section have suggested three important factors entering the structural energetics of low-coordinated transition-metal ions: ligand-field stabilization energies E_{LFSE} , direct electrostatic and steric interactions between ligands, and induced interactions E_{IND} between the ligands. In order to evaluate the relative importance of these contributions, we need a way of partitioning the calculated energy differences between them. We identify the direct ligand-ligand interactions with the empty-center results given in Fig. 2. We evaluate the ligand-field contribution to the energy differences ΔE_{LFSE} by assuming that the remaining components of the energy vary linearly with transition-metal atomic number, and that ΔE_{LFSE} vanishes for Zn^{2+} and Mn^{2+} . The linearity is a reasonable assumption, since the non- d -band contributions to the energy should be determined by the energies and radii of the sp states, which vary fairly linearly with atomic number, and the charge on the ion, which should vary little among the transition metal ions. We thus obtain ΔE_{LFSE} by subtracting from the calculated values a linear interpolation between Zn^{2+} and Mn^{2+} :

$$\Delta E_{\text{LFSE}}(Z) = \Delta E(Z) - [(Z - Z_{\text{Mn}})\Delta E(\text{Zn}) + (Z_{\text{Zn}} - Z)\Delta E(\text{Mn})]/(Z_{\text{Zn}} - Z_{\text{Mn}}), \quad (3)$$

where Z is the atomic number of the ion. These results, for N and O neighbors, are given in Figs. 3(a) and 3(b). We do not include the S neighbors here or below, for reasons discussed above. The general trends observed above, namely, that the

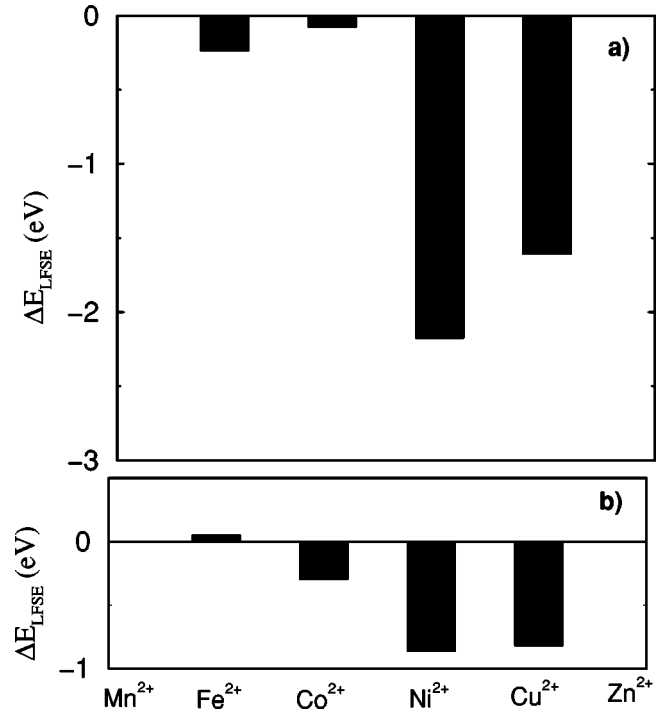


FIG. 3. ΔE_{LFSE} for N-coordinated (a) and O-coordinated (b) transition metal ions.

energy scale of E_{LFSE} is considerably smaller for O than for N, and that Cu and Ni have the largest magnitudes, are seen clearly in these plots. E_{LFSE} substantially exceeds the direct ligand-ligand interactions for Cu and Ni. Although the ligand-field stabilization energies are not precisely measurable, estimates can be made on the basis of observed ligand-field splittings if a one-electron picture of the total energy is used. This picture is most valid for the ions Cu^{2+} and Cr^{2+} , which each have one hole in the upper spin subband, since the dominant part of the electron-electron interaction is between opposite-spin electrons, and shifting an electron from an occupied orbital in the minority-spin complex to the unoccupied orbital should not greatly affect its interaction with the approximately spherical majority-spin charge density. The fact that the LFSE is measured relative to the average energy in the band implies that the magnitude of the energy difference favoring the square structure is equal to the difference between the energies of the (empty) highest orbitals in the subband in the two structures. According to a simplified ligand-field theory,¹³ these energies are $12.28Dq$ for the square structure and $1.78Dq$ for the tetrahedral structure, where $10Dq$ is the conventional ligand-field splitting in octahedral coordination. In a common parametrization¹³ of ligand-field theory, $10Dq = fg$, where f is a factor for the ligand and g is a factor for the transition metal. For NH_3 and H_2O , $f = 1.25$ and 1.00 , respectively; for Cu^{2+} , $g = 12.0$, where the energy is expressed in 10^3 cm^{-1} . We then obtain as experimental estimates $\Delta E_{\text{LFSE}} = 1.94$ and 1.55 eV, for NH_3 and H_2O neighbors, respectively; the calculated values are 1.61 and 0.82 eV. Since the experimental values are obtained from complexes having two additional axial neighbors, it is not clear whether the discrepancies come from our

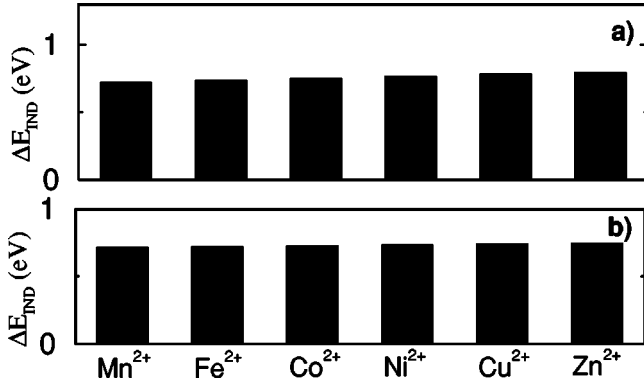


FIG. 4. ΔE_{IND} for N-coordinated (a) and O-coordinated (b) transition-metal ions.

ignoring these neighbors, or from problems with the underlying treatment of exchange and correlation.

We obtain the induced ligand-ligand interaction energy ΔE_{IND} by subtracting the empty-center results from the energy obtained by linear interpolation between the Mn and Zn results

$$\Delta E_{\text{IND}}(Z) = [(Z - Z_{\text{Mn}})\Delta E(\text{Zn}) + (Z_{\text{Zn}} - Z)\Delta E(\text{Mn})] / (Z_{\text{Zn}} - Z_{\text{Mn}}) - \Delta E_{\text{empty}}. \quad (4)$$

These values are shown in Fig. 4. Again, they greatly exceed the direct ligand-ligand interactions.

B. Tests of classical force fields

We now turn to the question of how well the energy terms derived here can be treated by classical force fields. A approximate real-space method for describing ligand-field energies has recently been presented,^{4,5} which gives E_{LFSE} in terms of a sum of angular ligand-ligand interactions, in the following form:

$$E_{\text{LFSE}} = - \left[\sum_{ij} e_{d\sigma,i} e_{d\sigma,j} [u(\theta_{ij}) - A] \right]^{1/2}, \quad (5)$$

where θ_{ij} is the angle between ligands i and j ,

$$u(\theta) = [P_2(\cos \theta)^2 - (1/5)], \quad (6)$$

and P_2 is the second-order Legendre polynomial. The $e_{d\sigma,i}$ are ligand-field interaction-energy parameters defined by

$$e_{d\sigma,i} = Ch_{d\sigma,i}^2/E_0, \quad (7)$$

where $h_{d\sigma,i}$ is the electronic σ -coupling strength between the ligand orbital responsible for the ligand-field splitting and the appropriately oriented transition-metal d orbital, E_0 is the energy difference between the ligand orbitals and the d orbitals, and C is a dimensionless prefactor determined by the d -band filling. The theoretical analysis corresponds to the above expression with $A=0$, but using nonzero values of A was found to give a better fit to the energies of small clusters with random structures.^{4,5} We find that the best fit is obtained with $A=0.133$.

The results presented above can then be used to derive values of the interactions $e_{d\sigma,i}$ in Eq. (5). Since the ligand molecules in our calculations are all at the same distance R , we can extract the values of $e_{d\sigma} = e_{d\sigma,i}$ from the calculated values of ΔE_{LFSE} . A straightforward calculation shows that

$$\Delta E_{\text{LFSE}} = (\sqrt{32/15 - 16A} - \sqrt{34/5 - 16A})e_{d\sigma} = -2.16e_{d\sigma}. \quad (8)$$

This gives a direct connection between the *ab initio* total-energy results and the parameters in the classical force field.

With regard to the induced-interaction energy, it is not *a priori* clear which of the two parts contributes the most. We write $\Delta E_{\text{IND}} = \Delta E_{\text{IND}}^{\text{hyb}} + \Delta E_{\text{IND}}^{\text{pol}}$, where $\Delta E_{\text{IND}}^{\text{hyb}}$ is the hybridization contribution and $\Delta E_{\text{IND}}^{\text{pol}}$ is the polarization contribution. Both can be described classically. For $\Delta E_{\text{IND}}^{\text{hyb}}$, a recent methodology²⁴ has developed classical force fields for the case of complete or nearly complete covalency. In order to treat the partial covalency effects that we believe result from hybridization here, we use a previously derived methodology,⁷ which treats interactions between formally occupied and unoccupied orbitals in fourth-order perturbation theory. According to this methodology, the fourth-order energy has the form

$$E^{(4)} = \left[\sum_{\alpha,\beta,\gamma,\delta} h_{\alpha\beta} h_{\beta\gamma} h_{\gamma\delta} h_{\delta\alpha} \right] / E_0^3, \quad (9)$$

where the $h_{\alpha\beta}$ are the couplings between the unoccupied and occupied orbitals. These are determined by the interaction strengths $h_{s\sigma}$ and $h_{p\sigma}$ between the occupied ligand orbitals and the transition-metal s and p orbitals, and the energy differences between the ligand orbitals and these orbitals. A simple approximation for evaluating the ratio $h_{p\sigma}/h_{s\sigma}$ is obtained by going to an sp^3 basis, and retaining only couplings between sp^3 orbitals pointing at each other. In this case one finds by a straightforward calculation that $h_{p\sigma}/h_{s\sigma} = \sqrt{3}$. This approximation is confirmed by the parametrized fits developed by Harrison.⁷ In addition, we ignore interactions between sp^3 orbitals on the same atom. With these approximations, the hybridization energy takes the form

$$E_{\text{IND}}^{\text{hyb}} = \left[\sum_{ij} e_{s\sigma,i} e_{s\sigma,j} w(\theta_{ij}) \right] / E_0, \quad (10)$$

where

$$w(\theta) = [1 + 6 \cos \theta + 9 \cos^2 \theta], \quad (11)$$

$e_{s\sigma} = h_{s\sigma}^2/E_0$, and E_0 is the energy difference between the ligand orbitals and the s orbitals on the transition metal ion.

We evaluate $\Delta E_{\text{IND}}^{\text{pol}}$, for NH_3 clusters, by placing point charges Q_N on the N sites and charges $Q_H = -Q_N/3$ on the H sites, with parallel procedures being followed for the clusters with oxygen ligands. Comparison of the angular dependence of this term with that derived above for $\Delta E_{\text{IND}}^{\text{hyb}}$ reveals that their angular dependence is almost identical. For this reason, we do not attempt to parametrize the two pieces of ΔE_{IND} separately, but rather treat the whole term with the functional form for $\Delta E_{\text{IND}}^{\text{hyb}}$ because of its simpler mathematical form.

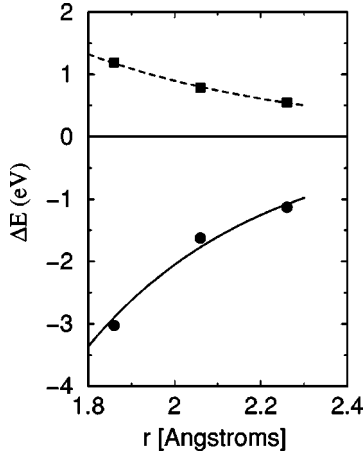


FIG. 5. Distance dependence of ΔE_{LFSE} and ΔE_{IND} for Cu^{2+} with N ligands. Circles: VASP points for ΔE_{LFSE} . Solid line: exponential fit for ΔE_{LFSE} . Squares: VASP points for ΔE_{IND} . Dashed line: exponential fit for ΔE_{IND} .

In implementing the force field given by Eq. (10), we can choose E_0 at will since changes in E_0 can always be absorbed in rescaling of the function $e_{s\sigma,i}$. We choose $E_0 = 6$ eV. We then obtain ΔE_{IND} in terms of $e_{s\sigma,i}$:

$$\Delta E_{\text{IND}} = 24e_{s\sigma}^2/E_0 = 4 \text{ eV}^{-1}e_{s\sigma}^2. \quad (12)$$

Having pinned down the values of the interaction parameters in the classical force field at the distance R used in the calculations, we turn to the evaluation of the distance dependence of the interactions. This is often assumed to have an exponential form. Figure 5 shows the distance dependence of ΔE_{LFSE} and ΔE_{IND} for Cu^{2+} with N neighbors. Both display a rapid decay with distance. For ΔE_{IND} the exponential form gives an excellent fit. For ΔE_{LFSE} the fit is not as good but still acceptable. According to Eqs. (5) and (10), exponential dependence of ΔE_{LFSE} and ΔE_{IND} implies a dependence of the form $e(r) = e(R)\exp[-\kappa(r-R)]$ for the interaction parameters entering the classical force fields. The values of κ for ΔE_{LFSE} and ΔE_{IND} , for Cu^{2+} and Zn^{2+} interacting with N and O neighbors, are given in Table II. As expected from the smaller size of the d orbitals relative to the sp orbitals $\kappa_{\text{LF}} > \kappa_{\text{IND}}$.

We test the classical force fields by comparing the classical force field results with *ab initio* results for the energy along the distortion path going from the square to the tetrahedral structure. In this distortion path, we begin with a square structure in the x - y plane, and rotate one pair of trans ligands up from the x - y plane by an angle $\Delta\theta$, and the other

TABLE II. Values of decay parameter κ (\AA^{-1}).

Ion	Ligand	κ_{IND}	κ_{LF}
Cu^{2+}	N	0.97	2.46
	O	0.96	5.19
Zn^{2+}	N	0.94	
	O	0.94	

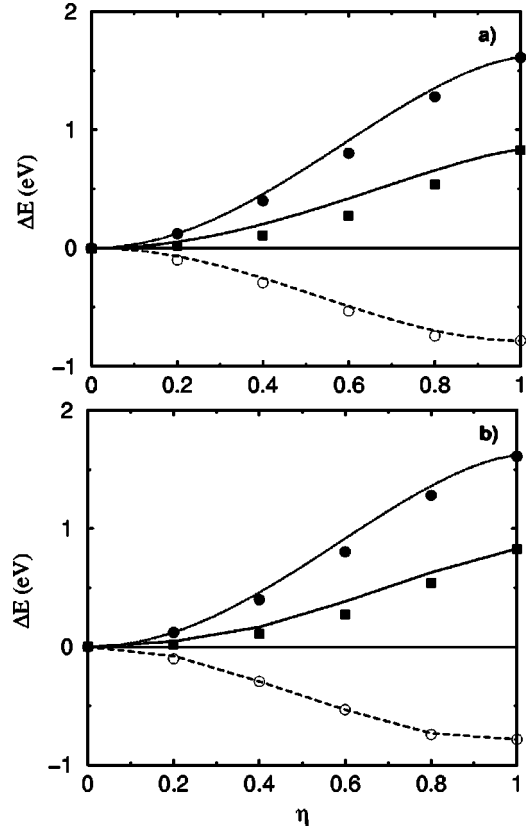


FIG. 6. Variation of E_{LFSE} (solid circles), E_{IND} (open circles), and their sum (squares) along square ($\eta=0$) to tetrahedral ($\eta=1$) distortion path for Cu^{2+} with N ligands. Dotted, dashed, and solid lines: classical approximations for E_{LFSE} , E_{IND} , and their sum, respectively. (a) E_{IND} fit to classical form for hybridization energy obtained using fourth-order perturbation theory. (b) E_{IND} fit to empty-cluster results.

one down by the same angle. One readily sees that the tetrahedral structure is obtained when $\Delta\theta = \Delta\theta_{\text{tet}} = (180^\circ - \theta_{\text{tet}})/2 = 35.25^\circ$, where $\theta_{\text{tet}} = 109.5^\circ$ is the tetrahedral bond angle. Our plots are given in terms of the distortion parameter $\eta = \Delta\theta/\Delta\theta_{\text{tet}}$, so that $\eta=0$ for the square structure and $\eta=1$ for the tetrahedral structure.

Figure 6(a) gives results for E_{LFSE} , E_{IND} , and their sum for Cu^{2+} with N neighbors, where the energies are referenced to the energies for the square structure. The parameters in the classical force field are obtained from the electronic total-energy calculations as described above. We see that the overall shape of both E_{LFSE} and E_{IND} are reproduced reasonably well by the classical force fields, the main discrepancy being that in each case the classical curve lies slightly above the calculated data points. In the case of E_{LFSE} , the discrepancy results partly because a classical force field cannot obtain the cusp at $\eta=1$ (tetrahedral structure) that results from Jahn-Teller effects around this point. When the two energies are added, the cancellation due to their sign difference causes the relative errors to be larger; at $\eta=0.4$, the error is about 100%. We find similar results using the classical interaction potential for $E_{\text{IND}}^{\text{pol}}$. The only functional form that we have found to give a better fit for E_{IND} is to assume that E_{IND}

$\propto E_{\text{empty}}$, where E_{empty} is the energy of an empty-centered cluster as a function of η . This results are shown in Fig. 6(b); the discrepancies in the total energy are reduced significantly. We do not know why this provides a better description than the hybridization energy or electrostatic forms.

V. CONCLUSION

The results described above have shown that the structural energetics of low-coordinated transition metal ions are dominated by the ΔE_{LFSE} and ΔE_{IND} terms. Both have magnitudes of roughly 1 eV per transition metal atom for N neighbors and smaller values for O neighbors. When ligand-field effects are absent, the energy stabilizing the tetrahedral structure is dominated by ΔE_{IND} , which is mediated by the ion, rather than by direct interactions between the ligands. When the square structure is preferred, the preference results from a competition between ΔE_{LFSE} and ΔE_{IND} , both having comparable magnitudes. Tests of a classical force field involving

a perturbation-theory derived term for the hybridization energy, and a previous classical form for the ligand-field energy, show that a reasonable description of ΔE_{LFSE} and ΔE_{IND} along the distortion path from square to tetrahedral coordination can be obtained. However, the cusplike behavior of ΔE_{LFSE} at the tetrahedral end of the curve is not obtained correctly, and cancellations between ΔE_{LFSE} and ΔE_{IND} can cause large errors in their sum. Nevertheless, we feel that the use of terms such as these in classical force fields would be a substantial improvement on existing codes, which usually ignore the ligand-field energy entirely and base the structural energetics mainly on direct ligand-ligand interactions.

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- ¹S.J. Lippard, *Principles of Bioinorganic Chemistry* (University Science Books, Mill Valley, 1994).
²K.C. Hass, *Solid State Phys.* **42**, 213 (1989).
³C.R. Landis, T. Cleveland, and T.K. Firman, *J. Am. Chem. Soc.* **120**, 2641 (1998).
⁴A.E. Carlsson, *Phys. Rev. Lett.* **81**, 477 (1998).
⁵A.E. Carlsson and S. Zapata, *Biophys. J.* **81**, 1 (2001).
⁶L. Rulisek and J. Vondrasek, *J. Inorg. Biochem.* **71**, 115 (1998).
⁷W.A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, Mineola, NY, 1989).
⁸G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
⁹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11 169 (1996).
¹⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
¹¹F.H. Allen and O. Kennard, *Chem. Design Autom. News* **8**, 31 (1993).
¹²L. Rulisek and Z. Havlas, *J. Am. Chem. Soc.* **122**, 10428 (2000).
¹³W.W. Porterfield, *Inorganic Chemistry: A Unified Approach* (Academic Press, San Diego, 1993).
¹⁴J.P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
¹⁵A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
¹⁶M.J. Frisch *et al.*, *Gaussian 98, Revision A.7* (Gaussian, Inc., Pittsburgh, 1998).
¹⁷P.J. Hay and W.R. Wadt, *J. Chem. Phys.* **82**, 270 (1985).
¹⁸P.J. Hay and W.R. Wadt, *J. Chem. Phys.* **82**, 299 (1985).
¹⁹J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
²⁰F. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience, New York, 1972).
²¹M.M. Harding, *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **56**, 857 (2000).
²²U. Ryde, M.H.M. Olsson, K. Pierloot, and B.O. Roos, *J. Mol. Biol.* **261**, 586 (1996).
²³W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life* (Wiley, New York, 1994).
²⁴D.M. Root, C.R. Landis, and T. Cleveland, *J. Am. Chem. Soc.* **115**, 4201 (1993).