In ligand-field theory the energy of all the states arising from a particular electron configuration can be written as a linear combination of the Slater integrals F^k,

$$E = \sum_{k=0}^{2l} C_k F^k$$

It can be shown[1,2] that all multiplet states arising from the same electron configuration have the same dependency on C_0, i.e. C_0 is a fixed number for that particular configuration. A well-known consequence of this property of ligand-field theory is that excitations within a configuration do not depend on F^0. However, on our simulations the high-spin to low-spin excitation is seen (Figure 1 in the main text) to depend on F^0. As explained in the main text this difference comes from the use, in our DFT-based calculation, of a single Slater determinant (with fractional occupations and spin contamination) to represent the atomic state when compared to the multideterminant representation (with states with well-defined $<S^2>$ values) used in ligand-field theory.

In order to show this, we use Eq. 8 in the main text to calculate the 4-center intra-atomic integrals setting $F^2=F^4=0$. We can observe that the only non-zero integrals are:

$$\left\langle \chi_0 \chi_0 \left| \frac{1}{|r-r'|} \right| \chi_0 \chi_0 \right\rangle = \left\langle \chi_0 \chi_1 \left| \frac{1}{|r-r'|} \right| \chi_0 \chi_1 \right\rangle = F^0$$

From these integrals we can now use Eq. 7 to evaluate the energy of the different configurations used. A summary of these calculations can be found on the following table. We can see that the energy of the different atomic configurations has a different dependency on F^0. Moreover, the high-spin low-spin energy difference in a d^8 system (Ni^{2+}) is $0.6F^0$ while in a d^7 system (Ni^{3+}) is $1.2F^0$, thus explaining how the slope in Figure 1 in the main text is double for Ni^{3+} than for Ni^{2+}.

Table Energies of the d-shell in terms of F^0, associated to different electronic configurations for in d-shell electronic occupation and spin and the orbital occupation associated to that state assuming a single Slater determinant representation.

Electronic configuration	Spin	Occupation per d orbital	State energy
d^7	High-spin	$(1.0\uparrow 0.4\downarrow)$	$33.2F^0$
d^7	Low-spin	$(0.8\uparrow 0.6\downarrow)$	$32.0F^0$
d^8	High-spin	$(1.0\uparrow 0.6\downarrow)$	$42.2F^0$
d^8	Low-spin	$(0.8\uparrow 0.8\downarrow)$	$41.6F^0$

References:

1. Bersuker, I. B. *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*; Wiley, 2010.

2. Griffith, J. S. *The Theory of Transition-Metal Ions*; Cambridge University Press, 1964