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The crystal dependent open-shell polarizability of F-elements: higher order contributions

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Abstract

It has earlier been shown that the use of a self consistent multipole electrostatic model to derive the crystal field parameters (CFP) actually gives the correct curve shape when the CFP are plotted against the various rare-earth ions (S. Edvardsson, M. Klintenberg, The use of CI calculated polarizabilities to study rare-earth CFP dependencies in the laser host RE:YLF. Mater. Sci. Forum, 1999;315–317:407). It is also known that the electrostatic contribution is important for the lower order parameters. In this connection, our primary interest is to revisit this model and investigate theoretically some aspects of the dipole polarizability (α_D). A few approximations were done in the earlier calculations: the treatment of unfilled shells, the neglect that also higher order terms of the type $A_{t0}r^tC_0^t$ contribute with t odd (not only the $A_{10}r^1C_0^1$ term), correlation effects and second order contributions in perturbation theory. The solutions of the inhomogeneous Schrödinger equation are solved by a powerful numerical method. The problem is reformulated and results instead in a simple linear equation system (symmetric tridiagonal matrix) which is stable and fast to solve. The various theoretical results will be used in future applications. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

This work theoretically reviews and also presents some new mathematical expressions in connection to the dipole polarizability of ions. First, we apply the full crystal-field hamiltonian to derive a general expression that should be useful for polarizabilities in the solid state; the standard expressions for the free-ion polarizability become a special case ($t=1$). Second, mathematical expressions for both open- and closed-shell ions are shown. The electronic correlations are also known to be fairly important for cations. As long as these effects are reasonably small they may be treated using perturbation theory. It is extremely convenient to submit the computed perturbed wavefunctions into the correlation formula presented. We also briefly outline some expressions needed for second order calculations. Finally, we conclude this work with a well known numerical recipe in order to get fast and reliable solutions. The derivations are done using a formalism which should be considered standard for the theoretical rare-earth spectroscopist. The type of approach presented here would also be useful in the calculation of the wavefunctions needed in intensity calculations for transitions within the f-shell. A beautiful review about experimental and theoretical considerations may be found in Ref. [1]. This book also lists a great number of references in the field of polarizability.

1.1. The first order dipole polarizability

Since the crystal-field hamiltonian is a one-particle operator we can treat each electron separately. This is true if all unperturbed wavefunctions are orthogonalized to all perturbed wavefunctions. One of the electrons in a rare-earth or actinide ion is assumed to be perturbed by the standard crystal field hamiltonian:

$$H_{cf}=\sum_{tp} A_{tp}r^tC_p^t(\theta,\varphi)$$

where

$$A_{tp}=(-1)^{p+1}\int \frac{\rho(\vec{r}\,')}{r'^{\,t+1}}C_{-p}^t(\alpha',\beta')\,\mathrm{d}\vec{r}\,'$$

represents the external densities. These ligand density distributions modify the wavefunction in first order into:

$$\psi=\psi_0+\psi_1$$

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where $\psi_0 = 1/ru_0Y_{lm}$ and $\psi_1 = 1/r\,\Sigma_{l'm'}\,u_{l'}Y_{l'm'}$. The induced charge density is then given by $|\psi_1|^2 + \psi_0\psi_1^* + \psi_1\psi_0^*$ and the induced dipole moment $\vec{\mu} = \Sigma_i\,q_i\vec{r}_i$, becomes in integral form:

$$\vec{\mu} = \int_V (|\psi_1|^2 + \psi_0\psi_1^* + \psi_1\psi_0^*)\,\vec{r}\mathrm{d}V$$

in atomic units. The induced dipole moment $\vec{\mu} = \alpha_{\mathrm{D}}\vec{E}$ expressed along the z-axis gives the isotropic scalar dipole polarizability:

$$\alpha_{\mathrm{D}} = -(A_{10})^{-1}\int_V r\cos\theta(|\psi_1|^2 + \psi_0\psi_1^* + \psi_1\psi_0^*)\,\mathrm{d}V \tag{1}$$

By the use of spherical harmonics, Eq. (1) is written:

$$\begin{aligned}\alpha_{\mathrm{D}} = &-(A_{10})^{-1}\sqrt{\frac{4\pi}{3}}\sum_{l_1'm_1'l_2'm_2'}\\ &\left[\int Y_{10}\frac{1}{r}u^*_{l_1'}u_{l_2'}Y^*{}_{l_1'm_1'}Y_{l_2'm_2'}\mathrm{d}V\right]\\ &-(A_{10})^{-1}\sqrt{\frac{4\pi}{3}}\sum_{l'm'}\int Y_{10}\frac{1}{r}u_0(u^*_{l'}Y_{lm}Y^*_{l'm'}\\ &+u_{l'}Y_{l'm'}Y^*_{lm})\,\mathrm{d}V\\ &=-(A_{10})^{-1}\sqrt{\frac{4\pi}{3}}\sum_{l_1'm_1'l_2'm_2'}\langle u_{l_1'}|r|u_{l_2'}\rangle\langle l_1'm_1'|Y_{10}|l_2'm_2'\rangle\\ &-(A_{10})^{-1}\sqrt{\frac{4\pi}{3}}\sum_{l'm'}[\langle u_{l'}|r|u_0\rangle\langle l'm'|Y_{10}|lm\rangle\\ &+\langle u_0|r|u_{l'}\rangle\langle lm|Y_{10}|l'm'\rangle]\end{aligned} \tag{2}$$

The first order wavefunction ψ_1 may be expanded according to the standard expression:

$$\psi_n^{(1)} = \sum_{k\neq n}\frac{\langle\psi_k^{(0)}|H_{cf}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}\psi_k^{(0)}$$

Here every term consists of an angular part $\langle l'm'|C_p^t|lm\rangle$ which is proportional to:

$$\begin{pmatrix} l' & t & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & t & l\\ -m' & p & m\end{pmatrix} \tag{3}$$

The first term of Eq. (2) (the $|\psi_1|^2$ part of Eq. (1)) only contributes when $l_1' + l_2' + 1$ is even. Eq. (3) gives that l_1' and l_2' are connected to l via t_1 and t_2, respectively. Now from Eq. (3) we have that $l_1' + t_1 + l$ and $l_2' + t_2 + l$ must be even integers, so $l_1' + l_2' + t_1 + t_2$ is even as well. In the case that $t_1 + t_2$ is even then $l_1' + l_2'$ is even; this is incompatible with the statement earlier that $l_1' + l_2' + 1$ is even, and hence these terms do not contribute in the $|\psi_1|^2$ part of Eq. (2). For example, this means that a constant field does not contribute since there is only one term in the hamiltonian $A_{10}rC_0^1$ ($t_1 + t_2$ even). However, the remaining cross-terms in $|\psi_1|^2$ with $l_1' + l_2'$ odd could actually be important (e.g. in a crystal) but should still be small in comparison with $\psi_0\psi_1^* + \psi_1\psi_0^*$.

These two terms in Eq. 2 only contribute if $m = m'$ and if $l' + l + 1$ is even. These then give the following contribution to the polarizability:

$$\begin{aligned}\alpha_{\mathrm{D}} = &-(A_{10})^{-1}\sum_{l'}[\langle u_{l'}|r|u_0\rangle + \langle u_0|r|u_{l'}\rangle][l', l]^{1/2}\\ &\times(-1)^m\begin{pmatrix} l' & 1 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & 1 & l\\ -m & 0 & m\end{pmatrix}\end{aligned} \tag{4}$$

From Eq. 4 we have $l' + l + 1 = $even, and from the angular part of Eq. (3), $l' + t + l = $even which gives $2l' + 2l + t + 1 = $ e*v*en $\Rightarrow t = $ odd integer. The fact that $m = m'$ gives that $p = 0$ (Eq. (3)), so the relevant crystal field perturbations become:

$$H_{cf} = \sum_{t=1,3,\ldots} A_{t0}r^tC_0^t$$

Now consider the well known first order equation from Rayleigh–Schrödinger perturbation theory:

$$(H_0 - E_0)\psi_1 = (E_1 - H_{cf})\psi_0$$

After some rather lengthy derivations we obtain a modified Sternheimer equation for the dipole polarizability:

$$\left[-\frac{\partial^2}{\partial r^2} + \frac{l'(l'+1)}{r^2} + 2(V_{nl}(r) - E_0(nl))\right]w^t(nl \rightarrow l') = r^tu_0(nl) \tag{5}$$

where $u_{l'} = -2\,\Sigma_t\,A_{t0}\langle l'm|C_0^t|lm\rangle\,w^t(nl \rightarrow l')$. There are certainly additional terms that contribute to $u_{l'}$ in the expression $\psi_1 = 1/r\,\Sigma_{l'm'}\,u_{l'}Y_{l'm'}$ earlier, but those do not contribute to the dipole polarizability. $w^t(nl \rightarrow l')$, from here after designated $w^t_{l'}$, is the perturbed function corresponding to the perturbation $A_{t0}r^tC_0^t$. Since A_{t0} is real the function $u_{l'}$ in Eq. (4) is real.

Using this definition of $u_{l'}$ Eq. (4) may then be written:

$$\begin{aligned}\alpha_{\mathrm{D}} &= \sum_{l'}\alpha_{\mathrm{D}}(nlm_lm_s \rightarrow l'm_lm_s)\\ &= 4\sum_t\sum_{l'}\frac{A_{t0}}{A_{10}}\langle u_0|r|w^t_{l'}\rangle\langle l'm|C_0^t|lm\rangle(-1)^m[l',l]^{1/2}\\ &\times\begin{pmatrix} l' & 1 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & 1 & l\\ -m & 0 & m\end{pmatrix}\\ &= 4\sum_t\sum_{l'}\frac{A_{t0}}{A_{10}}\langle u_0|r|w^t_{l'}\rangle[l', l]\begin{pmatrix} l' & 1 & l\\ 0 & 0 & 0\end{pmatrix}\\ &\begin{pmatrix} l' & 1 & l\\ -m & 0 & m\end{pmatrix}\\ &\times\begin{pmatrix} l' & t & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & t & l\\ -m & 0 & m\end{pmatrix}\end{aligned} \tag{6}$$

The interesting feature here is that now the polarizability depend on odd crystal field factors, i.e. they are crystal dependent. After a diagonalization of the energy matrix, the eigenvectors are given by:

$$\Psi_0 = \sum_i c_i\{k_1k_2\ldots k_n\}_i$$

for a *open-shell* ground state. The probability of finding the ion in the determinantal product state $\{k_1k_2\dots k_n\}_i$ is $|c_i|^2$. This means that the total α_D is a *weighted* sum over the single electron $\alpha'_\mathrm{D}s$:

$$\alpha_\mathrm{D} = \sum_i \sum_{l'} |c_i|^2 [\alpha_\mathrm{D}(nlm_{l_{1i}}m_{s_{1i}} \rightarrow l'm_{l_{1i}}m_{s_{1i}}) + \cdots + \alpha_\mathrm{D}(nlm_{l_{ni}}m_{s_{ni}} \rightarrow l'm_{l_{ni}}m_{s_{ni}})]$$

In the case of a complete shell there is only one product state:

$$\alpha_\mathrm{D} = \sum_{l'} [\alpha_\mathrm{D}(nlm_{l_1}m_{s_1} \rightarrow l'm_{l_1}m_{s_1}) + \cdots + \alpha_\mathrm{D}(nlm_{l_n}m_{s_n} \rightarrow l'm_{l_n}m_{s_n})]$$

This is just a summation over all m_{l_i} and m_{s_i}, and the spin summation can be replaced with a multiplication with 2 since Eq. (6) is spin-independent. In the usual approximation that only the term $t=1$ contributes in Eq. (6) we get:

$$\alpha_\mathrm{D} = 8 \sum_{l'} \langle u_0 | r | w^1_{l'} \rangle [l', l] \begin{pmatrix} l' & 1 & l \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_m \begin{pmatrix} l' & 1 & l \\ -m & 0 & m \end{pmatrix}^2$$

The last summation equals $\frac{1}{3}$, giving:

$$\alpha_\mathrm{D} = \frac{8}{3} \sum_{l'} \langle u_0 | r | w^1_{l'} \rangle [l', l] \begin{pmatrix} l' & 1 & l \\ 0 & 0 & 0 \end{pmatrix}^2$$

for a complete shell. This is of course just the very well known expression for the closed shell dipole polarizability originally derived by Sternheimer [2].

1.2. The electron correlation contribution

Taking also the electron–electron interactions into account the polarizability may be written as $\alpha_\mathrm{D} = \alpha_0 + \alpha_1$, where α_0 is the polarizability from the previous section and α_1 includes the correlation contribution. It is often noted that the correlation contribution is quite significant. An approximate way to account for higher order contributions (if α_1 is reasonably small) is to use the geometric series expansion which is often found to be satisfactory [3]:

$$\alpha_\mathrm{D} = \alpha_0 \left(1 - \frac{\alpha_1}{\alpha_0}\right)^{-1}$$

The correlation contributions (α_1) to the dipole polarizability may either be derived using the diagrammatic approach in many body perturbation theory [4] or by classical methods [5]. Their result may be simplified into:

$$\alpha_1 = -\sum_{ij} 2\langle \delta\psi_i \delta\psi_j | 1/r_{12} | \psi_{0i} \psi_{0j} \rangle - \langle \delta\psi_i \delta\psi_j | 1/r_{12} | \psi_{0j} \psi_{0i} \rangle - \langle \delta\psi_i \psi_{0j} | 1/r_{12} | \delta\psi_j \psi_{0i} \rangle$$

where the ψ_{0k} values ($k = i$ or j) are unperturbed relativistic Hartree–Fock functions and the perturbed functions $\delta\psi_k = -(1/A_{10})\,\psi_{1k}$ are given by:

$$\delta\psi_k = \frac{1}{r} \sum_t \sum_{l'_k} 2\frac{A_{t0}}{A_{10}} (-1)^m [l'_k, l_k]^{1/2} \begin{pmatrix} l'_k & t & l_k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_k & t & l_k \\ -m_k & 0 & m_k \end{pmatrix} w^t_{l_k'} Y_{l_k' m_k}$$

Note that the $w^t_{l_k'}$ are already known from the first order calculations i.e. they are solutions to the inhomogeneous Schrödinger equation (see Eq. (5)). This type of calculation usually involve many intra- and inter-shell interactions. The procedure results in consistent polarizabilities that often are in excellent agreement with experiment [6].

1.3. Outline of second order contributions

We will here carry out the first steps needed to perform higher order calculations. Next order equation in Rayleigh–Schrödinger theory is:

$$(H_0 - E_0)\,\psi_2 + (H_{cf} - E_1)\,\psi_1 - E_2\psi_0 = 0 \qquad (7)$$

By using the expansion:

$$\psi = \psi_0 + \psi_1 + \psi_2 = \frac{1}{r}\left[u_0 Y_{lm} + \sum_{l'm'} u_{l'} Y_{l'm'} + \sum_{l''m''} u_{l''} Y_{l''m''}\right]$$

in Eq. (7) we end up with:

$$(H_0 - E_0)\,u_{l''} + \sum_{l'm'} \left[\sum_{tp} A_{tp} r^t \langle l''m'' | C^t_p | l'm' \rangle u_{l'} - \delta(l', l'')\,\delta(m', m'')\,E_1 u_{l'} - \delta(l'', l)\,\delta(m'', m)\,E_2 u_0 \right] = 0 \qquad (8)$$

In this order, the induced density is essentially $\psi_0\psi_2^* + \psi_0^*\psi_2$. Following the same procedure beginning with Eq. (1) we end up with a similar expression to Eq. (4). Thus $l'' \neq l$, so the last term in Eq. (8) disappear. This rather complex equation may then be investigated for each crystal field term separately.

1.4. Numerical calculations

In order to calculate the dipole polarizabilities we need to solve the modified Sternheimer equation:

$$\left[-\frac{\partial^2}{\partial r^2} + \frac{l'(l'+1)}{r^2} + 2(V(r) - E_0) \right] w^t_{l'} = r^t u_0$$

We will here apply the finite difference method with a grid defined according to $r_0 = 0$, $r_1 = h, \dots, r_i = ih, \dots, r_N = R$. The boundary conditions are $w^t_{l',0} = 0$ and $w^t_{l',N} = 0$. Approximating the second derivative of $w^t_{l'}$ in the point r_i with:

$$\frac{\partial^2 w^t_{l'}(r_i)}{\partial r_i^2} = \frac{w^t_{l',i-1} - 2w^t_{l',i} + w^t_{l',i+1}}{h^2}$$

the differential equation connecting nearby points can then be written:

$$w^t_{l',i-1} + U_{ii} w^t_{l',i} + w^t_{l',i+1} = s(r_i)$$

with

$$U_{ii} = -2 - h^2\left(\frac{l'(l'+1)}{r_i^2} + 2(V(r_i) - E_0)\right)$$

and $s(r_i) = -h^2 r_i^t u_0$. Applying the boundary conditions and connecting all the grid points lead to $N-1$ linear equations. This results in a matrix equation of type $Aw = s$ where the solutions w are the perturbed radial wave functions. The matrix A is symmetric tridiagonal:

$$A = \begin{bmatrix} U_{11} & 1 & 0 & \cdots & \cdots & \cdots & 0 \\ 1 & U_{22} & 1 & 0 & \cdots & \cdots & 0 \\ 0 & 1 & U_{33} & 1 & 0 & \cdots & 0 \\ \vdots & & & \ddots & & & \vdots \\ \vdots & & & & \ddots & & \vdots \\ \vdots & & & & & \ddots & 1 \\ 0 & \cdots & \cdots & \cdots & \cdots & 1 & U_{N-1,N-1} \end{bmatrix}$$

Calculating the perturbed wave functions $w_{l'}^t$ and evaluating the various integrals $\langle u_0|r|w_{l'}^t\rangle$ is a numerical tough problem. The computations are usually calculated using step-lengths $h = 0.0001$ a.u and $h = 0.00005$ a.u, and then applying the Richardson extrapolation technique. This method turns out not only to be extremely stable but also fast using the numerical library LAPACK (see http://www.netlib.org/lapack/).

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