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# The energy matrix using determinantal product states applied to Ho:YAG

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## Abstract

A program written in C is applied for calculations of energy levels and wavefunctions of the lanthanides or actinides. Standard non-relativistic phenomenological operators are used. Simple determinantal product states are used to form the basis set. The complete energy matrix is diagonalized with all operators interacting simultaneously thus allowing mixing of all quantum numbers. The crystal field splitting can also be studied via the standard crystal field hamiltonian as well as the magnetic field influence on the energy levels. The program is here applied to the technologically interesting trivalent ion holmium which is used to form extremely strong magnets as well as the medical eye-safe laser Ho:YAG. Both experimentally fitted and calculated self-consistent crystal field parameters are used to study the energy structure. Crystal ionic polarizabilities with electron correlation included are partly calculated. Zeeman split levels are also studied.

*Keywords:* Energy matrix; Crystal field; Polarizability; Rare-earth

## 1. Introduction

The complexity of the f-elements of the periodic system is generally known to be tremendous. Even with the fast computers of today, accurate ab initio calculations have still only been able to attack the $f^2$ electronic configuration, e.g. the term structure was calculated using the multiconfiguration Dirac–Fock program GRASP [1]. Improved results were later obtained using the relativistic coupled-cluster method [2]. For three or more f-electrons we are still obliged to turn to phenomenological model hamiltonians which nevertheless are motivated in higher order perturbation theory [3,4]. However, some of the parameters may actually be calculated (with fair reliability) using ab initio methods, see e.g. [5]. The use of determinantal product states in our program is clearly a disadvantage for the group theoretical aspects of the energy levels, but is indeed appealing with regard to the simplicity in calculating the matrix elements for any number of electrons. This approach also means that there is no need to find out or generate any fractional parentage coefficients of Racah. These considerations have also been used and appreciated earlier in practical calculations by Garcia and Faucher [6]. Modification of the program to include also other operators such as spin–spin, spin–other orbit or Breit interaction etc. is straight forward. Free ion configuration interaction is accounted for through the use of standard CI operators; the program may also quite easily be modified to broaden the basis (CI) so that instead an ab initio calculation is performed. The crystal field splittings can be studied via the standard crystal field hamiltonian as well as the magnetic field influence on the energy levels. Diagonalization results in all energy eigenvalues and eigenvectors that in turn are partly responsible for the polarized dipole, quadrupole, . . . transitions within the unfilled f-shell. The program is tested here for the medical laser host Ho:YAG. The software is made available for interested parties [7].

## 2. The energy matrix

The standard non-spherical hamiltonian for an ion embedded in a crystal is written:

$$\begin{aligned}\hat{H} = {} & \sum_{k=2,4,6} F^k(nf, nf)\hat{f}_k + \sum_i \xi(r_i)\hat{l}_i \cdot \hat{s}_i \\ & + \alpha\hat{L}^2 + \beta\hat{G}(G_2) + \gamma\hat{G}(R_7) \\ & + \sum_{i=2,3,4,6,7,8} T^i\hat{t}_i + \sum_i \sum_{tp} (1-\sigma_t)A_{tp}r_i^t\hat{C}_{tp}(\theta_i, \phi_i) \\ & + \mu_B\vec{B} \cdot \sum_i \hat{l}_i + 2\hat{s}_i \qquad (1)\end{aligned}$$

As usual, the $F^k$ and $\xi(r)$ are the electrostatic and

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spin–orbit parameters. $f_k$ are angular parts of the electrostatic interactions. $\alpha$, $\beta$, $\gamma$ are the Trees parameters associated with the two-body correction terms for free ion configuration interaction effects [3,8]. $\hat{G}(G_2)$ and $\hat{G}(R_7)$ are Casimir's operators for groups $G_2$ and $R_7$, respectively. Other free-ion CI effects are included by means of three-body operators. Judd's investigations of these resulted in the operators $\hat{t}_i$ with corresponding parameters $T^i$ [4]. $A_{tp}$ represents the crystal environment which is related to the crystal field parameters (CFP) through $B_{tp} = (1 - \sigma_t) A_{tp} r^t$ and $\sigma_t$ are the shielding factors by Sternheimer [9]. The shielding factors $\sigma_t$ are unnecessary if a cluster calculation is performed since the adjustments of the rare-earth wavefunctions would then already been taken into account. The last term is the standard magnetic field hamiltonian. We have here neglected the two-body magnetic operators $p_f$ and the Marvin operators $m_h$ associated with spin–spin, spin–other orbit interactions. Most of the operators are standard and the derivations of their matrix elements will not be repeated here. However, the matrix elements of the three-particle operators associated with configuration interaction are nontrivial to calculate, see [7].

## 3. The crystal field

In the electrostatic approach $A_{tp}$ may be calculated according to:

$$A_{tp} = (-1)^{p+1} \int \frac{\rho(\vec{r}\,')}{r'^{\,t+1}} C_{t-p}(\alpha', \beta')\, \mathrm{d}\vec{r}\,' \tag{2}$$

with $\rho(\vec{r}\,')$ being the external charge densities and $C_{t-p}(\alpha', \beta')$ is a spherical tensor of rank $t$ and projection $-p$. For ionic host materials one may as a first approximation use the self-consistent electrostatic model, see e.g. [10,11]. In this model the density $\rho(\vec{r}\,')$ is expanded using monopole-, dipole- and quadrupole polarizabilities. The dipole moments are calculated self-consistently, i.e., electrostatic equilibrium of charges and induced dipoles at each ion site is ensured. The quadrupole polarizability may be calculated as in [12]. The correlation contributions were there neglected since they are known to be practically negligible [13]. The electron correlations for the dipole case will be calculated in present work. The crystal field parameters become

$$\begin{aligned} A_{tp} \approx (-1)^{p+1} \sum_j \Big[ & q_j r_j'^{\,-t-1} + \vec{\mu}_j \cdot \overrightarrow{e_{r_j'}}\, r_j'^{\,-t-2}(t+1) \\ & + \frac{1}{2} Q_j r_j'^{\,-t-3}(t+2)(t+1) \Big] C_{t-p}(\alpha_j', \beta_j') \end{aligned} \tag{3}$$

This approach usually works satisfactorily for lower order $A_{tp}$ in ionic hosts. In the case of higher order $A_{tp}$ they often become underestimated. This failure is usually attributed to neglect of covalency and charge penetration. However, it could also partly be due to site-distortion effects in the case of doping. This should certainly have a higher influence on high order $A_{tp}$ compared to low order $A_{tp}$. Another interesting approach would be to use the density $\rho(\vec{r}\,')$ from density functional theory (DFT) to derive the crystal field parameters from Eq. (2). Some initial work has already been carried out for metallic systems [14]. Here each Stark level acts back on the density of the environment which in turn interacts with the Stark level leading to a self-consistent process. This means that there are different densities $\rho(\vec{r}\,')$ for different Stark levels, i.e., $A_{tp}$ can no longer be chosen to be unique for all Stark levels. This effect actually seems to be important in the case of metallic systems but should be less pronounced for isolators since it is well known experimentally that one set of parameters is satisfactory in most cases. This type of approach is presently carried out in our group and will be presented in the near future.

## 4. The dipole polarizability

In perturbation theory the dipole polarizability $\alpha_D$ can mainly be divided into two parts. First the standard contribution $\alpha_0$ that for example may be calculated using the Sternheimer equation [12], and second the correlation contribution $\alpha_1$. In principle $\alpha_D$ is then given by $\alpha_0 + \alpha_1$. However, it is often noted that the correlation contribution is quite significant. An approximate way to account for higher order contributions (if $\alpha_1$ is reasonably small) is to use the geometric series expansion which is often found to be satisfactory [15].

$$\alpha_D = \alpha_0 \left( 1 - \frac{\alpha_1}{\alpha_0} \right)^{-1}$$

The correlation contributions ($\alpha_1$) to the dipole polarizability may either be derived using the diagrammatic approach in many body perturbation theory [16] or by classical methods [17]:

$$\begin{aligned} \alpha_1 = -\sum_{ij} & 2 \left\langle \delta\psi_i \delta\psi_j | 1/r_{12} | \psi_i \psi_j \right\rangle - \left\langle \delta\psi_i \delta\psi_j | 1/r_{12} | \psi_j \psi_i \right\rangle \\ & - \left\langle \delta\psi_i \psi_j | 1/r_{12} | \delta\psi_j \psi_i \right\rangle \end{aligned}$$

where the $\psi_k$'s ($k = i$ or $j$) are unperturbed relativistic Hartree–Fock functions [18] and the perturbed functions are given by [19]

$$\begin{aligned} \delta\psi_k = \frac{1}{r} \sum_{l_k'} & 2(-1)^m [l_k', l_k]^{1/2} \begin{pmatrix} l_k' & 1 & l_k \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} l_k' & 1 & l_k \\ -m_k & 0 & m_k \end{pmatrix} w_{l_k'} Y_{l_k' m_k}. \end{aligned}$$

The perturbed radial functions $w_{l_k'}$ are the solutions to the inhomogeneous Schrödinger equation, see e.g. [12]. This type of calculation usually involves many intra- and inter-shell interactions. The procedure results in consistent

Table 1
Electronic dipole and quadrupole polarizabilities in Å$^3$ and Å$^5$, respectively. The values for $O^{2-}$ are from [20]

| Ion | $\alpha_0$ | $\alpha_1$ | $\alpha_D$ | $\alpha_Q$ | $\alpha_D$ (cryst) | $\alpha_Q$ (cryst) |
|---|---|---|---|---|---|---|
| $Ho^{3+}$ | 0.820 | −0.0649 | 0.760 | 0.525 | 1.045 | 1.092 |
| $Y^{3+}$ | 0.833 | −0.262 | 0.633 | 0.516 | 0.867 | 1.061 |
| $Al^{3+}$ | 0.04175 | −0.00366 | 0.0384 | 0.0106 | 0.051 | 0.0158 |
| $O^{2-}$ | – | – | – | – | 1.349 | 3.694 |

polarizabilities that often are in excellent agreement with experiment. We have calculated the relevant polarizabilities in order to simulate the energy structure of Ho:YAG.

## 5. Results

The polarizabilities used are given in Table 1. Both the dipole and the quadrupole values were calculated here. However, these are free-ion polarizabilities and they need to be corrected to reflect the true crystal-ion polarizabilities. This correction can be done approximately by using the Watson sphere model [20] or by including higher order crystal field perturbations [19]. Here we simply use Table 1 of [20] to correct our free-ion values. The values of $\sigma_t$ and $\langle r^t \rangle$ needed to calculate $H_{cf}$ are from [12]. In the case of the correlation result for $Ho^{3+}$ we only included the filled shells from 4s, p, d and 5s, p in the calculation. It seems that correlation is less pronounced for the rare-earths compared to other lighter cations such as $Y^{3+}$. The energy program is certainly general, to illustrate this we plot the free ion energy levels of the whole actinide series in Fig. 1. The parameter values of Carnall are taken from [21,22]. Fig. 2 displays the energy levels in the case of $Ho^{3+}$:YAG up to about 21 000 cm$^{-1}$ only (limited by exp. data). The full 1001×1001 energy matrix was diagonalized. The first series (I) represents a free $Ho^{3+}$ ion, the next (II) is the calculated results using our polarizabilities, the third (III) is obtained using fitted parameters and the last set (exp.) is the experimental results [23]. The calculated higher order parameters ($B_{6p}$) are as usual too small (by a factor 2–3) leading to a contraction of the Stark levels in the various multiplets in

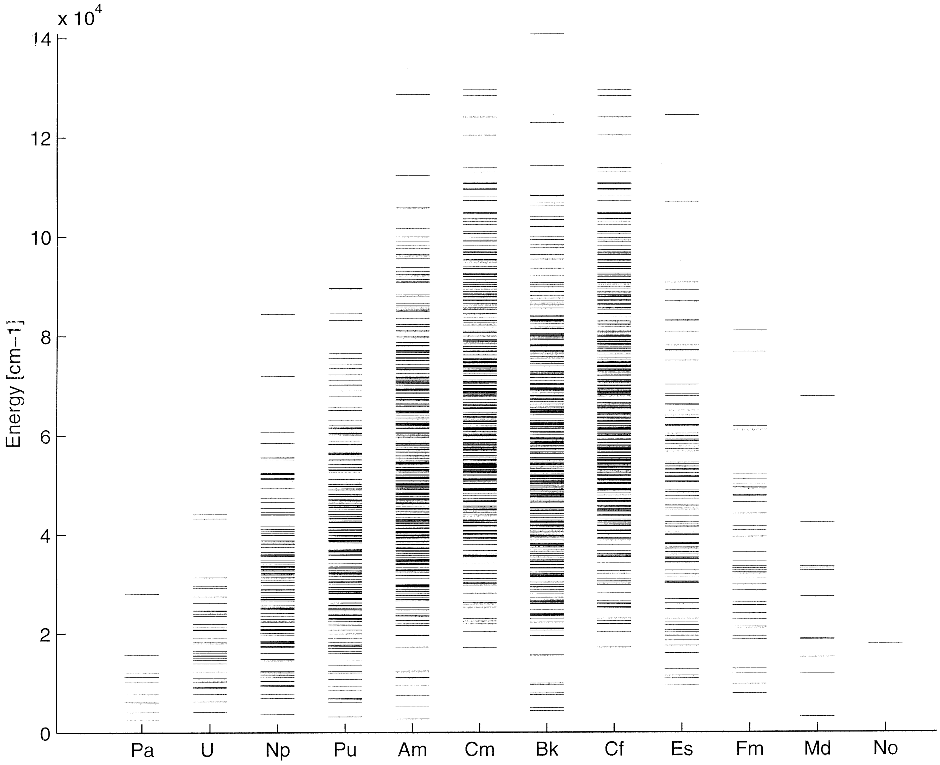

Fig. 1. The free-ion energy levels for the whole trivalent actinide series. Parameters are taken from Refs. [21,22].

Fig. 2. A possible cure would be to use an expansion of the radial 4f wavefunction in the crystal. However this effect is most probably small. It was shown earlier in a *free-ion* calculation of $Pr^{3+}$ that it is possible to calculate term levels correctly applying the relativistic coupled cluster method [2]. A significant artificial expansion of the radial wavefunction would certainly destroy their agreement with experiment. In the future we will apply densities obtained from DFT to investigate these problems further. Approximately fitted parameters used in the third set are respectively 73, 456, $-846$, $-1653$, $-133$, $-401$, 538, $-385$, and $-1115$ cm$^{-1}$ for $B_{tp} = B_{t-p}$ ($tp = 22$, 20, 44, 42, 40, 66, 64, 62 and 60). Magnetic studies may also be performed. The Zeeman split crystal field levels of the ground state $^5I_8$ are studied in Fig. 3 with $B \perp c$-axis for fields up to 1 Tesla (zero is set to the lowest Stark level). Only the lowest Stark levels up to about 140 cm$^{-1}$ are plotted because of scaling problems plotting all members of the ground state. In order to increase the reliability in these results we used the fitted $B_{tp}$'s.

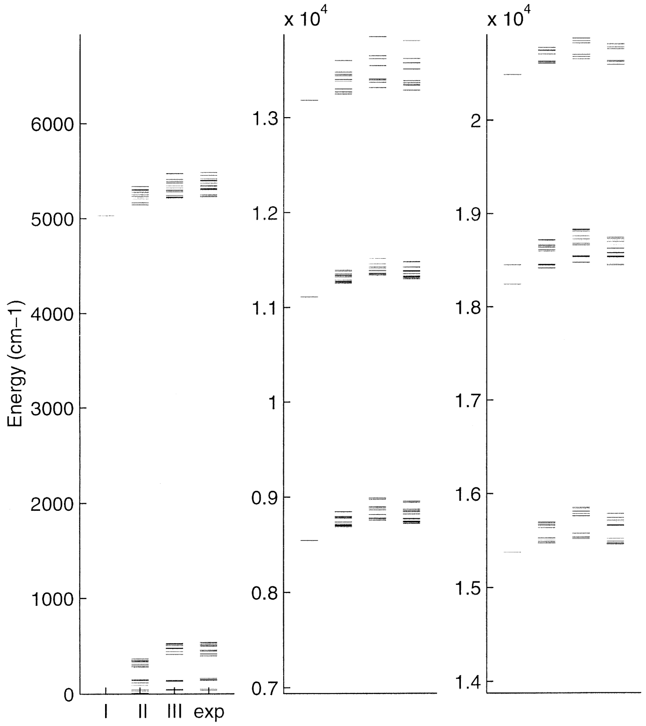

Fig. 2. The crystal field energy levels in the case $Ho^{3+}$:YAG. Set I: free-ion levels; set II: calculated Stark levels; set III: Stark levels using fitted parameters; the last set is the experimental result from Ref. [23].

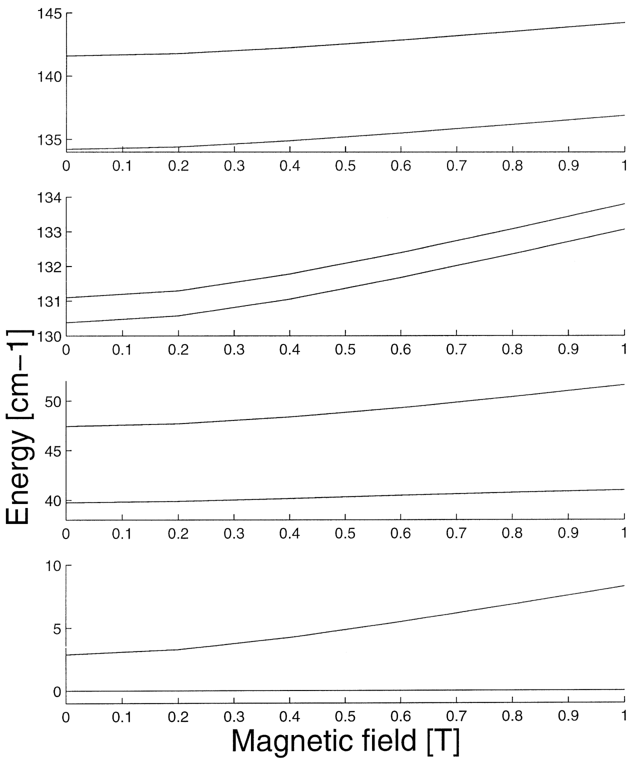

Fig. 3. A magnetic case study of the ground state $^5I_8$ of $Ho^{3+}$:YAG displaying the influence on the lowest Stark levels for fields ranging from 0 up to 1 Tesla. The zero energy is set to the first Stark level.

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