

The Mixing of $3d^n$ and $3d^{n-1}4s$ States in Crystalline Field Theory

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The effect upon the crystalline field energies of mixing $3d^n$ and $3d^{n-1}4s$ states under the $1/r_{12}$ term present in the Hamiltonian is investigated. It is shown that the inclusion of higher states will improve the agreement with theory and experiment somewhat, especially that some of the apparent term reduction ${}^3P-{}^3F'$ found, *e.g.*, in Ni^{2+} complexes is explained in this way. However, due to the approximations of the theory it is impossible to assert just how much a full configuration interaction will affect the levels in question.

The crystalline field theory has been remarkably successful in explaining the visible spectra of complexes of transition metal ions, by representing the energy states of interest with pure d^n wave functions^{1,2}. No doubt a better approximation of the energy states is one in which all permissible configuration interaction is included. The purpose of this note is to investigate in detail the effect of including one important such interaction, $3d^74s$ with $3d^8$, in the "weak" octahedral field calculation of Ni^{2+} . It is well known¹ that the states $(3d)^n$ and $(3d)^{n-1}(4s)^1$ cannot mix under an octahedral field V_0 . However, the term $1/r_{12}$ present in the full Hamiltonian is capable of performing a mixing of these atomic configurations. Consequently we first perform a scrambling of the various states under $1/r_{12}$, and then proceed to evaluate their crystal field energies.

THEORY

Proper wave functions in the SLM_TM_S scheme for $3d^8$ and $3d^74s$ terms were obtained using angular momentum operators, as outlined in Condon and Shortley³. The energy states of greatest interest in determining the visible spectra of Ni^{2+} complexes are the ground state 3F and the excited 3P level. For the configuration $3d^8$ there is one 3F and one 3P ; for $3d^74s$, there are two 3F 's and two 3P 's.

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The secular determinants of electrostatic interaction mixing these levels are

$${}^3F \begin{vmatrix} 1. a3d^8 & 2. b3d^74s & 3. c3d^74s \\ -E & 0 & \frac{2}{35}\sqrt{15} R^2 \\ 0 & \Delta_{12}-E & 0 \\ \frac{2}{35}\sqrt{15} R^2 & 0 & \Delta_{13}-E \end{vmatrix} = 0 \quad (1)$$

and

$${}^3P \begin{vmatrix} 1. a3d^8 & 2. b3d^74s & 3. c3d^74s \\ -E & 0 & \frac{\sqrt{210}}{35} R^2 \\ 0 & \Delta_{12}-E & 0 \\ \frac{\sqrt{210}}{35} R^2 & 0 & \Delta_{13}-E \end{vmatrix} = 0 \quad (2)$$

where Δ_{12} and Δ_{13} are the energy separations between respective $3d^74s$ levels and $3d^8$, and R^2 is the radial integral defined as

$$R^2(3d,3d; 3d,4s) = e^2 \int_0^\infty \int_0^\infty \frac{r_1^2}{r_1^3} R_1(3d)R_2(3d)R_1(3d)R_2(4s)dr_1dr_2 \quad (3)$$

Δ 's were taken as the experimental energy separations of the terms as given by Shenstone⁴. Term energies for some important states in the $3d^74s$ configuration were calculated using the Slater-Condon F_k and G_k parameters³, and are given in the Table. A reasonable fit of terms is obtained by taking $F_2(3d,3d) = 1\,770 \text{ cm}^{-1}$, $F_4(3d,3d) = 135 \text{ cm}^{-1}$ and $G_2(3d,4s) = 1\,900 \text{ cm}^{-1}$. A value is needed for $R^2(3d,3d; 3d,4s)$. It should reasonably lie between $F^2(3d,3d)$

Table 1. Energies of some important terms in the $3d^74s$ configuration of the free Ni^{2+} ion. All energies are given in cm^{-1} .

Term	Energy expressed in Slater-Condon parameters *	Predicted energy with $F_2 = 1\,770 \text{ cm}^{-1}$, $F_4 = 135 \text{ cm}^{-1}$ and $G_2 = 1\,900 \text{ cm}^{-1}$	Experimental term energy **
4F	$-5G_2 - 43F_2 - 324F_4$	55 406	55 406 (3)
$b\,{}^3F$	$-G_2 - 43F_2 - 324F_4$	63 006	62 606 (3)
4P	$-5G_2 - 28F_2 - 399F_4$	71 816	71 384 (2)
3G	$-4G_2 - 39F_2 - 239F_4$	75 857	75 647 (4)
$b\,{}^3P$	$-G_2 - 28F_2 - 399F_4$	79 416	78 483 (1)
$c\,{}^3P$	$-4G_2 - 34F_2 - 264F_4$	81 327	82 277 (1)
3H	$-4G_2 - 34F_2 - 264F_4$	81 327	82 194 (5)
$c\,{}^3F$	$-4G_2 - 19F_2 - 339F_4$	97 761	97 996 (3)

* See Ref.³ Each term also has common parameters $7F_0(3d,4s) + 21F_0(3d,3d)$.

** From Ref.⁴; J values in parentheses.

and $G^2(3d,4s)$ as it does in calculations made by Ufford⁵ on configuration interaction among $3d^3$, $3d^24s$ and $3d4s^2$. Ufford calculated R^2 in order to obtain the best fit of the free ion spectrum involved, but in our case there are less data available, so it is estimated as the geometric mean of G^2 and F^2 , giving $R^2 = 28\,700\text{ cm}^{-1}$ *.

The solutions of determinants (1) and (2) yield the following "best" wavefunctions for 3F and 3P in this approximation:

$$({}^3F) = \lambda_1[a {}^3F(3d^3)] + \lambda_2[c {}^3F(3d^24s)] \quad (4)$$

$$({}^3P) = \lambda_3[a {}^3P(3d^3)] + \lambda_4[c {}^3P(3d^24s)] \quad (5)$$

$$\lambda_1 = 0.9978, \quad \lambda_2 = 0.0656; \quad \lambda_3 = 0.9827, \quad \lambda_4 = 0.1852.$$

In an octahedral crystal field the 3F state splits into three levels, ${}^3T_{1g}$, ${}^3T_{2g}$ and ${}^3A_{2g}$ with energies calculated in the weak field approximation as follows **::

$$E({}^3T_{1g}) = (\lambda_1)^2({}^3T_{1g}(a3d^3) | V_0 | {}^3T_{1g}(a3d^3)) + (\lambda_2)^2({}^3T_{1g}(c3d^24s) | V_0 | {}^3T_{1g}(c3d^24s)) \quad (6)$$

$$E({}^3T_{2g}) = (\lambda_1)^2({}^3T_{2g}(a3d^3) | V_0 | {}^3T_{2g}(a3d^3)) + (\lambda_2)^2({}^3T_{2g}(c3d^24s) | V_0 | {}^3T_{2g}(c3d^24s)) \quad (7)$$

$$E({}^3A_{1g}) = (\lambda_1)^2({}^3A_{2g}(a3d^3) | V_0 | {}^3A_{2g}(a3d^3)) + (\lambda_2)^2({}^3A_{2g}(c3d^24s) | V_0 | {}^3A_{2g}(c3d^24s)) \quad (8)$$

and with

$$\begin{aligned} ({}^3T_{1g}(a3d^3) | V_0 | {}^3T_{1g}(a3d^3)) &= 6Dq, & ({}^3T_{1g}(c3d^24s) | V_0 | {}^3T_{1g}(c3d^24s)) &= -Dq \\ ({}^3T_{2g}(a3d^3) | V_0 | {}^3T_{2g}(a3d^3)) &= -2Dq, & ({}^3T_{2g}(c3d^24s) | V_0 | {}^3T_{2g}(c3d^24s)) &= \frac{1}{3}Dq \\ ({}^3A_{2g}(a3d^3) | V_0 | {}^3A_{2g}(a3d^3)) &= -12Dq, & ({}^3A_{2g}(c3d^24s) | V_0 | {}^3A_{2g}(c3d^24s)) &= 2Dq \end{aligned}$$

we obtain

$$\begin{aligned} E({}^3T_{1g}) &= 5.97 Dq \\ E({}^3T_{2g}) &= -1.99 Dq \\ E({}^3A_{2g}) &= -11.94 Dq \end{aligned} \quad (9)$$

The 3P state is not split and gives a ${}^3T_{1g}$ level in the octahedral field. The secular determinant mixing ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ under V_0 is ***

$$\begin{array}{cc|c} 1. & {}^3T_{1g}(F) & 2. & {}^3T_{1g}(P) & \\ {}^3T_{1g} & \left| \begin{array}{cc} 5.97 Dq - E & 3.99 Dq \\ 3.99 Dq & 15\,617 - E \end{array} \right| & = & 0 & (10) \end{array}$$

* Recall, as defined in Ref.³, $G^2 = 5G_2$ and $F^2 = 49F_2$; in this case $G^2 = 9\,500\text{ cm}^{-1}$ and $F^2 = 86\,730\text{ cm}^{-1}$.

** Details of the calculation of levels in the weak field approximation are given in Refs.^{1,2}

*** The off-diagonal element, $({}^3T_{1g}(F) | V_0 | {}^3T_{1g}(P))$ is equal to $(\lambda_1)(\lambda_3)({}^3T_{1g}(F)(a3d^3) | V_0 | {}^3T_{1g}(P)(a3d^3)) + (\lambda_2)(\lambda_4)({}^3T_{1g}(F)(c3d^24s) | V_0 | {}^3T_{1g}(P)(c3d^24s))$ with $({}^3T_{1g}(F)(3d^3) | V_0 | {}^3T_{1g}(P)(3d^3)) = 4Dq$ and $({}^3T_{1g}(F)(c3d^24s) | V_0 | {}^3T_{1g}(P)(c3d^24s)) = \frac{11}{7} \sqrt{14} Dq$. The ${}^3F-{}^3P$ term interval, $15\,617\text{ cm}^{-1}$, is the value from Ref.⁴ for the Ni^{2+} free ion.

The value of Dq is determined from the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition, which for $\text{Ni}(\text{H}_2\text{O})^{2+}$ gives ${}^6 Dq = 854 \text{ cm}^{-1}$. Solving (10) we obtain

Transition	Predicted energy (cm^{-1}) for $3d^8 + 3d^74s$	Predicted energy for $3d^8$ only	Spectral maxima found * (cm^{-1})
${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	14 288	14 297	{ 13 500 ** 15 400
${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	26 820	26 820	25 300

DISCUSSION

It is apparent from these results that the calculated energies are only very slightly affected by the inclusion of $3d^74s$ with $3d^8$, suggesting that no serious error is involved in the $3d^8$ approximation of the states. On the other hand, in the pure $3d^8$ case the predicted energy of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is too large by approximately $1\,500 \text{ cm}^{-1}$. This discrepancy has been attributed by some authors^{8,9} to be a reduction in the ${}^3F - {}^3P$ term interval in going from a free to a complexed ion, as a result of the delocalization of metal ion electrons in the latter (covalent bonding). However, the molecular orbital treatment of chrome alum carried out by Tanabe and Sugano¹⁰ has cast some doubt on this interpretation, since the calculation did not lead to smaller values for the electron repulsion integrals (F_k 's).

It is however significant that a more complete calculation than the above, mixing ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ with higher ${}^3T_{1g}$'s arising from pure $3d^74s$ terms will result in an improvement of the predicted energy of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, since the ${}^3T_{1g}(P)$, with more $3d^74s$ character (eqn. 5), will be depressed relative to ${}^3T_{1g}(F)$. The magnitude of this depression of ${}^3T_{1g}(P)$ can be roughly estimated at about 30 cm^{-1} by looking at the various off-diagonal elements and term separations involved. For the same reason the extension of configuration interaction to include the two 3F 's and the two 3P 's in the $3d^64s^2$ configuration will result in another improvement, but it is difficult to estimate the magnitude of interaction since the $3d^64s^2$ levels haven't been located experimentally for Ni^{2+} .

Interaction with states of the configuration $3d^74d$ may also be of importance, since there are seven 3F 's and five 3P 's in $3d^74d$. A calculation which included all these possibilities would be quite tedious to perform, but to get an idea of the effect we carried out a calculation similar to the one above for Ti^{2+} ion,

* From Ref.⁶

** These two maxima are now believed to result from spin-orbit splitting of the ${}^3T_{1g}(F)$. See Ref.⁷ for details.

mixing the ${}^3F(3d^2)$ and ${}^3P(3d^2)$ levels with the one ${}^3F(3d4d)$ and one ${}^3P(3d4d)$, respectively. This gives a result in the right direction, "moving" the ${}^3T_{1g}(P)$ some 50 cm^{-1} closer to the 3F levels.

By summing the expected contributions from the inclusion of $3d^74s$, $3d^64s^2$ and $3d^74d$ levels, a definite improvement in the predicted energy of the ${}^3A_{2g}-{}^3T_{1g}(P)$ transition for Ni^{2+} complexes results. Thus it is tempting to suggest that it may be possible to resolve the apparent ${}^3F-{}^3P$ term interval reduction in the limits of crystalline field theory by inclusion of all possible configuration interaction. Furthermore, this explanation would of course be consistent with the experimental observation that the apparent reduction in the ${}^3F-{}^3P$ term interval is larger as the Dq value becomes larger, since the magnitude of the depression of ${}^3T_{1g}(P)$ with respect to the 3F levels increases with increasing Dq . In any case, we see that by the inclusion of configuration interaction in the crystalline field theory a result is obtained which if extended to its limits could possibly account for the apparent reduction of the ${}^3F-{}^3P$ term interval. Although some degree of covalent bonding must of necessity exist in metal complexes it is not at all clear at present just how this interval is affected by this type of bonding.

APPENDIX

Some other examples in which inclusion of $3d^{n-1}4s$ and $3d^{n-2}4s^2$ with $3d^n$ levels might be of interest in crystalline field calculations are the following:

1. $3d^3$. Ground state 4F . There is a 4F state for the configuration $3d^24s$ but it doesn't mix with the $3d^3$ 4F state ⁵.

2. $3d^6$. Ground state 5D . There are 5D 's for both $3d^54s$ and $3d^44s^2$ configurations. Complete matrices of electrostatic interaction are given by Trees and Harvey ¹¹. This case is of little practical interest in an octahedral field calculation since the 5D splits into only two levels, with the splitting parameter Dq taken from experiment. The configuration interaction calculation would only change the Dq value.

3. $3d^7$. Ground state 4F , with an excited 4P state approximately $14\,500\text{ cm}^{-1}$ above it ¹². This case is somewhat analogous to the $3d^8$ case, there being two 3F 's and two 3P 's in both $3d^64s$ and $3d^54s^2$ configurations. The electrostatic matrix elements have not been worked out.

4. $3d^9$. Ground state 2D . There are 2D 's in both $3d^84s$ and $3d^74s^2$ configurations, but the electrostatic matrix elements have not been calculated. As in 5D , the octahedral field calculation would only change the Dq value.

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