The energy level splitting of the d-orbitals due to their interaction with the ligands in a complex has important structural and thermodynamic effects on the chemistry of transition-metal complexes. Although these two types of effects are interrelated, they are considered separately here.

### Structural Effects

There are two major kinds of structural effects: effects on the ionic radii of metal ions with regular octahedral or tetrahedral geometries, and structural distortions observed for specific electron configurations.

#### Ionic Radii

Figure 1 is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. The dashed line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge \( Z_{\text{eff}} \), assuming a spherical distribution of the 3d electrons. Because these radii are based on the structures of octahedral complexes and \( \text{Cr}^{2+} \) and \( \text{Cu}^{2+} \) do not form truly octahedral complexes, the points for these ions are shown as open circles.

![Figure 1: The Effect of d-Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals.](image)

Only \( \text{Ca}^{2+} \), \( \text{Mn}^{2+} \) (high-spin \( d^5 \)), and \( \text{Zn}^{2+} \) (\( d^{10} \)) lie on the smooth dashed curve. All other divalent ions fall below this curve because they have asymmetrical distributions of d electrons. To explain why an asymmetrical distribution of d electrons makes a metal ion smaller than expected, consider the \( \text{Ti}^{2+} \) ion, which has a \( d^2 \) configuration with both electrons in the \( t_{2g} \) orbitals. Because the \( t_{2g} \) orbitals are directed between the ligands, the two d-electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than predicted; the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five d orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving the metal a larger ionic radius.
A similar effect is observed for the V$^{2+}$ ion, which has a d$^3$ configuration. Because the three electrons in the t$_{2g}$ orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs from Ti$^{2+}$ to V$^{2+}$. Consequently, the observed ionic radius of the V$^{2+}$ ion is significantly smaller than that of the Ti$^{2+}$ ion.

Skipping the Cr$^{2+}$ ion for the moment, consider the d$^5$ Mn$^{2+}$ ion. Because the nuclear charge increases by +2 from V$^{2+}$ to Mn$^{2+}$, Mn$^{2+}$ might be expected to be smaller than V$^{2+}$. The two electrons added from V$^{2+}$ to Mn$^{2+}$ occupy the e$_g$ orbitals, however, which are oriented directly toward the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually increases significantly from $\text{V}^{2+}$ to Mn$^{2+}$, despite the higher nuclear charge of the latter.

The same effects are observed in the second half of the first-row transition metals. In the Fe$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ ions, the extra electrons are added successively to the t$_{2g}$ orbitals, resulting in increasingly poor shielding of the ligands from the nuclei and in abnormally small ionic radii. Skipping over Cu$^{2+}$, adding the last two electrons causes a significant increase in the ionic radius of Zn$^{2+}$, despite its greater nuclear charge.

**The Jahn–Teller Effect**

Because simple octahedral complexes are not observed for the Cr$^{2+}$ and Cu$^{2+}$ ions, only estimated values for their radii are shown in Figure \ref{PagelIndex{1}}). Since both Cr$^{2+}$ and Cu$^{2+}$ ions have electron configurations with an odd number of electrons in the e$_g$ orbitals. Because the single electron (in the case of Cr$^{2+}$) or the third electron (in the case of Cu$^{2+}$) can occupy either one of two degenerate e$_g$ orbitals, both systems have degenerate ground states. The Jahn–Teller theorem states that such non-linear systems are not stable; they undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the Jahn–Teller effect. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the e$_g$ orbitals, such as the Cr$^{2+}$ and Cu$^{2+}$ ions.

Consider an octahedral Cu$^{2+}$ complex, [Cu(H$_2$O)$_6$]$^{2+}$, which is elongated along the z axis. As indicated in Figure \ref{PagelIndex{2}}), this kind of distortion splits both the e$_g$ and t$_{2g}$ sets of orbitals. Because the axial ligands interact most strongly with the d$_{z^2}$ orbital, the splitting of the e$_g$ set (\(\delta_1\)) is significantly larger than the splitting of the t$_{2g}$ set (\(\delta_2\)), but both \(\delta_1\) and \(\delta_2\) are much, much smaller than the \(\Delta_0\). This splitting does not change the centerpoint of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the e$_g$ set contains one electron (as in the d$^4$ ions, Cr$^{2+}$ and Mn$^{3+}$) or three electrons (as in the d$^9$ ion, Cu$^{2+}$), the distortion decreases the energy of the system. For Cu$^{2+}$, for example, the change in energy after distortion is \(2(−\delta_1/2) + 1(\delta_1/2) = −\delta_1/2\). For Cu$^{2+}$ complexes, the observed distortion is always an elongation along the z axis by as much as 50 pm; in fact, many Cu$^{2+}$ complexes are distorted to the extent that they are effectively square planar. In contrast, the distortion observed for most Cr$^{2+}$ complexes is a compression along the z axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.
**Jahn–Teller distortions** are most important for $d^9$ and high-spin $d^4$ complexes; the distorted system is more stable than the undistorted one.

*Figure \( \PageIndex{2} \): The Jahn–Teller Effect*

Increasing the axial metal–ligand distances in an octahedral $d^9$ complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of $e_g$ orbitals to split in energy by an amount $\delta_1$; $\delta_1$ and $\delta_2$ are much smaller than $\Delta_0$. As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.

**Thermodynamic Effects**

As previously noted, crystal field splitting energies (CFSEs) can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.
Hydration Energies

The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:

\[ M^{2+}_{(g)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} \]  

Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. In Figure 1, a plot of the hydration energies of the fourth-period metal dications versus atomic number forms a curve with two valleys. Note the relationship between the plot in Figure 1 and the plot of ionic radii in Figure 1, the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of d electrons (Ca$^{2+}$, Mn$^{2+}$, and Zn$^{2+}$) lie on the dashed lines. In Figure 1, the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the [M(H$_2$O)$_6$]$^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Therefore, CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

**Figure 1:** Thermochemical Effects of d-Orbital Splittings. (a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for Ti$^{2+}$ and Cr$^{2+}$, are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the Ti$^{2+}$ ion in water are not stable, and Cr$^{2+}$ does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed lines), again illustrating the importance of CFSEs.

Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted against atomic number in part (b) of Figure 1. Recall that the lattice energy is defined as the negative of the enthalpy change for the reaction below. Like hydration energies, lattice energies are determined indirectly from a thermochemical cycle.

\[ M^{2+} (g) + 2Cl^- (g) \rightarrow MCl_2 (s) \]

The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) of Figure 1, with only Ca$^{2+}$, Mn$^{2+}$, and Zn$^{2+}$ lying on the smooth curve. It is not surprising that the explanation for
the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except MnCl$_2$ and ZnCl$_2$, are more stable than expected due to CFSE.

**Summary**

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy $\Delta_t$. The crystal field stabilization energy (CFSE) is the additional stabilization of a complex due to placing electrons in the lower-energy set of d orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic number. The Jahn–Teller theorem states that a non-linear molecule with a spatially degenerate electronic ground state undergoes a geometrical distortion to remove the degeneracy and lower the overall energy of the system.