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Addendum et Erratum

Ligand Field Distortion Parameters

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The original publication [1] did not demonstrate the derivations of Eqs. (7) and (8). These are given here for completeness and to correct a coefficient error in the expansion of (7). The ligand field perturbation Hamiltonian can be derived from the spherical harmonic addition theorem and is of form:

$$V_G = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{4\pi}{2n+1} \frac{r_<^n}{r_>^{n+1}} Y_{m_j}^{n*} \cdot Y_{m_i}^{n} \tag{1}$$

In a finite group G representing the physical environment this can be rewritten as a sum over the number of fully symmetric A_1 components projected from the spherical harmonics:

$$V_G = \sum_{n=0}^{\infty} \sum_{\alpha=1}^{Z} \frac{4\pi}{2n+1} \frac{r_<^n}{r_>^{n+1}} \alpha A_1^* \cdot \alpha A_1 \tag{2}$$

In the case of d electrons in an octahedral field $n = 4$, $\alpha = 1$

$$V_{O_h} = \frac{4\pi}{9} \frac{Ze^2 r_<^4}{r_>^5} A_1^* \cdot A_1 \tag{3}$$

Expanding the A_1^* tensor component of an octahedron in terms of spherical harmonics of order 4 yields:

$$\begin{aligned} V_{O_h} &= \frac{4\pi}{9} \frac{Ze^2 r_<^4}{r_>^5} \left[\sqrt{\frac{7}{12}}\, Y_0^4 + \sqrt{\frac{5}{24}}\,(Y_4^4 + Y_{-4}^4)\right]^* A_1 \\ &= \frac{4\pi}{9} \frac{Ze^2 \overline{r_4}}{a^5} \left[\sqrt{\frac{7}{12}} \left(\sqrt{\frac{1}{2\pi}} \sqrt{\frac{9}{128}}\ (8(2) + 3(4))\right)\right. \\ &\quad \left. + \sqrt{\frac{5}{24}} \left(\sqrt{\frac{1}{2\pi}} \sqrt{\frac{9}{128}} \sqrt{\frac{35}{2}}\,(4+4)\right)\right] A_1 \end{aligned} \tag{4}$$

after substitution of ligand positions in a ligand field approximation. On simplification this becomes:

$$V_{O_h} = \frac{4\pi Ze^2\overline{r_4}\sqrt{7}\sqrt{9}}{9\sqrt{2\pi}\sqrt{128}\sqrt{12}\,a^5}(48)A_1$$

$$= \frac{\sqrt{7\pi}}{24\sqrt{3}}\frac{Ze^2\overline{r^4}}{a^5}(48)A_1$$

$$= \frac{2\sqrt{7\pi}}{\sqrt{3}}\frac{Ze^2\overline{r^4}}{a^5}A_1 \tag{5}$$

Expanding the remaining A_1 representing the one-electron operator this expression yields:

$$V_{O_h} = \frac{2\sqrt{7\pi}}{\sqrt{3}}\frac{Ze^2\overline{r^4}}{a^5}\left[\sqrt{\tfrac{7}{12}}\,Y_0^4 + \sqrt{\tfrac{5}{24}}\,(Y_4^4 + Y_{-4}^4)\right] \tag{6}$$

The conventional form of the operator uses an unnormalized linear combination of spherical harmonics and thus:

$$V_{O_h} = \frac{2\sqrt{7\pi}}{\sqrt{3}}\frac{Ze^2\overline{r^4}}{a^5}\sqrt{\tfrac{7}{12}}\left[Y_0^4 + \sqrt{\tfrac{5}{14}}(Y_4^4 + Y_{-4}^4)\right]$$

$$= \frac{7\sqrt{\pi}}{3}\frac{Ze^2\overline{r^4}}{a^5}\left[Y_0^4 + \sqrt{\tfrac{5}{14}}(Y_4^4 + Y_{-4}^4)\right] \tag{7}$$

which is the conventional form. Instead of completing this simplification, the expansion of (4) may be retained during the expansion of the second A_1 component in (6). Then:

$$V_{O_h} = \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a^5}\left[\sqrt{\tfrac{7}{12}}\,Y_0^4 + \sqrt{\tfrac{5}{24}}(Y_4^4 + Y_{-4}^4)\right]^* \left[\sqrt{\tfrac{7}{12}}\,Y_0^4 + \sqrt{\tfrac{5}{24}}\,(Y_4^4 + Y_{-4}^4)\right]$$

This simplifies using (1) to:

$$V_{O_h} = \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a^5}\left[\tfrac{7}{12}\,Y_0^{4*}Y_0^4 + \tfrac{5}{24}(Y_4^{*4}Y_4^4 + Y_{-4}^{4*}Y_{-4}^4)\right]$$

$$V_{O_h} = \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a^5}\left[\frac{1}{\sqrt{2\pi}}\sqrt{\frac{9}{128}}\left(\frac{7}{12}\right)\left(\frac{8(2)}{a^5} + \frac{3(4)}{b^5}\right)Y_0^4 + \frac{1}{\sqrt{2\pi}}\sqrt{\frac{315}{256}}\left(\frac{5}{24}\right)\left(\frac{4}{b^5}Y_4^4 + \frac{4}{b^5}Y_{-4}^4\right)\right]$$

$$= \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a^5}\frac{1}{\sqrt{2\pi}}\sqrt{\frac{9}{128}}\sqrt{\frac{7}{12}}\left[\sqrt{\frac{7}{12}}\left(\frac{8(2)}{a^5} + \frac{3(4)}{b^5}\right)Y_0^4 + \frac{5\sqrt{5}}{2\sqrt{24}}\left(\frac{4}{b^5}Y_4^4 + \frac{4}{b^5}Y_{-4}^4\right)\right]$$

$$= \frac{\sqrt{7\pi}}{24\sqrt{3}}Ze^2\overline{r^4}\left[\sqrt{\frac{7}{12}}\left(\frac{16}{a^5} + \frac{12}{b^5}\right)Y_0^4 + \frac{5\sqrt{5}}{2\sqrt{24}}\left(\frac{4}{b^5}Y_4^4 + \frac{4}{b^5}Y_{-4}^4\right)\right] \tag{8}$$

which is what Eq. (7a) of paper *should be*.

The reparametrization of Eqs. (7a) and (7b) to yield Eq. (8) is carried out most easily as a comparison of strong and weak field formulations of the tetragonal Hamiltonian.

Let, in the strong field model:

$$P|A_{1g}|_{D_{4h}} = DQ\,|A_{1g}0\,|_{O_h} + DT|E_g0|_{O_h} \tag{9a}$$

In a weak field model;

$$P|A_{1g}|_{D_{4h}} = P_0|\,Y_0^4| + \frac{1}{\sqrt{2}}P_4|\,(Y_4^4 + Y_{-4}^4)| \tag{9b}$$

Equating these two expressions:

$$\begin{aligned} DQ|A_{1g}0|_{O_h} + DT|E_g0|_{O_h} &= P_0|\,Y_0^4| + \frac{1}{\sqrt{2}}P_4|(Y_4^4 + Y_{-4}^4)| \\ &= \sqrt{\tfrac{7}{12}}DQ|\,Y_0^4| + \sqrt{\tfrac{5}{24}}DQ|(Y_4^4 + Y_{-4}^4)| \\ &\quad + \sqrt{\tfrac{5}{12}}DT|\,Y_0^4| - \sqrt{\tfrac{7}{24}}DT|(Y_4^4 + Y_{-4}^4)| \end{aligned} \tag{10}$$

by expansion of the totally symmetric linear combinations of $|A_{1g}0|_{O_h}$ and the anti-symmetric combination $|E_g0|_{O_h}$. Now equating terms of common harmonics:

$$P_0|\,Y_0^4| = \sqrt{\tfrac{7}{12}}DQ|\,Y_0^4| + \sqrt{\tfrac{5}{12}}DT|\,Y_0^4|$$

and

$$\frac{1}{\sqrt{2}}P_4|(Y_4^4 + Y_{-4}^4)| = \sqrt{\tfrac{5}{24}}DQ|(Y_4^4 + Y_{-4}^4)| + \sqrt{\tfrac{7}{24}}DT|(Y_4^4 + Y_{-4}^4)| \tag{11}$$

Solving for DQ and DT:

$$\begin{aligned} DQ &= \sqrt{\tfrac{5}{12}}P_4 + \sqrt{\tfrac{7}{12}}P_0 \\ DT &= \sqrt{\tfrac{7}{12}}P_4 + \sqrt{\tfrac{5}{12}}P_0 \end{aligned} \tag{12}$$

If these expressions are expanded by substitution of ligand positions where

$$\begin{aligned} P_0 &= \frac{4\pi}{9}Ze^2\overline{r^4}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\left(\frac{16}{a^5} + \frac{12}{b^5}\right) \\ P_4 &= \frac{4\pi}{9}Ze^2\overline{r^4}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\sqrt{\frac{35}{2}}\left(\frac{4}{b^5} + \frac{4}{b^5}\right) \end{aligned} \tag{13}$$

then substitution yields:

$$\begin{aligned} DQ &= \frac{4\pi}{9}Ze^2\overline{r^4}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\left[\sqrt{\frac{7}{12}}\left(\frac{16}{a^5} + \frac{12}{b^5}\right) + \sqrt{\frac{5}{24}}\sqrt{\frac{35}{2}}\left(\frac{4}{b^5} + \frac{4}{b^5}\right)\right] \\ &= \frac{4\pi}{9}Ze^2\overline{r^4}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\sqrt{\frac{7}{12}}\left[\frac{16}{a^5} + \frac{12}{b^5} + \frac{20}{b^5}\right] \\ &= \frac{4\pi}{9}Ze^2\overline{r^4}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\sqrt{\frac{7}{12}}(16)\left[\frac{1}{a^5} + \frac{2}{b^5}\right] \end{aligned} \tag{14}$$

which except for $(4\pi/9)$ is Eq. (8a).

The reformulation of this equation to (15) and (25) involved two errors in the paper. Thus by substitution of (12) of the paper into the equation above:

$$(DQ)_4 = \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\left[\sqrt{\frac{7}{12}}\left(\frac{8(n_A)(z)}{(a\sec\theta)^4} - \frac{24(n_E)(x)(\tan^2\theta)}{(a\,\mathrm{cosec}\,\theta)^4} + \frac{3(n_E)(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right) + \sqrt{\frac{5}{24}}\sqrt{\frac{35}{2}}\left(\frac{2(n_E)(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right)\right] \tag{15}$$

in which the cotan θ function is replaced by a tan θ function, implying projection onto the equatorial plane, and the final term is *positive* not negative. The simplified form of (15) then becomes:

$$(DQ)_4 = \frac{4\pi}{9}\frac{Ze^2\overline{r^4}}{a}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}(16)\left[\frac{(z)}{(a\sec\theta)^4} - \frac{(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right] \tag{16}$$

After simplification Eq. (15) of the paper becomes:

$$(DQ)_4 = \frac{2\sqrt{7\pi}}{\sqrt{3}}\frac{Ze^2\overline{r^4}}{a}\left[\frac{(z)}{(a\sec\theta)^4} - \frac{(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right] \tag{17}$$

and (16) is

$$(DQ)_4 = \frac{9}{8}\left(\frac{-2n_3}{18} + \frac{n_4}{6}\right)\frac{2\sqrt{7\pi}}{3\sqrt{3}}\frac{Ze^2\overline{r^4}}{a}\left[\frac{(z)}{(a\sec\theta)^4} - \frac{(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right] \tag{18}$$

Identical alterations should be made to Eqs. (25) for consistency, the new form of (25) is:

$$(DQ)_3 = \frac{9}{8}\left(\frac{2n_3}{18} - \frac{n_4}{6}\right)\frac{Ze^2\overline{r^4}}{a}\sqrt{\frac{1}{2\pi}}\sqrt{\frac{9}{128}}\left[\sqrt{\frac{7}{27}}\left(\frac{8(n_A)(z)}{(a\sec\theta)^4} - \frac{24(n_E)(x)(\tan^2\theta)}{(a\,\mathrm{cosec}\,\theta)^4} + \frac{3(n_E)(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right) + \sqrt{\frac{20}{54}}\sqrt{35}\left(\frac{2(n_E)(x)\tan\theta}{(a\,\mathrm{cosec}\,\theta)^4}\right)\right]$$

$$= \frac{9}{8}\left(\frac{2n_3}{18} - \frac{n_4}{6}\right)\frac{4}{9}\frac{\sqrt{7\pi}}{\sqrt{3}}\frac{Ze^2\overline{r^4}}{a}\left[\frac{(z)}{(a\sec\theta)^4} - \frac{(x)}{(a\,\mathrm{cosec}\,\theta)^4}\right] \tag{19}$$

As is clearly apparent, these expansions give the expected:

$$(DQ)_3 = -\tfrac{2}{3}(DQ)_4 \tag{20}$$

References

1. Hollebone, B. R., Donini, J. C.: Theoret. Chim. Acta (Berl.) 39, 33 (1975)

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