

Crystal field module for the general relativistic atomic structure package^{☆,☆☆}

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ABSTRACT

The latest version of the GRASP2018 package [Froese Fischer et al. (2019)], based on the multiconfigurational Dirac–Hartree–Fock method, is extended to account for effects of crystal fields in complex systems. Instead of using the simplified treatment of the crystal field effects based on the Stevens' operator-equivalent method the program uses the fully *ab-initio* method in which the external ions are treated as point charges at fixed positions. In addition, examples of how to use the CF_HAMILTONIAN program are given in source directory grasp2018/src/appl/CF_Hamiltonian/Sample_Runs.

Program summary

Program Title: CF_HAMILTONIAN

CPC Library link to program files: <https://doi.org/10.17632/fksxwwjbx6.1>

Licensing provisions: MIT license

Programming language: Fortran 95.

External routines/libraries used: GRASP2018 modules: LIBMOD, LIB9290, LIBRANG90; GRASP2018 routines: starttime, setdbg, getmixblock, getmixa, getmixc, setmc, factt, setcon, setcsla, stoptime; and LAPACK library.

Nature of problem: The CF_HAMILTONIAN program is designed as a part of the GRASP2018 package for the computation of Stark splitting in crystal field in the point charge crystal field approximation.

Solution method: The point charge crystal field approach is used. It allows user to include different Atomic State Functions (ASF) mixing such as ASF mix with the same total *J* values, ASF mixing with different total *J* values, ASF mixing with different parities.

Additional comments including restrictions and unusual features: The restrictions of the program are coming from the restrictions of GRASP2018 package and it is suitable for systems for which the point charge crystal field approximation is appropriate.

The Stark level splitting of the atomic energy terms in the point-charge crystal field approach is performed by the program CF_HAMILTONIAN.

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1. Introduction

The rare earth ions in ionic crystals show very sharp lines in absorption as well as emission spectra. In many cases, the line widths are as narrow as lines emitted by free ions. This feature is very different from rather broad spectra of defects in solids, such as F-centers. As suggested in [1], it means that in principle it is possible to investigate interactions between the ions and crystal

fields by optical methods with a degree of accuracy similar to that possible with free atoms and ions. Trivalent erbium Er^{3+} is studied as one of those rare earth free ions [2] and those in a variety of host compounds [3].

Since it was found that hydrogen permeation is reduced drastically by an oxide Er_2O_3 layer (1 μm) on metallic substrates [4], the erbium oxide is a primary candidate of tritium permeation barriers of blanket systems in nuclear fusion devices. To evaluate degradation or durability as the permeation barrier, it is essential to characterize crystallinity change inside the oxides due to neutron irradiation anticipated in the nuclear fusion devices. Recently, degradation of the crystallinity by high energy ion bombardment was inferred from ion beam induced luminescence spectra [5,6]. To characterize the crystallinity change inside the

[☆] This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

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target oxide, we need to know luminescence spectra in the damaged crystals, which is, however, hitherto unknown. Motivation of this work is to develop a theoretical method to predict ion spectra in the damaged crystals. To this end, we need to use *ab-initio* methods for calculations of free ion spectra in order to investigate crystal field effects without recourse to empirical parameters in atomic energy terms. Then, Stark level splitting of the atomic energy terms is investigated using the point-charge crystal field approach for a perfect crystal of the erbium oxide whose crystallographic data is available from databases [7].

Most authors [8–15] have used semi-empirical methods to obtain spectroscopic data for the free ion Er^{3+} . These methods rely on measurements of Stark components in different types of erbium doped crystals (LaF_3 , LaCl_3 , LiYF_3 and ZnGa_2O_4) that determine centers of gravity. Then, by using different approximations, the energy spectrum is derived for the free ion. The situation is similar for the Stark components themselves. The components are measured in experiments and to obtain higher levels, the crystal-field theory [16,17] and Superposition Models (SPM) [18] are used.

The modern highly developed experimental accuracy of determining a number of spectroscopic constants of atoms and ions requires the theoretical results to be correspondingly accurate. That accuracy can be achieved by accounting jointly for relativistic and correlation effects. There is a whole series of theoretical methods considering correlation effects in many-electron atoms and ions: different versions of the many-body perturbation theory, the configuration interaction method, the random phase approximation with exchange, the incomplete variable separation method, multiconfiguration approximation, etc. Recently the majority of theoretical *ab initio* calculations of energy spectra of atoms and ions with open shells have been carried out using configuration interaction (CI), multiconfiguration Hartree-Fock [19,20] (MCHF) or multiconfiguration Dirac-Hartree-Fock [21,22] (MCDHF) methods. As a rule, relativistic effects are taken into account by the MCDHF method. Usually in carrying out the calculations the well-known program GRASP2018 [23] (A General-Purpose Relativistic Atomic Structure program) is used. Our analysis demonstrates that the configuration interaction method and the GRASP2018 [23] package are hitherto the best tools for the investigation of the crystal field effects in ionic solids. These methods are based on the accurate four-component one-electron radial wave functions which were calculated including correlation and relativistic effects. In order to achieve the research aims, we added a new crystal field program into the GRASP2018 package.

The program installation is presented in Section 2. The point charge crystal field approach is presented in Section 3 and the program based on this approximation are presented in Section 4. Input data and output data of the program is presented in Sections 5 and 6, respectively. The test case is presented and described in Section 7.

2. Installation of the program

CF_HAMILTONIAN has been developed as a (new) component of the GRASP2018 package [23]. The steps below should be followed to ensure a proper installation in the bash shell. The installation procedure assumes that the GRASP2018 package has already been installed.

- (1) Go to the main directory grasp2018 of the GRASP2018 package. Type

```
source make-environment_XXX
```

where XXX is the compiler name (see the README file of the GRASP2018 package). The GRASP2018 environment variables are now set.

- (2) Copy the file CF_Hamiltonian.tar.gz to the directory grasp2018/src/appl of the GRASP2018 package. Untar it by typing

```
tar -zxvf CF_Hamiltonian.tar.gz
```

A directory CF_Hamiltonian will appear.

- (3) In the grasp2018/src/appl/CF_Hamiltonian directory, execute the installation by typing

```
makeclean
```

```
make
```

This will generate an executable file CF_HAMILTONIAN in the directory grasp2018/bin.

The subdirectory grasp2018/src/appl/CF_Hamiltonian/Sample_Runs lists a number of script files for illustration of the CF_HAMILTONIAN program usage to obtain Stark splitting in crystal field in the point charge crystal field approximation.

3. Method of accounting for the crystal field effects

In order to calculate the splitting of the ionic energy levels γJ in solids, the crystal field effects must be included. Instead of using the simplified treatment of the crystal field effects based on the Stevens' operator-equivalent method [24,25] we used the fully *ab-initio* method. Treating the external ions as point charges at fixed positions, the crystal field operator can be presented in the following form in a. u. [26]:

$$\begin{aligned} H_{CF} &= - \sum_{j=1}^A \sum_{i=1}^N \frac{Z_j}{|\vec{R}_j - \vec{r}_i|} \\ &= \sum_{j=1}^A \sum_{i=1}^N \sum_{k=0}^{\infty} \sum_{q=-k}^k (-1)^{q+1} \sqrt{\frac{4\pi}{2k+1}} B_k(r_i, R_j, Z_j) \\ &\quad \times C_q^k(\theta_i, \phi_i) Y_{-q}^k(\theta_j, \phi_j), \end{aligned} \quad (1)$$

where

$$B_k(r, R, Z) = Z \begin{cases} r^k/R^{k+1}, & r < R, \\ R^k/r^{k+1}, & r > R. \end{cases} \quad (2)$$

and A is the number of the external ions, Z_j and R_j , θ_j , ϕ_j are the charges and the spherical coordinates of the external ions, N stands for a number of the electrons. Charges and positions of the external ions are the parameters (which depend on the compound) in the calculations. Using first order perturbation theory (diagonalization of the H_{CF} operator matrix), splitting of the degenerate atomic energy levels (and shift of $J = 0$ state energy) in the crystal electric field (Stark effect) can be calculated.

The matrix element of the crystal field operator H_{CF} has the form:

$$\begin{aligned} &\langle \gamma J M_J | H_{CF} | \gamma' J' M_J' \rangle \\ &= \sum_{j=1}^A \sum_{k=0}^{\infty} \sum_{q=-k}^k \sum_{r,s} \sum_{a,b} c_r c_s (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \\ &\quad \times \sqrt{2J+1} d_{ab}^k(r, s) [\kappa_a \| C^k \| \kappa_b] (-1)^{q+1} Z_j \sqrt{\frac{4\pi}{2k+1}} \\ &\quad \times Y_{-q}^k(\theta_j, \phi_j) \left(\int_0^{R_j} \frac{r^k}{R_j^{k+1}} (P_a P_b + Q_a Q_b) dr \right. \\ &\quad \left. + \int_{R_j}^{\infty} \frac{R_j^k}{r^{k+1}} (P_a P_b + Q_a Q_b) dr \right), \end{aligned} \quad (3)$$

where

$$[\kappa_a \| C^k \| \kappa_b] = (-1)^{j_a-1/2} \sqrt{2j_b+1} \begin{pmatrix} j_a & k & j_b \\ 1/2 & 0 & -1/2 \end{pmatrix} \times \pi(l_a, l_b, k). \quad (4)$$

Here P_a and Q_a are the large and small components of the relativistic one-electron radial wave function, $d_{ab}^k(rs)$ are the spin-angular coefficients that arise from using Racah's algebra in the decomposition of the one-electron operator matrix element [27], and $\pi(l_a, l_b, k)$ is defined:

$$\pi(l_a, l_b, k) = \begin{cases} 1; & \text{if } l_a + k + l_b \text{ even,} \\ 0; & \text{otherwise.} \end{cases} \quad (5)$$

Degenerated γJ levels split due to the crystal field into a number of sub-levels ($a = 1, \dots, 2J + 1$):

$$|\gamma_a J M_J\rangle_a = \sum_{k=1}^{N_{\text{CSFs}}} \sum_{m=-j}^j c_{km}^{(a)} |\gamma_k J M_J = m\rangle. \quad (6)$$

Using this method, splitting of energy levels (E_a) and weights (c_{ia}) can be obtained. Depending on the symmetry of the crystal some of the energy levels can also be degenerated.

Crystal field interaction also mixes different atomic state functions (ASFs) - J mixing effects. In this case taking into account ASFs the wave functions of crystal field sub-levels with different J values can be expressed:

$$|\gamma J M_J\rangle_a = \sum_{k=1}^{N_{\text{CSFs}}} \sum_{j=j_{\min}}^{j_{\max}} \sum_{m=-j}^j c_{kjm}^{(a)} |\gamma_k J = j M_J = m\rangle. \quad (7)$$

In order to be able to perform such calculations, the GRASP2018 [23] package has been extended to include program for the crystal field operator matrix element calculation and diagonalization of matrix of full atomic Hamiltonian (including matrix elements between different ASFs).

4. The program structure

The GRASP2018 package is written in FORTRAN95, therefore, the new crystal field program is based on the same language. Along with the new modules to be created (we shall describe them later), the new program uses common libraries and subroutines of the GRASP2018 package. The detailed structure of these modules is represented by Fig. 1. Routines `starttime`, `setdbg`, `getmixblock`, `getmixa`, `getmixc`, `setmc`, `factt`, `setcon`, `setcsla`, and `stoptime` are the original modules of the program GRASP2018 and perform the same functions as in the GRASP2018 package. For example, after calling `setmc` - to set up machine - and precision-dependent parameters and perform other-dependent initialization, `setcon` - to set up physical constants and conversion factors, and `factt` - to generate a table of factorials for later use by `clrx` and `dracah`. All these modules of the GRASP2018 program have an auxiliary character and they organize the calculations in the crystal-field approximation.

The subroutine `ions_input` is reading all information about the crystal geometry from the file `crystaldata` before the program calls to the main routine. The calculations themselves must be performed by the routine `cf_hamil` (see Fig. 1).

The subroutine `y_k` from Fig. 1 performs the calculation of the spherical functions Y_q^k . The routine `matel_cf_hamil` computes the spin-angular part of reduced matrix elements of the crystal field operator. It calls to the utility `clrx` for getting the value of the coefficient

$$C(a, k, b) = \begin{pmatrix} j_a & k & j_b \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}. \quad (8)$$

The sub-programme `ions_param` collects the specific crystal-dependent values of the A (the number of the external ions), Z_j (the charge of the external ions) and R_j, θ_j, ϕ_j (the coordinates of the external ions). Namely this subroutine contains the information on the parameters of a concrete crystal. If there is a need to consider crystals of the same symmetry, one has to change the values of the parameters mentioned above. Thus, such algorithm allows easily to extend the domain of tasks to be considered. The calculation of the linear combination of radial integrals

$$\int_0^{R_j} \frac{r^k}{R_j^{k+1}} (P_a P_b + Q_a Q_b) dr + \int_{R_j}^{\infty} \frac{R_j^k}{r^{k+1}} (P_a P_b + Q_a Q_b) dr \quad (9)$$

of crystal field operator is carried out by the routine `rint_cf_hamil`. The standard subroutine `quad` is the utility routine that performs finite-difference quadratures $\int_0^{\infty} f(r) dr$ for given $f(r)$.

Routine `cf_hamil` contains two subroutines (`onescalar` and `oneparticlejj_cf`) which perform the spin-angular integration of one-particle operator. The subroutine `onescalar` is located in the `LIBRANG90` library of the GRASP2008 package and the subroutine `oneparticlejj_cf` is the modification of subroutine `oneparticlejj` from the `LIBRANG90`. The routine `wig_3j` calculates the Wigner 3-j symbol. The routine `itta` checks triangular conditions $l + j \geq k, l + k \geq j$ and $j + k \geq l$.

Subroutine `zgcev` is from the library LAPACK. It computes the eigenvalues and the left and/or right eigenvectors of a general complex matrix generalized eigenproblem.

5. Input data

In order to run `CF_HAMILTONIAN`, following files used in the GRASP2018 package have to be available:

- (1) a GRASP2018 isotope data file `isodata`.
- (2) a GRASP2018 configuration state function file (`name.c`), which defines the CSFs by specifying orbital occupation numbers and angular couplings.
- (3) a GRASP2018 mixing coefficients file (`name.(c)m`), which lists the mixing coefficients for each configuration state function for each atomic state function.
- (4) a GRASP2018 radial wave function file (`name.w`), which contains relativistic radial wave functions on a grid for all subshells specified in `name.c`.

The scheme of the use of `CF_HAMILTONIAN` in the GRASP2018 calculations sequence is shown in Fig. 2. The `CF_HAMILTONIAN` program is controlled interactively, (see Fig. 3):

Default settings ? (Y/N)

we recommend to answer Y. The non-default mode is used for debugging the `CF_HAMILTONIAN` program.

In the second question

Name of state

You need to type the name to be used for defining the files.

Mixing coefficients from a CI calc.?

Type Y if input files are from `rci` calculations or N if they are from `rmcdhf` calculations.

For which State ?

Max ?

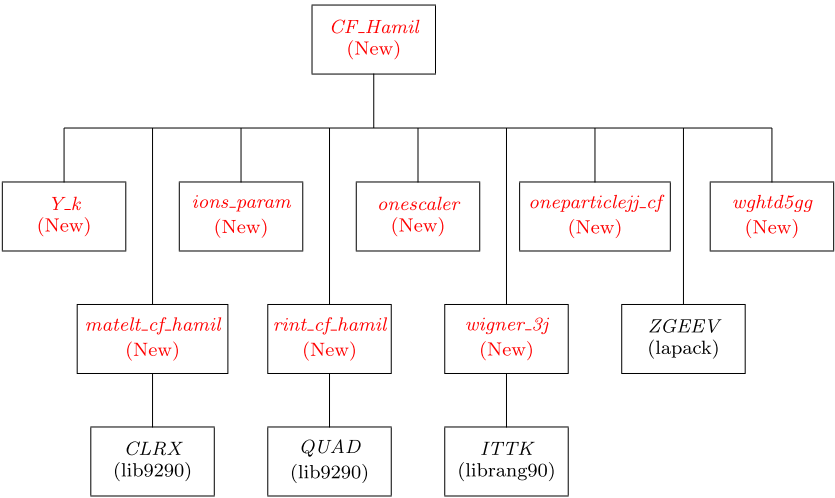


Fig. 1. Structure of subroutine CF_HAMIL: the new modules of programs are marked in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

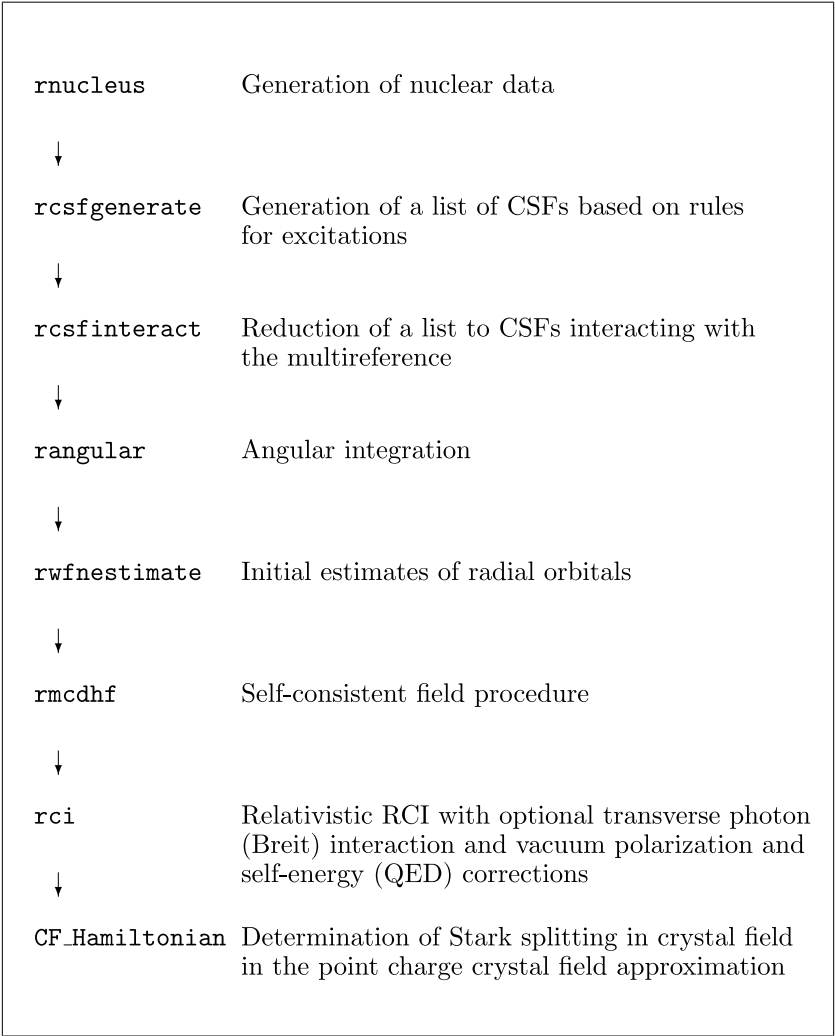


Fig. 2. Typical sequence of program calls to compute Stark splitting in crystal field in the point charge crystal field approximation.

Type number of the highest energy level which needs to be investigated.

Min ?

Type number of the lowest energy level which needs to be investigated. The interaction between different J values will be included in the calculation if the levels with different J values are typed in the input.

```

READ(55,'(A20,A10,A10,I10,2X,F5.2,5X,A4)') &

CF_Hamiltonian: Calculate the crystal-field splitting of ion
in crystal compound (Fortran 95 version)
(C) Copyright by G. Gaigalas and D. Kato,
(2019).
Input files: isodata, name.c, name.w,
name.(c)m
Output files: name.(c)CF-Hamil, name.(c)CFm

Default settings?
> Y
Name of state
> 5
Mixing coefficients from a CI calc.?
> Y
For which State ?
Max ?
> 38
Min ?
> 38

```

Fig. 3. Interactive dialog for CF_HAMILTONIAN.

```

Er(2) 0(3) SYMMETRY = NO 6 1.00 CART
1.601703E+00 -1.371274E+00 -7.969532E-01 -2.000000E+00
-1.146548E+00 -1.035308E+00 1.615332E+00 -2.000000E+00
-1.601703E+00 1.371274E+00 -7.969532E-01 -2.000000E+00
1.146548E+00 1.035308E+00 1.615332E+00 -2.000000E+00
1.269459E+00 1.488895E+00 -1.253960E+00 -2.000000E+00
-1.269459E+00 -1.488895E+00 -1.253960E+00 -2.000000E+00

```

Fig. 4. The input file Crystalldata.

The input file Crystalldata is needed for running the program, too. This file must be created by a user. Its format is presented in Fig. 4. The definition of the problem is described in the first line of the file

```
Er(2) 0(3) SYMMETRY = NO 6 1.00 CART
```

This line is read by the command

```

READ(55,'(A20,A10,A10,I10,2X,F5.2,5X,A4)') &
NAME_CRYSTAL,LAB1,LAB2,ion_max_number,Vector_L,COORD

```

from subroutine Ions_input.f90.

Energy levels for ...
Rydberg constant is 109737.31534
No - Serial number of the state; Pos - Position of the state within the
J/P block; Splitting is the energy difference from lowest level with same J values

No	Pos	J	2*M_J	Energy Total (a.u.)	Levels (cm ⁻¹)	Levels (meV)	Splitting (cm ⁻¹)	Splitting (meV)
16	1	15/2	-15	-12975.6475459				
1	1	15/2	-15	-12975.6475459	0.00	0.00	0.00	0.00
1	1	15/2	-15	-12975.6473809	36.21	4.49	36.21	4.49
16	1	15/2	-15	-12975.6473809	36.21	4.49	36.21	4.49
15	1	15/2	-13	-12975.6471338	90.46	11.22	90.46	11.22
2	1	15/2	-13	-12975.6471338	90.46	11.22	90.46	11.22
6	1	15/2	-5	-12975.6468664	149.14	18.49	149.14	18.49
11	1	15/2	-5	-12975.6468664	149.14	18.49	149.14	18.49
10	1	15/2	-3	-12975.6466520	196.21	24.33	196.21	24.33
7	1	15/2	-3	-12975.6466520	196.21	24.33	196.21	24.33
8	1	15/2	-1	-12975.6465227	224.57	27.84	224.57	27.84
9	1	15/2	-1	-12975.6465227	224.57	27.84	224.57	27.84
4	1	15/2	-9	-12975.6457791	387.77	48.08	387.77	48.08
13	1	15/2	-9	-12975.6457791	387.77	48.08	387.77	48.08
12	1	15/2	-7	-12975.6456571	414.54	51.40	414.54	51.40
5	1	15/2	-7	-12975.6456571	414.54	51.40	414.54	51.40

Fig. 5. The Stark level splitting of the atomic energy terms in the point-charge crystal field approach for a perfect crystal Er₂O₃ of the erbium oxide Er³⁺ (from file 5_without_J_mix.CF-Hamil).

The character type variable NAME_CRYSTAL = Er(2) 0(3) is used for the notation in the output. The SYMMETRY = must be assigned to LAB2=NO. The variable ion_max_number = 6 shows that crystal field is made up of 6 neighboring ions. The integer type variable Vector_L = 1 is the scaling factor for coordinates. The character type variable COORD = CART shows that the Cartesian coordinates are used in the input. The program supports the Spherical coordinates system if variable COORD is assigned to COORD = SPHE.

In the next lines the coordinates for each ion (first three numbers from the left) and ion charge must be typed. These lines are read by the commands

```

DO I = 1,ion_max_number
  READ(55,'(3X,D13.6,3(3X,D13.6))')X1(I),X2(I),X3(I),QQ(I)
END DO

```

The meaning of variables X1(I), X2(I), X3(I) for cartesian coordinates are: X1(I) x-axis coordinates, X2(I) y-axis coordinates, and X3(I) z-axis coordinates in angstroms. The meaning of variables X1(I), X2(I), X3(I) for spherical coordinates are: X1(I) radius r , X2(I) θ , and X3(I) ϕ (angle unit in degrees). The beginning of these coordinates is assigned to the ion for which calculation of Stark splitting is being performed.

6. Output data

Data generated when running a CF_HAMILTONIAN session are stored in the files name.CF-Hamil and name.CFm if input was taken from rmcdf calculation or in the files name.cCF-Hamil and name.cCFm if input was taken from rci calculation. The energy structure of crystal field is listed in the file name.(c)CF-Hamil (see Fig. 5). The file name.(c)CFm contains the expansion coefficients $C_{km}^{(a)}$ or $C_{kjm}^{(a)}$ of atomic state function (6) or (7) (see Fig. 6).

7. Test case: Stark splitting effects for Er³⁺ in Er₂O₃

Here we present an example in which the calculation of Stark splitting of the ground state $4f^{11} 4f_{15/2}^0$ of Er³⁺ in Er₂O₃ is performed. In this calculation atomic state function taken from relativistic configuration interaction calculations is used. The input of


```

Er(2) 0(3)    SYMMETRY =NO          2159  1.00
The space of CF expansion is      16

 1 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=-15
 2 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=-13
 3 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=-11
 4 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= -9
 5 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= -7
 6 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= -5
 7 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= -3
 8 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= -1
 9 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=  1
10 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=  3
11 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=  5
12 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=  7
13 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J=  9
14 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= 11
15 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= 13
16 Number of Energy level 38 Parity - Pos 1 J=15/2 2*M_J= 15

End of the list of CF expansion.

Energy level No. before CF 38 after CF 16 Parity - Pos 1 J=15/2 2*M_J= 15
Energy = -12975.6475459 16
 0.0675 0.1496 -0.0478 -0.2669 0.0204
 0.2679 -0.0154 -0.2598 0.0114 0.1141
-0.0094 0.0130 0.0127 -0.2029 0.0093
 0.4520

Energy level No. before CF 38 after CF 1 Parity - Pos 1 J=15/2 2*M_J=-15
Energy = -12975.6475459 1
 0.4577 0.0220 -0.2053 -0.0516 0.0138
 0.0425 0.1127 -0.0346 -0.2567 0.0120
 0.2645 -0.0005 -0.2631 -0.0018 0.1508
 0.0000

Energy level No. before CF 38 after CF 1 Parity - Pos 1 J=15/2 2*M_J=-15
Energy = -12975.6473809 1
 0.6024 0.0138 -0.0725 -0.0094 -0.0301
-0.0102 -0.0399 0.0175 0.2136 -0.0128
-0.3001 0.0018 0.4011 0.0130 -0.2227
-0.0640

Energy level No. before CF 38 after CF 16 Parity - Pos 1 J=15/2 2*M_J= 15
Energy = -12975.6473809 16
 0.2202 -0.2123 -0.0075 0.3841 -0.0119
-0.2906 -0.0014 0.2078 0.0529 -0.0395
-0.0764 -0.0298 0.1145 -0.0662 -0.0466
 0.5627

Energy level No. before CF 38 after CF 15 Parity - Pos 1 J=15/2 2*M_J= 13
Energy = -12975.6471338 15
 0.0665 0.0132 0.0158 0.0055 -0.3749
-0.0064 0.2153 -0.0143 -0.1102 0.0308
-0.0347 -0.0223 -0.0560 0.0042 0.5375
 0.0000

Energy level No. before CF 38 after CF 2 Parity - Pos 1 J=15/2 2*M_J=-13
Energy = -12975.6471338 2
-0.0369 0.5361 -0.0197 -0.0567 -0.0120
-0.0349 0.0101 -0.1096 -0.0130 0.2154
 0.0094 -0.3750 0.0245 0.0167 0.0174
 0.0657
.....

```

Fig. 6. The expansion coefficients $c_{km}^{(a)}$ of atomic state function (6) for erbium oxide Er^{3+} in the Er_2O_3 compound (from file 5_without_J_mix.CFm).

this calculation is presented in (Fig. 3). The sequence of these calculation (Fig. 2) is listed in the script file Ex_run in the directory grasp2018/src/appl/CF_Hamiltonian/Sample_Runs.

The crystal Er_2O_3 coordinates are listed in the input file Crystaldata. The coordinates of a compound are presented in the spherical coordinate system in degrees, for 2159 neighboring

ions. The present coordinates are obtained by molecular statics calculations based on density functional theories performed with VASP code [28,29]. The two test cases are presented:

- **Case 1.** Computation of energy (Stark) levels (in cm^{-1}) of Er^{3+} in Er_2O_3 without J -mixing induced by the crystal field. Interactive input of this case is shown in Fig. 3.

Table 1

Comparison of computed energy (Stark) levels (in cm^{-1}) of Er^{3+} ($4f^{11}4f_{15/2}^0$) in Er_2O_3 crystal field (without and with J -mixing) with other theories and experiment.

Experiment			Semi-empirical			Theoretical (our results)	
[30]	[31]	[32]	[30]	[31]	[32]	Without J -mixing	With J -mixing
0	0	0	1	2	0	0.00	0.00
38	36	39.5	36	37	11.6	36.21	35.47
75	69	75.3	66	65	79.4	90.46	91.95
88	86	89.0	93	81	107.7	149.14	153.96
159	162	260.1	169	157	154.8	196.21	202.47
265	263	349.6	262	265	176.7	224.57	230.55
490	484	488.6	477	483	194.3	387.77	393.48
505	503	531.2	502	506	249.8	414.54	419.59

- **Case 2.** Computation of energy (Stark) levels (in cm^{-1}) of Er^{3+} in Er_2O_3 with J -mixing of 41 different levels. The list of all levels included in calculations is presented in the file `Output_rlevels_5` in the directory `grasp2018/src/appl/CF_Hamiltonian/Sample_Runs`

All output files are presented in the

`grasp2018/src/appl/CF_Hamiltonian/Sample_Output`.

Comparison of computed energy (Stark) levels (in cm^{-1}) of Er^{3+} in Er_2O_3 without and with J -mixing induced by the crystal field is shown in Table 1. The results show that for Stark splitting of Er^{3+} in the Er_2O_3 crystal calculations it is important to choose appropriate expansion of CSFs in ASF for given J value and number of neighboring ions.

It is noted that the present calculations omit chemical bonding or covalency with orbitals of adjacent *ligand* ions, i.e. O ions. The energy level splitting of the central Er ion is assumed to be solely caused by electrostatic fields exerted by ambient O and Er ions of the nominal charge states, -2 and $+3$, respectively. The chemical bonding effects can be treated by amalgamation of molecular orbital theories and the crystal-field theory which has been known as *ligand-field theory*, e.g. [33,34]. However, this is not incorporated in the present program code. While the present results show a fairly good agreement with experiments especially for the lowest levels, the chemical bonding effects, e.g. [35,36], may be the reason for imperfect agreement.

8. Conclusions

The program is based on the generalized multiconfiguration Dirac–Hartree–Fock method for large-scale *ab-initio* calculations of the crystal-field energy levels. By using the program it is possible to investigate how correlation effects in ion make influence on Stark effects. This investigation as well as inclusion of mixture of several levels (not only with the same J value) allow us to get the most accurate crystal-field energy levels.

Possible explanations for an imperfect agreement between the results obtained from CF_HAMILTONIAN and an experiment may be explained by the nature of mixing of $4f$ and ligand orbitals, and point to the necessity for further refinements to the present theory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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