

Magnetic atoms in solids: solution

Alessandro Vindigni

17/10/2022

Magnetic moments of transition-metal ions for some octahedral complexes

In textbooks different definitions may be found for the atomic magnetic moment. Here we assume that the magnitude of the magnetic moment (in absolute value) is given by the maximal possible projection of the operator $\hat{\mu}$ along an applied magnetic field. For the free ion and neglecting spin-orbit coupling, this definition corresponds to

$$\mu_{\text{Hund}} = \mu_{\text{B}}(2S_{\text{Hund}} + L_{\text{Hund}})$$

having replaced M_S and M_L with their maximal positive values. For a transition-metal ion in a perfect octahedral field (O_h) of ligands, instead, we consider a toy model (not fully justified!) in which

$$\mu_{O_h} = \mu_{\text{B}}(2S_{O_h} + L_{O_h})$$

where $L_{O_h} = L' = 1$ for T_{1g} and T_{2g} multi-electron configurations and $L_{O_h} = 0$ otherwise. Usually experimental estimates of the magnetic moments are given in terms of the Curie constant (see next chapters), which is proportional to $g^2 S(S+1)$ when there is no orbital contribution. To compare the magnetic moments defined above with experimental values, we will assume that the orbital and the spin components of μ_{Hund} contribute *independently* to the Curie constant. Therefore, we compare the quantity $p = \sqrt{4S(S+1) + L(L+1)}$ obtained for the free ions and with our toy model against experimental values.

1. Determine S_{O_h} and L_{O_h} associated with the single-electron configurations indicated in the column " O_h el. conf." and write the value in the corresponding column.

ion	free-ion el. conf.	S_{Hund}	L_{Hund}	p_{Hund}	O_h el. conf.	S_{O_h}	L_{O_h}	p_{O_h}	p_{exp}
Ti ³⁺	(3d) ¹	1/2	2	3	t_{2g}^1	1/2	1	2.2	1.6-1.7
V ³⁺	(3d) ²	1	3	4.5	t_{2g}^2	1	1	3.2	2.7-2.9
Cr ³⁺	(3d) ³	3/2	3	5.2	t_{2g}^3	3/2	0	3.9	3.7-3.9
Cr ²⁺ /Mn ³⁺	(3d) ⁴	2	2	5.5	$t_{2g}^3 e_g^1$ (high S)	2	0	4.9	4.7-4.9
Cr ²⁺ /Mn ³⁺	(3d) ⁴	2	2	5.5	t_{2g}^4 (low S)	1	1	3.2	3.2-3.3
Mn ²⁺ /Fe ³⁺	(3d) ⁵	5/2	0	5.9	$t_{2g}^3 e_g^2$ (high S)	5/2	0	5.9	5.6-6.1
Mn ²⁺ /Fe ³⁺	(3d) ⁵	5/2	0	5.9	t_{2g}^5 (low S)	1/2	1	2.2	1.8-2.1
Fe ²⁺ /Co ³⁺	(3d) ⁶	2	2	5.5	$t_{2g}^4 e_g^2$ (high S)	2	1	5.1	5.1-5.7

ion	free-ion el. conf.	S_{Hund}	L_{Hund}	p_{Hund}	O_h el. conf.	S_{O_h}	L_{O_h}	p_{O_h}	p_{exp}
Fe^{2+}/Co^{3+}	$(3d)^6$	2	2	5.5	t_{2g}^6 (low S)	0	0	0	0
Co^{2+}	$(3d)^7$	3/2	3	5.2	$t_{2g}^5 e_g^2$ (high S)	3/2	1	4.1	4.3-5.2
Co^{2+}	$(3d)^7$	3/2	3	5.2	$t_{2g}^6 e_g^1$ (low S)	1/2	0	1.7	1.8
Ni^{2+}	$(3d)^8$	1	3	4.5	$t_{2g}^6 e_g^2$	1	0	2.8	2.9-3.3
Cu^{2+}	$(3d)^9$	1/2	2	3	$t_{2g}^6 e_g^3$	1/2	0	1.7	1.7-2.2

Experimental values taken from this Table ([https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Modules_and_Websites_\(Inorganic_Chemistry\)/Crystal_Field_Theory/Magnetic_Moments_of_Transition_Metals](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Modules_and_Websites_(Inorganic_Chemistry)/Crystal_Field_Theory/Magnetic_Moments_of_Transition_Metals)).

- Use the underlying script to compute the values of p_{Hund} and p_{O_h} for different transition metals ions; assume the values of S_{O_h} and L_{O_h} determined at the previous point to compute p_{O_h} . Copy the values p_{Hund} and p_{O_h} obtained in this way in the corresponding cells of the table above.

```
mu_effective_TM <- function(S,L){
  mu_sq <- 4*S*(S+1) + L*(L+1)
  return (sqrt(mu_sq))
}
S_Hund=1/2
L_Hund=2
mu_effective_TM(S_Hund,L_Hund)
```

```
## [1] 3
```

```
S_0h=1/2
L_0h=1
mu_effective_TM(S_0h,L_0h)
```

```
## [1] 2.236068
```

- What are the electronic configurations for in which the value of p estimated with the toy model (O_h) reproduces significantly better experimental estimates? For which configurations the difference is instead negligible?

Answer

A better agreement is found for electronic configurations for which $L' = 0$. The agreement is generally less satisfactory when $L' = 1$ and it seems to get worse as the number of electrons increases.

Magnetic moments of rare-earth ions

Determine the values of S , L , and J compatible with the three Hund's rules for the following rare-earth ions. With the help of the underlying scripts compute the Landé factor given by Equation

$$g_J = 1 + (g_s - 1) \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)},$$

and the relative $p_{th} = g_J \sqrt{J(J + 1)}$ (see previous assignment). Compare the latter against experimental results given in the last column on the right.

```
g_Lande <- function(S,L,J){
  num = J*(J+1) + S*(S+1) - L*(L+1)
  den = 2*J*(J+1)
  g_J = 1 + num/den
  return(g_J)
}
```

```
mu_effective_RE <- function(S,L,J){
  g_J <- g_Lande(S,L,J)
  return (g_J*sqrt(J*(J+1)))
}
```

```
S=1/2
L=3
J=5/2
g_Lande(S,L,J)
```

```
## [1] 0.8571429
```

```
mu_effective_RE(S,L,J)
```

```
## [1] 2.535463
```

ion	free-ion el. conf.	S	L	J	g.s. term	g_J	p_{th}	p_{exp}
Ce ³⁺	(4f) ¹	1/2	3	5/2	² F _{5/2}	0.86	2.5	2.4
Pr ³⁺	(4f) ²	1	5	4	³ H ₄	0.8	3.6	3.5
Nd ³⁺	(4f) ³	3/2	6	9/2	⁴ I _{9/2}	0.73	3.6	3.5
Pm ³⁺	(4f) ⁴	2	6	4	⁵ I ₄	0.6	2.7	-
Sm ³⁺	(4f) ⁵	5/2	5	5/2	⁶ H _{5/2}	0.29	0.8	1.5
Eu ³⁺	(4f) ⁶	3	3	0	⁷ F ₀	0	0	3.4
Gd ³⁺	(4f) ⁷	7/2	0	7/2	⁸ S _{7/2}	2	7.9	8

ion	free-ion el. conf.	S	L	J	g.s. term	g_J	p_{th}	p_{exp}
Tb ³⁺	(4f) ⁸	3	3	6	⁷ F ₆	1.5	9.7	9.5
Dy ³⁺	(4f) ⁹	5/2	5	15/2	⁶ H _{15/2}	1.33	10.6	10.6
Ho ³⁺	(4f) ¹⁰	2	6	8	⁵ I ₈	1.25	10.6	10.4
Er ³⁺	(4f) ¹¹	3/2	6	15/2	⁴ I _{15/2}	1.2	9.6	9.5
Tm ³⁺	(4f) ¹²	1	5	6	³ H ₆	1.17	7.6	7.3
Yb ³⁺	(4f) ¹³	1/2	3	7/2	² F _{7/2}	1.14	4.5	4.5

Values taken from *Solid State Physics*, N. W. Ashcroft and N. D. Mermin.

For which ions the agreement between the computed p and the experimental value is not satisfactory?

For Sm³⁺ and Eu³⁺ the observed magnetic moments is much larger than the theoretical one. The contribution comes from the Van Vleck susceptibility: read the article "[CourseLibrary/Articles/Van_Vleck_Eu_JAP_1968.pdf](#)" for more details.