SUPPORTING INFORMATION

First-principles study of optical absorption energies, ligand field and spin-Hamiltonian parameters of Cr^{3+} ions in emerald

Mihail Atanasov*[2,3],Emiliana-Laura Andreici Eftimie[1], Nicolae M. Avram*[1,4], Mikhail G. Brik[4,5,6,7] and Frank Neese[2]

[1)]Department of Physics, West University of Timisoara, Bd. V. Parvan, No. 4,300223, Timisoara, Romania
[2)] Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany
[3)] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. Georgi Bontchev Street, Bl.11, 1113 Sofia, Bulgaria
[4)] Academy of Romanian Scientists, Ilfov 3, 050044-Bucharest, Romania
[5)]CQUPT-BUL Innovation Institute &College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing, 400065, People's Republic of China
[6)] Institute of Physics, University of Tartu, W. Ostwald Str. 1, Tartu, 50411, Estonia
[7)]Faculty of Science and Technology, Jan Długosz University, Armii Krajowej 13/15, PL-42200, Częstochowa, Poland

E-mail: *nicolae.avram@e-uvt.ro ; *mihail.atanasov@kofo.mpg.de ; *neese@kofo.mpg.de

Contents

1 CAS(3,5) results of SA-CASSCF/MR-methods and SS-CASSCF/CASP2 in emerald **S2**

2 QC expansion **S3**

3 Energies deviations ΔE in CAS (3,5) for CASSCF/MR-PT methods using SA and SS protocol from experimental values. Contributions from orbital relaxation and dynamical correlation to d-d transitions energies in emerald **S3**

4 AILFT **S6**

4.1 Ligand field one-electron matrix V_{LF} **S6**

4.2 AILFT energy levels **S7**

5.State specific multiplet calculations **S9**

6. Vibronic analysis and calculation of vibronic landshapes **S14**

7. Generation of embedded host environment based on the Gelle-Lepettit method **S20**

8. Angular Overlap Model Calculations **S23**

9.Periodic DFT geometry optimizations **S33**

References **S40**

§1. CAS(3,5) results of SA-CASSCF/MR-methods and SS-CASSCF / CASP2 in emerald.

Table S1. Electronic transitions states energies (in cm^{-1}) of Cr^{3+}: $Be_3Si_6Al_2O_{18}$ from SA-CASSCF/ MR-methods and SS-CASSCF/CASPT2 calculations with a minimal active space.

Energy levels		Exp. [1] [a][2] [b][3]	*STATE - AVERAGE*						*STATE - SPECIFIC*	
O_h	D_3		CASSCF (3,5)	SC-NEVPT2 (3,5)	HQD-NEVPT2 (3,5)	DCD-CAS2(3) (3,5)	CASPT2 (3,5)	SORCI (3,5)	CASSCF (3,5)	CASPT2 (3,5)
$^4A_{2g}(^4F)$	$^4A_2$	**0**	0	0	0	0	0	0	0	0
$^2E_g(^2G)$	^2E	**14686**	19102	16674	16651	16611	16750	16885	19963	14211
$^2T_{1g}(^2G)\{$	$^2A_2$	**-**	19694	17268	17261	17220	17472	17039	-	-
	^2E	**[a]15140**	20452	17909	17881	17850	17983	17628	21344	15288
$^4T_{2g}(^4F)\{$	$^4A_1$	**15700**	14532	16935	16923	16734	14208	17077	15568	14655
	^4E	**16800**	15235	17662	17646	17491	15455	17721	16612	13527
$^2T_{2g}(^2G)\{$	^2E	**} 21037**	26972	24467	24379	24267	23226	23438	28080	20053
	$^2A_1$		28520	25925	25819	25727	24659	24797	29384	21423
$^4T_{1g}(^4F)\{$	^4E	**22800**	22894	25093	24714	24458	23262	24003	24228	21052
	$^4A_2$	**24000**	24718	26599	25996	25709	25070	24938	-	-
$^2A_{1g}(^2G)$	$^2A_1$	**[b]28902**	30971	31228	31252	31059	28461	31289	32406	25415
$^2T_{2g}(^2H)\{$	$^2A_1$	**30700**	33123	33192	33175	32954	30668	32831	34512	27230
	^2E	**31650**	34120	33876	33795	33603	31739	33496	35299	29804
$^2T_{1g}(^2P)\{$	$^2A_2$	**30700**	34415	34255	34363	34156	31802	33990	-	-
	^2E	**31650**	35432	35177	34783	34591	32226	34466	-	-
$^2E_g(^2H)$	^2E	**-**	37363	36515	36541	36368	34535	35910	-	-
$^2T_{1g}(^2H)\{$	^2E	**36300**	40750	40029	39891	39648	37435	38847	42167	33395
	$^2A_2$	**~37400**	41208	40350	40201	39962	37306	38890	-	-
$^4T_{1g}(^4P)\{$	$^4A_2$	**[a]37730**	34526	35973	36553	36363	34658	36599	34442	31645
	^4E	**[a]41320**	38603	39856	40207	40052	38250	39792	39608	35081
$^2T_{2g}(^2D)\{$	^2E	**39900**	47895	46744	45568	45164	44044	43319	48918	43123
	$^2A_1$	**~39900**	47838	46652	45661	45315	43397	43501	-	-
$^2A_{2g}(^2F)$	$^2A_2$	**41800**	47915	48336	47309	46988	45399	45597	-	-
Spin-allowed RMS errors (cm^{-1}) →			1803	1664	1345	1246	1890	1154	1522	3993
Spin-forbidden RMS errors (cm^{-1}) →			5172	4059	3673	3466	2305	2738	6253	2179
TOTAL RMS errors(cm^{-1}) →			**4378**	**3472**	**3118**	**2939**	**2180**	**2347**	**5030**	**2991**

§2. QC expansion

Table S2. Results for SA-CASSCF(3,5)/NEVPT2 multiplets energies (in cm^{-1}) using the embedded clusters $[CrO_6Be_3]^{3-}$, $[Cr(OSi)_6Be_3]^{21}$ and $[Cr(O_2Si)_6Be_3]^9$ in comparison to $[CrO_6]^{9-}$.

Energy levels		**Exp.**	*Ab-initio*	$[CrO_6]^{9-}$	$[CrO_6Be_3]^{3-}$	$[Cr(OSi)_6Be_3]^{19}$	$[Cr(O_2Si)_6Be_3]^9$
O_h	D_3	**[1] [a][2]**	methods				
$^4A_{2g}(^4F)$	$^4A_2$	**0**	SA-CASSCF	0	0	0	0
			SC-NEVPT2	0	0	0	0
$^2E_g(^2G)$	^2E	**14686**	SA-CASSCF	19111	19119	19147	19113
			SC-NEVPT2	16714	16713	16733	16685
$^2T_{1g}(^2G)\{$	$^2A_2$	**-**	SA-CASSCF	19704	19712	19780	19748
			SC-NEVPT2	17304	17304	17360	17319
	^2E	**[a]15140**	SA-CASSCF	20461	20478	20454	20420
			SC-NEVPT2	17947	17955	17913	17864
$^4T_{2g}(^4F)\{$	$^4A_1$	**15700**	SA-CASSCF	14510	14510	14299	14298
			SC-NEVPT2	16923	16937	16596	16592
	^4E	**16800**	SA-CASSCF	15212	15232	14923	14948
			SC-NEVPT2	17648	17681	17234	17270
$^2T_{2g}(^2G)\{$	^2E	**}21037**	SA-CASSCF	26978	26996	26993	26964
			SC-NEVPT2	24539	24552	24524	24484
	$^2A_1$		SA-CASSCF	28526	28555	28374	28339
			SC-NEVPT2	25994	26016	25776	25717
$^4T_{1g}(^4F)\{$	^4E	**22800**	SA-CASSCF	22868	22891	22577	22606
			SC-NEVPT2	25082	25119	24680	24715
	$^4A_2$	**24000**	SA-CASSCF	24691	24707	24224	24220
			SC-NEVPT2	26596	26629	26004	25975
$^4T_{1g}(^4P)\{$	$^4A_2$	**[a]37730**	SA-CASSCF	34498	34494	34337	34312
			SC-NEVPT2	35948	35964	35566	35528
	^4E	**[a]41320**	SA-CASSCF	38570	38623	37993	38021
			SC-NEVPT2	39833	39907	38972	39015
RMS errors(cm^{-1}) →			SA-CASSCF	3873	3878	3940	3918
			SC-NEVPT2	2435	2443	2407	2382

§3. Energies deviations ΔE in CAS (3,5) for CASSCF/MR-PT methods using SA and SS protocol from experimental values. Contributions from orbital relaxation and dynamical correlation to d-d transitions energies in emerald.

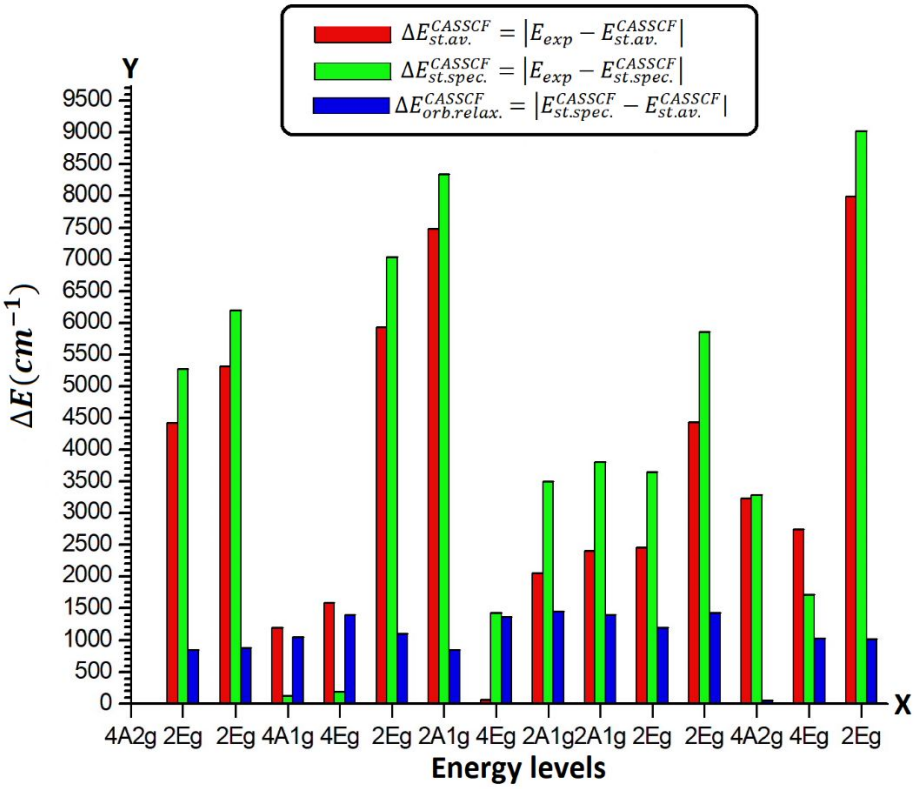

Figure S1. CASSCF (3,5)

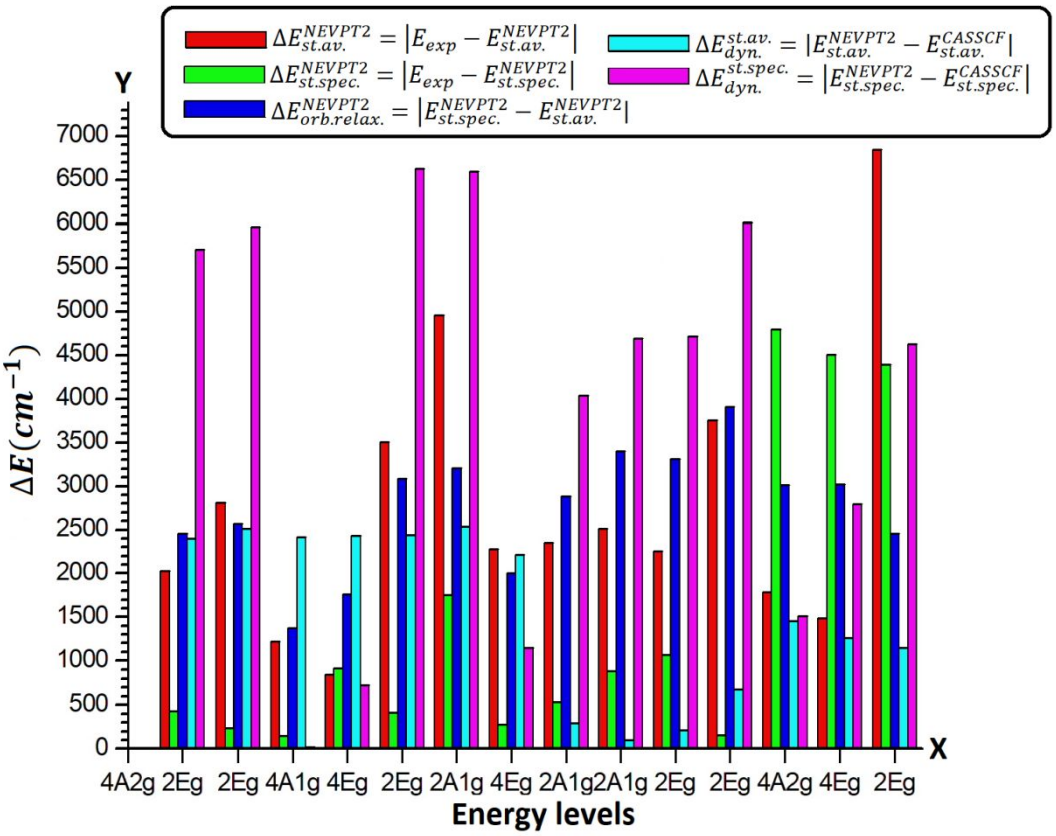

Figure S2. NEVPT2 (3,5)

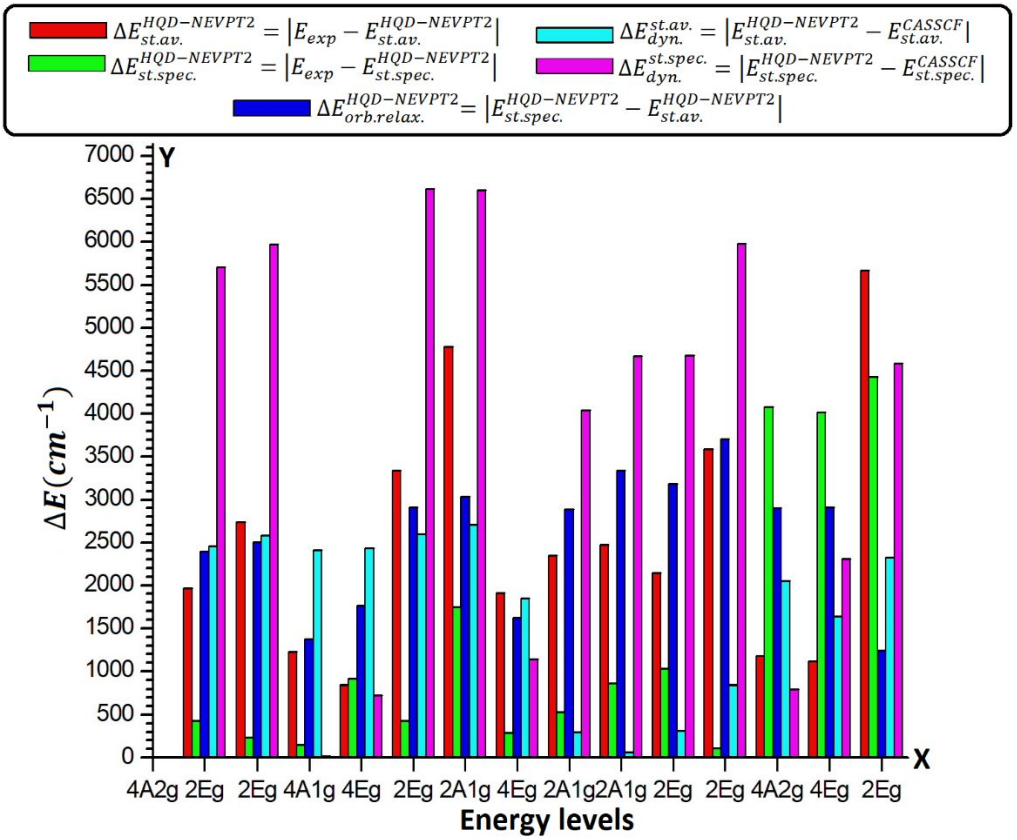

Figure S3. HQD- NEVPT2 (3,5)

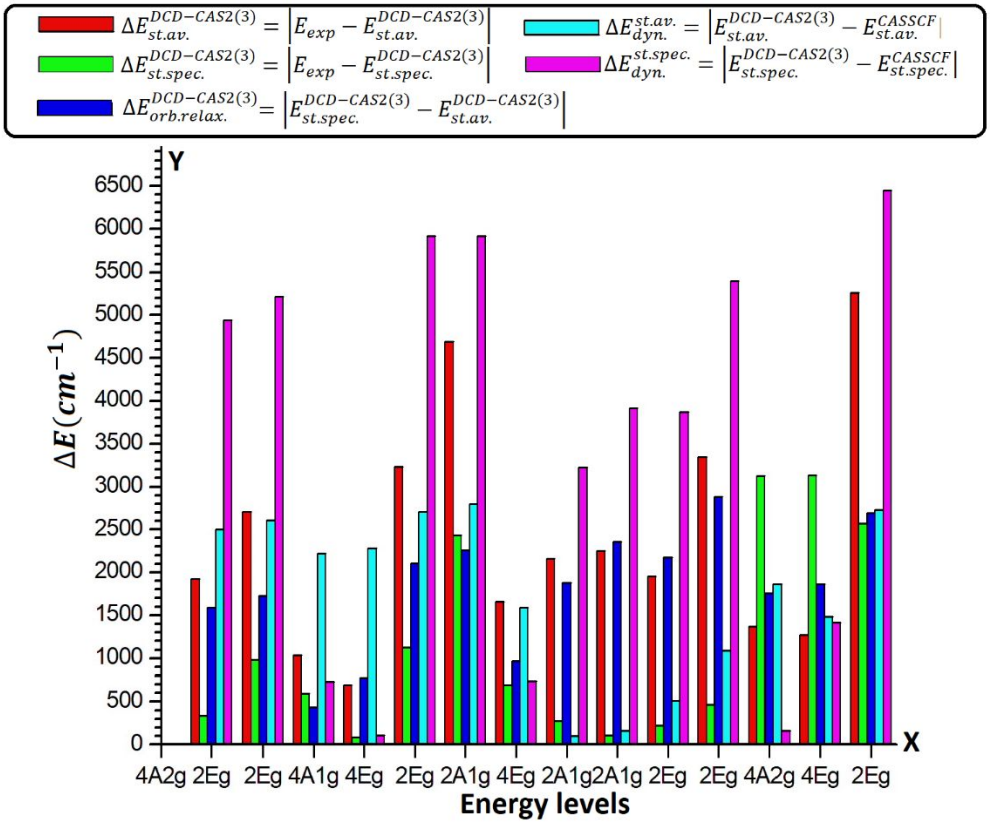

Figure S4. DCD-CAS2(3) (3,5)

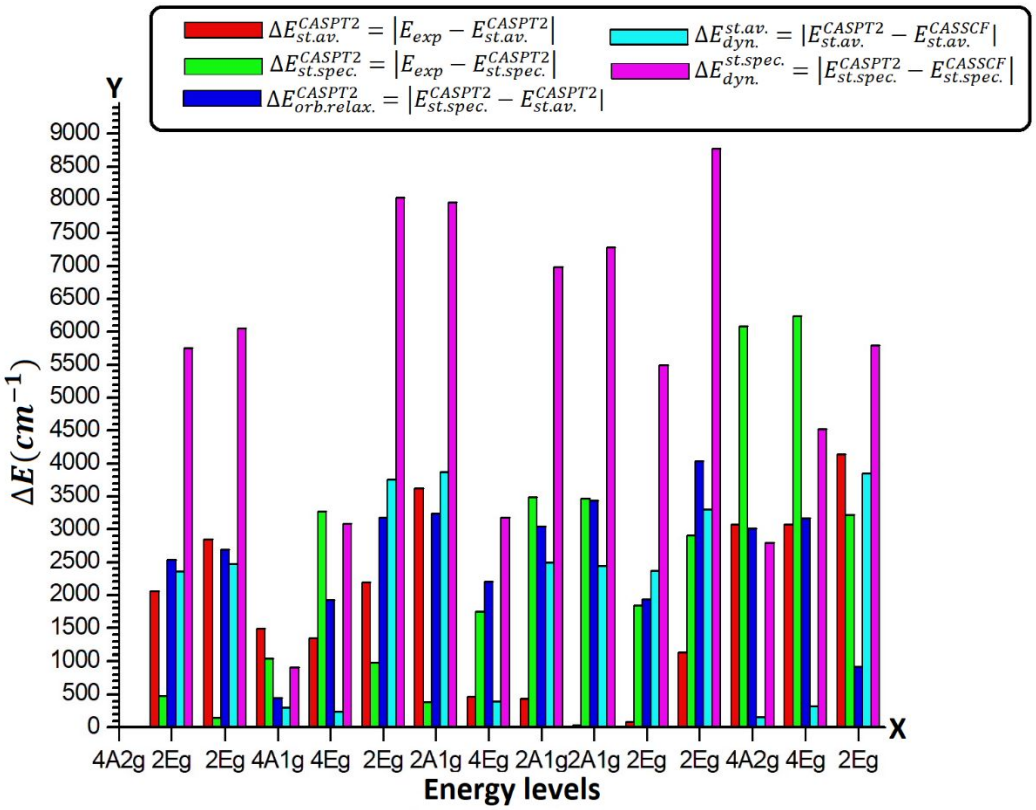

Figure S5. CASPT2 (3,5)

§4. AILFT

4.1 Ligand field one-electron matrix V_{LF}

Ligand field one-electron matrix V_{LF} (DCD-CAS2(3)) (a.u.):

d_{xy}	d_{yz}	d_{z2}	d_{xz}	d_{x2-y2}
−2.025962	0.036677	0.000004	0.000023	0.000004
0.036677	−2.014520	−0.000003	−0.000008	0.000037
0.000004	−0.000003	−2.064440	−0.000002	−0.000002
0.000023	−0.000008	−0.000002	−2.014564	−0.036694
0.000004	0.000037	−0.000002	−0.036694	−2.025905

(S1)

Eigenvalues (cm^{-1}) and corresponding orbitals: 0-d_{z2}; 1552.8-d_{xy}; 1553.5-d_{x2-y2}; 17847.9-d_{xz}; 17825.5-d_{yz};

Ligand field one-electron matrix V_{LF} (CASPT2) (a.u.):

d_{xy}	d_{yz}	d_{z2}	d_{xz}	d_{x2-y2}
−2.028932	0.031960	−0.000005	0.000015	0.000018
0.031960	−2.019272	−0.000003	−0.000016	0.000037
−0.000005	−0.000003	−2.062160	−0.000002	0.000003
0.000015	−0.000016	−0.000002	−2.019300	−0.031980
0.000018	0.000037	0.000003	−0.031980	−2.028865

(S2)

Eigenvalues (cm^{-1}) and corresponding orbitals: 0-d_{z2}; 1258.0-d_{xy}; 1261.1-d_{x2-y2}; 15443.3-d_{xz}; 15457.4-d_{yz};

4.2 AILFT energy levels

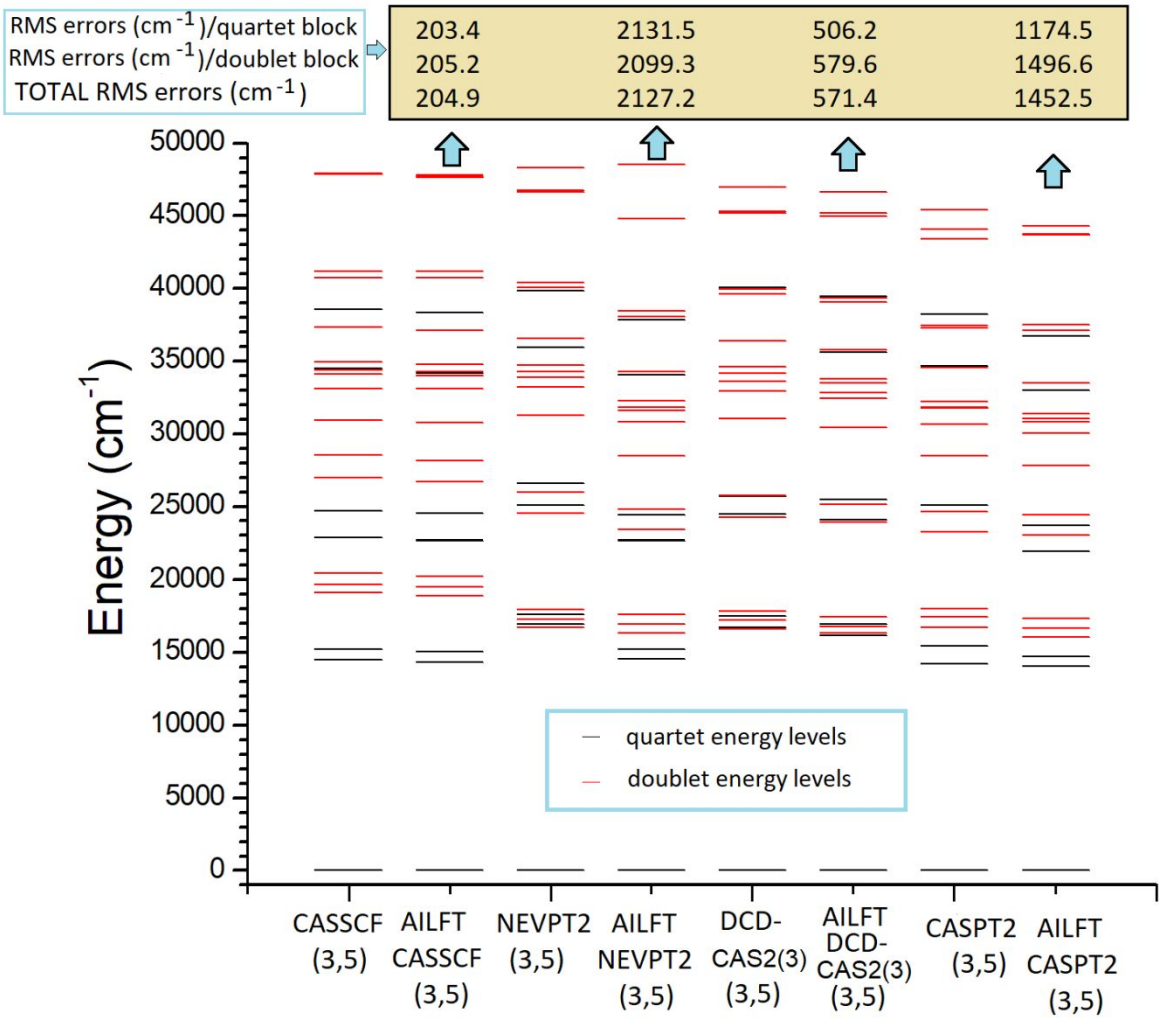

Figure S6. Comparison between energy levels obtained by AI and AILFT methods CAS (3,5).

From this figure it can be seen that recalculated energy levels by AILFT CASSCF (3,5) method (second column in Figure S6), are close with those of AI CASSCF (3,5) (first column in Figure S6), highlighted by correspondent RMS errors. This means that AILFT extractions from CASSCF calculations are more successful than those based on NEVPT2, where deviations are large as 2127 cm^{-1}. One can also see that multistate method DCD-CAS2(3) has, compared to NEVPT2 and CASPT2 methods, an AILFT fit with smaller value of RMS error between ab initio and LFEs. These finding are in agreement with observations reported in [4] for other octahedral $3d^3$ complexes (Cr^{3+} with ligands F−, Cl−, Br−, I−, CN−, NH3).

§5. State specific multiplet calculations

Ab Initio calculation of energies and wave functions of individual ligand field multiples is a rarely used practice. The reason is, that one normally assumes that ligand field theory is at work, such that one is doing this in one step taking state averaging over all states of the d^n configuration of transition metal in complexes. However, for Cr^{3+} in emerald it turned out that state averaging is not the best option. Since nicely resolved d-d absorption spectra are available it was worth trying to attempt state specific calculations to allow a comparison and to test the theory. The first step toward this goal is doing a standard state average CASSCF calculation.

emeraldic.inp

```
!DKH DKH-def2-TZVPP AutoAux TightSCF Grid5 FinalGrid6 SOMF(1X) RI-JK Conv PAtom
 %rel method DKH              # relativistic method
     order 2 # order of DKH treatment (1-5).  maximum value is 2 or SOC
      picturechange true # include the DKH correction to SOC
  end

  %method
SpecialGridAtoms 24
SpecialGridIntAcc 7
```

```
end
%pointcharges "SD.pc"

%casscf         nel     3
                norb    5
                    mult   4,2
                nroots  10,40
                actorbs dorbs
                    switchstep nr
                    trafostep ri
 end

* xyz -9 4
cr      0.000000000000      0.000000000000      0.000000000000
o       0.702755007287      1.571706375966      0.961746349055
o      -1.712515152519     -0.177249499037      0.961746349055
o       1.009760145234     -1.394456876930      0.961746349055
o      -1.010725439782     -1.394795408710     -0.959773945048
o       1.713290976916     -0.177916202748     -0.959773945048
o      -0.702565537133      1.572711611457     -0.959773945048
be>     2.000000000000      0.000232417861      2.704985823138      0.001557569383          NewECP "SDD" end
be>     2.000000000000     -2.342702648644     -1.352291631798      0.001557569383          NewECP "SDD" end
be>     2.000000000000      2.342470230785     -1.352694191341      0.001557569383          NewECP "SDD" end
al>     3.000000000000      0.000000000000      0.000000000000     -4.629229868599          NewECP "SDD" end
al>     3.000000000000      0.000000000000      0.000000000000      4.631409611309          NewECP "SDD" end
si>     4.000000000000     -1.574984830215      1.752292586031     -2.330284349944          NewECP "SDD" end
si>     4.000000000000      1.554235642388      3.605402553803     -2.323365402895          NewECP "SDD" end
si>     4.000000000000     -0.730037479258     -2.240123166558     -2.330284349944          NewECP "SDD" end
si>     4.000000000000      2.305022309475      0.487830580526     -2.330284349944          NewECP "SDD" end
si>     4.000000000000      2.345252381270     -3.148708826676     -2.323365402895          NewECP "SDD" end
si>     4.000000000000     -3.899488023656     -0.456693727127     -2.323365402895          NewECP "SDD" end
si>     4.000000000000     -1.554496391215      3.605328612928      2.325350975521          NewECP "SDD" end
si>     4.000000000000      3.899554363395     -0.456430941581      2.325350975521          NewECP "SDD" end
si>     4.000000000000     -2.345057972178     -3.148897671348      2.325350975521          NewECP "SDD" end
si>     4.000000000000     -2.304735328998      0.487837513378      2.332290888944          NewECP "SDD" end
si>     4.000000000000      0.729887984995     -2.239878100601      2.332290888944          NewECP "SDD" end
si>     4.000000000000      1.574847344003      1.752040587223      2.332290888944          NewECP "SDD" end
o>     -2.000000000000     -2.825143473877      0.743914796652     -2.313398407606          NewECP "SDD" end
o>     -2.000000000000     -1.766650776435     -3.472966305326     -2.366707499729          NewECP "SDD" end
o>     -2.000000000000      0.768322624787     -2.818603416039     -2.313398407606          NewECP "SDD" end
o>     -2.000000000000      2.056820849090      2.074688619387     -2.313398407606          NewECP "SDD" end
o>     -2.000000000000     -2.124351658682      3.266447604671     -2.366707499729          NewECP "SDD" end
o>     -2.000000000000      3.891002435117      0.206518700654     -2.366707499729          NewECP "SDD" end
o>     -2.000000000000      1.767548685558     -3.471638502476      2.369030913635          NewECP "SDD" end
o>     -2.000000000000     -3.890301478680      0.205077187119      2.369030913635          NewECP "SDD" end
o>     -2.000000000000      2.122752793122      3.266561315357      2.369030913635          NewECP "SDD" end
o>     -2.000000000000     -2.057820773724      2.074994127948      2.314911453248          NewECP "SDD" end
o>     -2.000000000000     -0.768087240644     -2.819622130455      2.314911453248          NewECP "SDD" end
o>     -2.000000000000      2.825908014369      0.744628002507      2.314911453248          NewECP "SDD" end
o>     -2.000000000000      0.670545225333      1.499643257013      3.672945844596          NewECP "SDD" end
```

```
o>    -2.000000000000    0.963456544521   -1.330530828031    3.672945844596    NewECP "SDD" end
o>    -2.000000000000   -1.634001769853   -0.169112428983    3.672945844596    NewECP "SDD" end
o>    -2.000000000000   -0.670227854094    1.499988292156   -3.670835011013    NewECP "SDD" end
o>    -2.000000000000    1.634141893435   -0.169559798109   -3.670835011013    NewECP "SDD" end
o>    -2.000000000000   -0.963914039339   -1.330428494048   -3.670835011013    NewECP "SDD" end
o>    -2.000000000000   -0.677911034098    3.862314123155    0.966954580683    NewECP "SDD" end
o>    -2.000000000000    3.683817665097   -1.344068884543    0.966954580683    NewECP "SDD" end
o>    -2.000000000000   -3.005906630998   -2.518245238613    0.966954580683    NewECP "SDD" end
o>    -2.000000000000    0.677978375661    3.862231424575   -0.964693524869    NewECP "SDD" end
o>    -2.000000000000    3.005801341147   -2.518262208826   -0.964693524869    NewECP "SDD" end
o>    -2.000000000000   -3.683779716806   -1.343969215749   -0.964693524869    NewECP "SDD" end
*
```

The CASSCF method yields many particle state energies with orbital degeneracies which are strictly fulfilled; this allows to count degenerate levels and assign symmetry. In D_3 symmetry there are two non-degenerate representations A_1 and A_2 which can be identified using one AOM calculation with ligand field parameters as input for the AOMX program package (see Section 8) . These parameters can be taken from the AILFT section of the ORCA output. This allows one to identify the states in the D_3 point group as listed below

```
------------------------------
SA-CASSCF TRANSITION ENERGIES
------------------------------

LOWEST ROOT (ROOT 0 ,MULT 4) =  -1584.516853273 Eh -43116.896 eV

STATE   ROOT MULT  DE/a.u.    DE/eV    DE/cm**-1
  0:    0   4  0.000000     0.000  00000.0   4A2(1)
  1:    1   4   0.066211     1.802  14531.7   4A1(1)
  2:    2   4   0.069412     1.889  15234.1   4E(1)
  3:    3   4   0.069417     1.889  15235.3   4E(1)
  4:    0   2   0.087036     2.368  19102.1   2E(1)
  5:    1   2   0.087037     2.368  19102.4   2E(1)
  6:    2   2   0.089731     2.442  19693.8   2A2(1)
  7:    3   2   0.093189     2.536  20452.5   2E(2)
  8:    4   2   0.093189     2.536  20452.5   2E(2)
  9:    4   4   0.104308     2.838  22893.0   4E(2)
 10:    5   4   0.104322     2.839  22895.9   4E(2)
 11:    6   4   0.112626     3.065  24718.5   4A2(2)
 12:    5   2   0.122895     3.344  26972.2   2E(3)
 13:    6   2   0.122895     3.344  26972.4   2E(3)
 14:    7   2   0.129948     3.536  28520.3   2A1(1)
 15:    8   2   0.141112     3.840  30970.6
 16:    9   2   0.150919     4.107  33122.8
```

17: 10 2 0.155461 4.230 34119.7
18: 11 2 0.155468 4.231 34121.3
19: 12 2 0.156802 4.267 34414.1
20: 13 2 0.156809 4.267 34415.5
21: 7 4 0.157311 4.281 34525.8 $^4A_2(3)$
22: 14 2 0.161442 4.393 35432.4
23: 15 2 0.170240 4.632 37363.3
24: 16 2 0.170243 4.633 37364.1
25: 8 4 0.175887 4.786 38602.8 $^4E(3)$
26: 9 4 0.175892 4.786 38603.9 $^4E(3)$

To compute the energy of each state separately we need reading the emerald.gbw file and use of the command "weights[0]=…" Here it is of crucial importance the weight with equal weights states which belong to the same degenerate manifold, otherwise symmetry will break down. Explicitly we have the following relevant part of inputs:

State specific calculations on the S=3/2 states

$^4A_2(1)$ ground state:

```
%casscf        nel    3
            norb   5
                mult   4
            nroots  1
                switchstep nr
                trafostep ri
                nevpt2 sc
 end
```

$^4A_1$ excited state:

```
%casscf        nel    3
            norb   5
                mult   4
            nroots  2
            actorbs locorbs
            weights[0]=0,1
                switchstep nr
                trafostep ri
                nevpt2 sc
 end
```

$^4E(1)$ excited state:

```
%casscf        nel    3
            norb   5
                mult   4
            nroots  4
            actorbs locorbs
```

```
            weights[0]=0,0,1,1
                orbstep superci
                switchstep diis
                trafostep ri
                shiftup 1
                shiftdn 1
                nevpt2 sc
 end
```

^{4}E(2) excited state:

```
%casscf        nel    3
            norb   5
                mult   4
            nroots  6
            actorbs locorbs
            weights[0]=0,0,0,0,1,1
                switchstep nr
                trafostep ri
                nevpt2 sc
 end
```

^{4}E(3) excited state:

```
 %casscf        nel    3
            norb   5
                mult   4
            nroots  10
            actorbs locorbs
            weights[0]=0,0,0,0,0,0,0,0,1,1
                switchstep nr
                trafostep ri
                nevpt2 sc
 end
```

$^4A_2$(3) excited state:

```
%casscf        nel    3
            norb   5
                mult   4
            nroots  8
            actorbs locorbs
            weights[0]=0,0,0,0,0,0,0,1
                switchstep nr
                trafostep ri
                nevpt2 sc
 end
```

Please, notice that the calculation for $^4A_2$(2) did not converge!

State specific calculations on the lowest S=1/2 states:

^{2}E(1) excited state (emitting):

```
%casscf        nel    3
               norb   5
                    mult   2
               nroots  2
               actorbs locorbs
               weights[0]=1,1
                    switchstep nr
                    trafostep ri
                    nevpt2 sc
 end
```

^{2}E(2) state:

```
%casscf        nel    3
               norb   5
                    mult   2
               nroots  5
               actorbs locorbs
               weights[0]=0,0,0,1,1
                    switchstep nr
                    trafostep ri
                    nevpt2 sc
 end
```

^{2}E(3)

```
%casscf        nel    3
               norb   5
                    mult   2
               nroots  7
               actorbs locorbs
               weights[0]=0,0,0,0,0,1,1
                    switchstep nr
                    trafostep ri
                    nevpt2 sc
 end
```

$^2A_2$(1) excited state:

```
%casscf        nel    3
               norb   5
                    mult   2
               nroots  3
               actorbs locorbs
               weights[0]=0,0,1
                     orbstep superci
                    switchstep diis
                   shiftup 0.5
                   shiftdn 0.5
                    trafostep ri
```

```
                nevpt2 sc
maxiter 200
 end
```

$^2A_1(1)$ excited state:

```
%casscf        nel    3
            norb   5
                 mult   2
            nroots  8
            actorbs locorbs
            weights[0]=0,0,0,0,0,0,0,1
                  orbstep superci
                 switchstep diis
                shiftup 2
                shiftdn 2
                 trafostep ri
                 nevpt2 sc
 end
```

§6. Vibronic analysis and calculation of vibronic landscapes of d-d transitions

State specific energies have been computed taking a scan along the Q_α stretching mode with increments of the Cr-O distance $R_o \pm \delta R$: R_o-0.05, R_o-0.025, R_o+0.025, Ro+0.05 Å around the reference distance R_o. Total energies for each state have been fitted using a $(1/2)K_\alpha Q_\alpha^2 + V_\alpha Q_\alpha + E_{FC}$ a dependence on the $Q_\alpha = \sqrt{6}\delta R$.

In this way we obtain the following energy expressions (in cm^{-1}):

$E[^4A_2(1)] = 149382Q_\alpha^2 - 25518Q_\alpha$

$E[^4A_1(1)] = 157939Q_\alpha^2 - 39165Q_\alpha + 15542$

$E[^4A_2(3)] = 169208Q_\alpha^2 - 54161Q_\alpha + 32932$

$E[^4E(1)] = 157491Q_\alpha^2 - 39295Q_\alpha + 15876$

$E[^4E(2)] = 155641Q_\alpha^2 - 40388Q_\alpha + 23069$

$E[^4E(3)] = 166482Q_\alpha^2 - 51343Q_\alpha + 36808$

$E[^2E(1)] = 148711Q_\alpha^2 - 23970Q_\alpha + 14234$

$E[^2E(2)] = 148395Q_\alpha^2 - 23962Q_\alpha + 15357$

$E[^2E(3)] = 148339Q_\alpha^2 - 25919Q_\alpha + 21416$

$E[^2A(1)] = 147639Q_\alpha^2 - 25947Q_\alpha + 22753$

It is well known, that force field parameters derived from Hartree-Fock, and from post-Hartree-Fock methods are systematically overestimated compared to values extracted from experimental IR and Raman spectra. The same, though to lesser extent, is also valid for gradients. In the calculations we have used the following scaling factors based on a spectroscopic calibration, adjusting the force field constant K_α and the gradient V_α using the following relations:

$$K_\alpha^{eff} = 0.21 K_\alpha^{NEVPT2}$$

$$V_\alpha^{eff} = 0.87 V_\alpha^{NEVPT2}$$

The adjustment holds true for the here considered case of Cr^{3+} in emerald and was chosen in such a way to reproduce the shape of the $^4A_2 \rightarrow {}^4T_2$ in the non-polarized with a $h\nu_{\alpha 1} = 370\,\mathrm{cm}^{-1}$ and a Hunag-Rhys factor S=3.0.

Figure 6 has been constructed using the following MatLab script:

```
clear all
clc

% potential energy diagrams
Qalfa1=[-0.72:0.01:0.72];
% ground state 4A2
deltaEFC=0;
Kalfa=61545;
Valfa=0;
Qalfamin1=Valfa/Kalfa
dRmin1=Qalfamin1/sqrt(6)
Ealfa4A21=deltaEFC+(1/2)*Kalfa*Qalfa1.^2-Valfa*Qalfa1;
% 4A2(4T1(2)), units cm-1
deltaEFC=32930;
Kalfa=69714;
Valfa=24920;
Qalfamin2=Valfa/Kalfa
dRmin2=Qalfamin2/sqrt(6)
Qalfa2=[-0.33:0.01:1.05];
Ealfa4A23=deltaEFC+(1/2)*Kalfa*Qalfa2.^2-Valfa*Qalfa2;
% 4A1(4T2), units cm-1
deltaEFC=15537;
Kalfa=65071;
Valfa=11873;
Qalfamin3=Valfa/Kalfa
dRmin3=Qalfamin3/sqrt(6)
Qalfa3=[-0.58:0.01:0.90];
Ealfa4A1=deltaEFC+(1/2)*Kalfa*Qalfa3.^2-Valfa*Qalfa3;

% 4E(4T2)

deltaEFC=15875;
Kalfa=64886;
Valfa=11987;
```

```
Qalfamin4=Valfa/Kalfa
dRmin4=Qalfamin4/sqrt(6)
Qalfa4=[-0.58:0.01:0.90];
Ealfa4E1=deltaEFC+(1/2)*Kalfa*Qalfa4.^2-Valfa*Qalfa4;

% 4E(4T11)

deltaEFC=23076;
Kalfa=64124;
Valfa=12937;
Qalfamin5=Valfa/Kalfa
dRmin5=Qalfamin5/sqrt(6)
Qalfa5=[-0.52:0.01:0.92];
Ealfa4E12=deltaEFC+(1/2)*Kalfa*Qalfa5.^2-Valfa*Qalfa5;

% 4E(4T12)

deltaEFC=36806;
Kalfa=68590;
Valfa=22468;
Qalfamin6=Valfa/Kalfa
dRmin6=Qalfamin6/sqrt(6)
Qalfa6=[-0.39:0.01:1.05];
Ealfa4E13=deltaEFC+(1/2)*Kalfa*Qalfa6.^2-Valfa*Qalfa6;


% 2E(2E)

deltaEFC=14233;
Kalfa=61269;
Valfa=-1347;
Qalfamin7=Valfa/Kalfa
dRmin7=Qalfamin7/sqrt(6)
Qalfa7=[-0.72:0.01:0.72];
Ealfa2E1=deltaEFC+(1/2)*Kalfa*Qalfa7.^2-Valfa*Qalfa7;

% 2E(2T1)

deltaEFC=15377;
Kalfa=61139;
Valfa=-1353;
Qalfamin8=Valfa/Kalfa
dRmin8=Qalfamin8/sqrt(6)
Qalfa8=[-0.72:0.01:0.72];
Ealfa2E2=deltaEFC+(1/2)*Kalfa*Qalfa8.^2-Valfa*Qalfa8;

%  2E(2T2)

deltaEFC=21415;
Kalfa=61116;
Valfa=-349;
Qalfamin9=Valfa/Kalfa
dRmin9=Qalfamin9/sqrt(6)
Qalfa9=[-0.72:0.01:0.72];
Ealfa2E3=deltaEFC+(1/2)*Kalfa*Qalfa9.^2-Valfa*Qalfa9;

%  2A1(2T2)

deltaEFC=22752;
```

```
Kalfa=60827;
Valfa=-373;
Qalfamin10=Valfa/Kalfa
dRmin10=Qalfamin10/sqrt(6)
Qalfa10=[-0.72:0.01:0.72];
Ealfa2A1=deltaEFC+(1/2)*Kalfa*Qalfa10.^2-Valfa*Qalfa10;

plot(Qalfa2,Ealfa4A23,'-',Qalfa1,Ealfa4A21,'-',Qalfa3,Ealfa4A1,'-',
Qalfa4,Ealfa4E1,'-',Qalfa5,Ealfa4E12,'-',Qalfa6,Ealfa4E13,'-',
Qalfa7,Ealfa2E1,'-',Qalfa8,Ealfa2E2,'-',Qalfa9,Ealfa2E3,'-
',Qalfa10,Ealfa2A1,'-')
XMIN=-0.72;
XMAX=1.05;
YMIN=0;
YMAX=45000;
axis([XMIN XMAX YMIN YMAX])
```

The spectrum (Figure 7) was simulated using the following MatLab script:

```
clear all
clc
format long
% Qalfa progression
%          1       2              3        4           5
% 4A2 -> 4A1(4T2) 4A2(4T1(2)) 4E(4T2) 4E(4T1(1))  4E(4T1(2))
S4=     [2.92 11.62 2.99 3.55 9.68];
ndim4=max(size(S4));
E4zpt=  [14454 28476 14768 21771 33126];
homega4=[370 383 370 368 380];
fosc4=[16.3 0.0  18.2  8.5 4.8];
S2=     [0.04  0.04  0.0  0.0];
ndim22=max(size(S2));
E2zpt=  [14218 15362 21414 22751];
homega2=[359 359 359 358];
fosc2=[4.3 1.6 0.7  0.2];
ndim22=max(size(S2));

% 4A2 to S=3/2 d-d transitions
isum=0.0;
esum=0.0;
I(40)=zeros;
E(40)=zeros;
for i=1:ndim4
factor=exp(-S4(i));
huangrhys=S4(i);
for j=1:8
isum=isum+1;
esum=esum+1;
 I4(isum)=factor*huangrhys^(j-1)/factorial(j-1);
 E4(esum)=E4zpt(i)+(j-1)*homega4(i);
end
end

% x=[min(E4)-1000:1:max(E4)+1000];
x=[12000:10:30000];
ndim2=max(size(x));


% result=[E'  I']
```

```
% disp(result)
% ndim=max(size(result));

% spin-allowed transitions
% zspectrum
ndim=8;
b=E4(1:8);
c=I4(1:8);
f=fosc4(1);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/1000;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope1(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope1(j)=envelope1(j)+y(i,j);
end
end

% xy spectrum  4E(1)

b=E4(17:24);
c=I4(17:24);
f=fosc4(3);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/1000;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope2(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope2(j)=envelope2(j)+y(i,j);
end
end

% xy spectrum  4E(2)
b=E4(25:32);
c=I4(25:32);
f=fosc4(4);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/1000;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope3(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope3(j)=envelope3(j)+y(i,j);
end
end
```

```
% xy spectrum  4E(2)

b=E4(33:40);
c=I4(33:40);
f=fosc4(5);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/1000;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope4(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope4(j)=envelope4(j)+y(i,j);
end
end

envelope4z=envelope1;
envelope4xy=envelope2+envelope3+envelope4;
%
% plot(x,envelope4z,'-',x,envelope4xy,'-')

% spin-forbidden transitions


% 4A2 to S=1/2 d-d transitions
isum=0.0;
esum=0.0;
I2(32)=zeros;
E2(32)=zeros;
for i=1:ndim22
factor=exp(-S2(i));
huangrhys=S2(i);
for j=1:8
isum=isum+1;
esum=esum+1;
 I2(isum)=factor*huangrhys^(j-1)/factorial(j-1);
 E2(esum)=E2zpt(i)+(j-1)*homega2(i);
end
end


% xy spectrum  2E(1)

b=E2(1:8);
c=I2(1:8);
f=fosc2(1);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/50;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope5(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope5(j)=envelope5(j)+y(i,j);
```

```
end
end



% xy spectrum  2E(2)
b=E2(9:16);
c=I2(9:16);
f=fosc2(2);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/50;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope6(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope6(j)=envelope6(j)+y(i,j);
end
end

% xy spectrum  2E(3)

b=E2(17:24);
c=I2(17:24);
f=fosc2(3);
y(8,ndim2)=zeros;
for i=1:8
 for j=1:ndim2
y(i,j)=(x(j)-b(i))/50;
y(i,j)=f*c(i)*exp(-y(i,j)*y(i,j));
     end
end
envelope7(ndim2)=zeros;
for j=1:ndim2
for i=1:8
envelope7(j)=envelope7(j)+y(i,j);
end
end
%   spin   allowed    allowed   allowed  forbidden  forbidden  forbidden
envelopexy=envelope2+envelope3+envelope4+envelope5+envelope6+envelope7;

plot(x,envelope4z,'-',x,envelopexy,'-')

axis([12000 30000  0  14])
```

§7. Generation of embedded host environment based on the Gelle-Lepettit method

7. 1 Gellé -Lepetit method

The Gellé -Lepetit method [5] allows to calculate the Madelung potential and design the embedded cluster around an impurity ion in a supercell of a given crystal. It works by the cancel out of given number of successive multipolar

moments of the crystal supercell. This method was applied to obtain the QC, BR and PC of emerald crystal using the 1x1x2 optimized supercell, the Env 15 softwer and the following files:

S 1.1. The input file

```
&envin
 prefix='SD',
 nfi_in='SD_0.cell',
 ncel = 0,
 nch = 116,
 sortie='orca',
 a= 9.25524107, b= 9.25524107, c= 18.51489404,
 alpha= 90.0, beta=90.0,gamma=120.000000,
 atom0='Ctr',
 pos0 = 3.333333333333E-01, -3.333333333333E-01, 1.249444485904E-01,
 nmag=1,
 atommag='Cr',
 posmag= 3.333333333333E-01,-3.333333333333E-01,1.249444485904E-01,
 dsys=2.0, dpseud=5.2,
 &end
```

S 1.2. The cell file

```
BE   -4.979021040594E-01  4.145567827934E-03  1.250285738022E-01    2.0
 BE   -4.999970259207E-01 -1.837319650455E-05 -3.749795366598E-01    2.0
 BE   -4.145567827933E-03  4.979523281127E-01  1.250285738022E-01    2.0
 BE    1.837319650452E-05 -4.999786527242E-01 -3.749795366598E-01    2.0
 BE   -4.979523281127E-01  4.979021040594E-01  1.250285738022E-01    2.0
 BE    4.999786527242E-01  4.999970259207E-01 -3.749795366598E-01    2.0
 BE    4.993976517886E-01 -2.529378483096E-05 -1.253486194027E-01    2.0
 BE   -4.994590019109E-01 -4.717867745963E-05  3.753128133843E-01    2.0
 BE    2.529378483100E-05  4.994229455734E-01 -1.253486194027E-01    2.0
 BE    4.717867745997E-05 -4.994118232335E-01  3.753128133843E-01    2.0
 BE   -4.994229455734E-01 -4.993976517886E-01 -1.253486194027E-01    2.0
 BE    4.994118232335E-01  4.994590019109E-01  3.753128133843E-01    2.0
 CR    3.333333333333E-01 -3.333333333333E-01  1.249444485904E-01    3.0
 AL    3.333333333333E-01 -3.333333333333E-01 -3.750209816237E-01    3.0
 AL   -3.333333333333E-01  3.333333333333E-01  1.250040383774E-01    3.0
 AL   -3.333333333333E-01  3.333333333333E-01 -3.749879007554E-01    3.0
 AL   -3.333333333333E-01  3.333333333333E-01 -1.252771096651E-01    3.0
 AL   -3.333333333333E-01  3.333333333333E-01  3.752811073035E-01    3.0
 AL    3.333333333333E-01 -3.333333333333E-01 -1.250829001267E-01    3.0
 AL    3.333333333333E-01 -3.333333333333E-01  3.750895264560E-01    3.0
 SI    2.724707118510E-01 -1.147141555955E-01 -9.155398550900E-04    4.0
 SI    2.726586925066E-01 -1.171441659495E-01 -4.998941293865E-01    4.0
 SI   -2.738280847363E-01  1.164831801927E-01 -5.418435739343E-04    4.0
 SI   -2.724469808798E-01  1.171094031002E-01 -4.997977394021E-01    4.0
 SI    1.147141555955E-01  3.871848674465E-01 -9.155398550900E-04    4.0
 SI    1.171441659495E-01  3.898028584560E-01 -4.998941293865E-01    4.0
 SI   -3.871848674465E-01 -2.724707118510E-01 -9.155398550900E-04    4.0
 SI   -3.898028584560E-01 -2.726586925066E-01 -4.998941293865E-01    4.0
 SI    3.903112649290E-01  2.738280847363E-01 -5.418435739343E-04    4.0
 SI    3.895563839800E-01  2.724469808798E-01 -4.997977394021E-01    4.0
 SI   -1.164831801927E-01 -3.903112649290E-01 -5.418435739343E-04    4.0
 SI   -1.171094031002E-01 -3.895563839800E-01 -4.997977394021E-01    4.0
 SI    3.895060586149E-01  1.171102086506E-01 -2.501981143837E-01    4.0
 SI    3.902784793311E-01  1.164739551960E-01  2.505379826661E-01    4.0
 SI   -2.723958499643E-01 -3.895060586149E-01 -2.501981143837E-01    4.0
 SI   -2.738045241351E-01 -3.902784793311E-01  2.505379826661E-01    4.0
 SI   -1.171102086506E-01  2.723958499643E-01 -2.501981143837E-01    4.0
 SI   -1.164739551960E-01  2.738045241351E-01  2.505379826661E-01    4.0
 SI    1.171659346214E-01 -2.726538822764E-01 -2.501089446355E-01    4.0
 SI    1.147455954205E-01 -2.724698468959E-01  2.509128113531E-01    4.0
 SI    2.726538822764E-01  3.898198168978E-01 -2.501089446355E-01    4.0
 SI    2.724698468959E-01  3.872154423165E-01  2.509128113531E-01    4.0
 SI   -3.898198168978E-01 -1.171659346214E-01 -2.501089446355E-01    4.0
 SI   -3.872154423165E-01 -1.147455954205E-01  2.509128113531E-01    4.0
 O     7.449144605487E-02 -2.405211840111E-01 -3.520466741145E-06   -2.0
 O     7.343120249905E-02 -2.381410348506E-01 -4.998745476272E-01   -2.0
 O    -7.419455050833E-02  2.333731379296E-01 -2.882774974361E-03   -2.0
 O    -7.323336798673E-02  2.380610629926E-01 -4.998081063218E-01   -2.0
```

O	2.405211840111E-01	3.150126300660E-01	-3.520466741145E-06	-2.0
O	2.381410348506E-01	3.115722373497E-01	-4.998745476272E-01	-2.0
O	-3.150126300660E-01	-7.449144605487E-02	-3.520466741145E-06	-2.0
O	-3.115722373497E-01	-7.343120249905E-02	-4.998745476272E-01	-2.0
O	3.075676884379E-01	7.419455050833E-02	-2.882774974361E-03	-2.0
O	3.112944309793E-01	7.323336798673E-02	-4.998081063218E-01	-2.0
O	-2.333731379296E-01	-3.075676884379E-01	-2.882774974361E-03	-2.0
O	-2.380610629926E-01	-3.112944309793E-01	-4.998081063218E-01	-2.0
O	3.112386789310E-01	2.380566202389E-01	-2.502141053059E-01	-2.0
O	3.077475342618E-01	2.335387970036E-01	2.528971610670E-01	-2.0
O	-7.318205869210E-02	-3.112386789310E-01	-2.502141053059E-01	-2.0
O	-7.420873725827E-02	-3.077475342618E-01	2.528971610670E-01	-2.0
O	-2.380566202389E-01	7.318205869210E-02	-2.502141053059E-01	-2.0
O	-2.335387970036E-01	7.420873725827E-02	2.528971610670E-01	-2.0
O	2.381118644501E-01	-7.341841479475E-02	-2.501098581124E-01	-2.0
O	2.404322031646E-01	-7.445333025681E-02	2.499741381067E-01	-2.0
O	7.341841479475E-02	3.115302792448E-01	-2.501098581124E-01	-2.0
O	7.445333025681E-02	3.148855334215E-01	2.499741381067E-01	-2.0
O	-3.115302792448E-01	-2.381118644501E-01	-2.501098581124E-01	-2.0
O	-3.148855334215E-01	-2.404322031646E-01	2.499741381067E-01	-2.0
O	-4.994266827362E-01	1.464404351639E-01	-1.771798108566E-01	-2.0
O	-4.976682160208E-01	1.459535584614E-01	3.232024042592E-01	-2.0
O	4.990626293697E-01	-1.462041156210E-01	-1.770999430880E-01	-2.0
O	4.993327548327E-01	-1.462351407360E-01	3.233223510867E-01	-2.0
O	-1.464404351639E-01	3.541328820998E-01	-1.771798108566E-01	-2.0
O	-1.459535584614E-01	3.563782255178E-01	3.232024042592E-01	-2.0
O	-3.541328820998E-01	4.994266827362E-01	-1.771798108566E-01	-2.0
O	-3.563782255178E-01	4.976682160208E-01	3.232024042592E-01	-2.0
O	3.547332550092E-01	-4.990626293697E-01	-1.770999430880E-01	-2.0
O	3.544321044313E-01	-4.993327548327E-01	3.233223510867E-01	-2.0
O	1.462041156210E-01	-3.547332550092E-01	-1.770999430880E-01	-2.0
O	1.462351407360E-01	-3.544321044313E-01	3.233223510867E-01	-2.0
O	3.544879190089E-01	-1.461920935303E-01	-7.331944657865E-02	-2.0
O	3.547018992249E-01	-1.462053759331E-01	4.270859087859E-01	-2.0
O	4.993199874608E-01	-3.544879190089E-01	-7.331944657865E-02	-2.0
O	4.990927248420E-01	-3.547018992249E-01	4.270859087859E-01	-2.0
O	1.461920935303E-01	-4.993199874608E-01	-7.331944657865E-02	-2.0
O	1.462053759331E-01	-4.990927248420E-01	4.270859087859E-01	-2.0
O	-1.459614955514E-01	4.976321522896E-01	-7.320226388244E-02	-2.0
O	-1.463975257829E-01	4.993705577814E-01	4.271942730778E-01	-2.0
O	-4.976321522896E-01	3.564063521590E-01	-7.320226388244E-02	-2.0
O	-4.993705577814E-01	3.542319164357E-01	4.271942730778E-01	-2.0
O	-3.564063521590E-01	1.459614955514E-01	-7.320226388244E-02	-2.0
O	-3.542319164357E-01	1.463975257829E-01	4.271942730778E-01	-2.0
O	-4.926917162187E-01	-1.372444162780E-01	1.768889181065E-01	-2.0
O	4.990832590823E-01	-1.462972513166E-01	-3.231152394448E-01	-2.0
O	-4.989782128639E-01	1.485359301106E-01	1.771702176709E-01	-2.0
O	-4.992441899080E-01	1.462341591354E-01	-3.231505025786E-01	-2.0
O	1.372444162780E-01	-3.554472999407E-01	1.768889181065E-01	-2.0
O	1.462972513166E-01	-3.546194896010E-01	-3.231152394448E-01	-2.0
O	3.554472999407E-01	4.926917162187E-01	1.768889181065E-01	-2.0
O	3.546194896010E-01	-4.990832590823E-01	-3.231152394448E-01	-2.0
O	-3.524858570255E-01	4.989782128639E-01	1.771702176709E-01	-2.0
O	-3.545216509566E-01	4.992441899080E-01	-3.231505025786E-01	-2.0
O	-1.485359301106E-01	3.524858570255E-01	1.771702176709E-01	-2.0
O	-1.462341591354E-01	3.545216509566E-01	-3.231505025786E-01	-2.0
O	-3.524837397911E-01	1.485256124869E-01	7.284080042560E-02	-2.0
O	-3.545040316271E-01	1.462414820844E-01	-4.268186581693E-01	-2.0
O	-4.989906477220E-01	3.524837397911E-01	7.284080042560E-02	-2.0
O	-4.992544862886E-01	3.545040316271E-01	-4.268186581693E-01	-2.0
O	-1.485256124869E-01	4.989906477220E-01	7.284080042560E-02	-2.0
O	-1.462414820844E-01	4.992544862886E-01	-4.268186581693E-01	-2.0
O	1.371190012884E-01	4.926494803844E-01	7.310650974104E-02	-2.0
O	1.462401739262E-01	-4.990799900355E-01	-4.268950283457E-01	-2.0
O	-4.926494803844E-01	-3.555304790960E-01	7.310650974104E-02	-2.0
O	4.990799900355E-01	-3.546798360383E-01	-4.268950283457E-01	-2.0
O	3.555304790960E-01	-1.371190012884E-01	7.310650974104E-02	-2.0
O	3.546798360383E-01	-1.462401739262E-01	-4.268950283457E-01	-2.0

The calculations generated the xyz and PC files that can be obtained from the authors upon request.

§8. Angular Overlap Model calculations

Angular overlap model calculations were carried out with the aid of the AOMX program package.[6] Here we include three type of examples of their usage in this report.

8.1. Assignment and labelling of multiplets from ORCA calculations.

Symmetry is available in ORCA for Abelian point groups only. In these point groups there are no degenerate representations. In the D_3 point group the irreducible representations are A_1, A_2 and E. From the ORCA output E representations can easily be identified from the twofold degeneracy of CASSCF computed state energies, but one cannot descriminate between A_1 and A_2. To this end, one can repeat the calculation using the AOMX program just taking the set of LF parameters from the AILFT output, but one has to derive the AOM parameters for the Cr-O bond beforehand (see Section 8.2 for an example); for the CASSCF calculation the resulting parameters are (in cm^{-1}):

e_σ=5774, e_π=484, B=1064, C=3950.

Input:

```
no Spin-Orbit coupling

3 D3

VAR
esg = 5774
epi =  484
B =   1064
C =   3950
*
zeta = 0

RTP
1.972  60.81  30.0
1.972  60.81  150.0
1.972  60.81  270.0
1.972  119.19 -30.0
1.972  119.19  90.0
1.972  119.19 210.0

AOM
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi
```

```
VEE 0 B C

CTL PLFM

RUN
```

Output:

```
   Program AOMX, 09-Jun-96 Version
         Author Heribert Adamsky, Theoretical Chemistry, HHU Duesseldorf, FRG
         MDET=252, MLIG=150, MVAR=40, MAOP=10, MOCS=10, MEEX=20

no Spin-Orbit coupling

3   electrons

rotation group: D3

esg        = 5774
epi        = 484
B          = 1064
C          = 3950
*
zeta       = 0

  1 R      = 1.972      THETA  = 60.81      PHI    = 30.0
  2 R      = 1.972      THETA  = 60.81      PHI    = 150.0
  3 R      = 1.972      THETA  = 60.81      PHI    = 270.0
  4 R      = 1.972      THETA  = 119.19     PHI    = -30.0
  5 R      = 1.972      THETA  = 119.19     PHI    = 90.0
  6 R      = 1.972      THETA  = 119.19     PHI    = 210.0

  1 ESIG   = esg        EPIS   = epi        EPIC   = epi
  2 ESIG   = esg        EPIS   = epi        EPIC   = epi
  3 ESIG   = esg        EPIS   = epi        EPIC   = epi
  4 ESIG   = esg        EPIS   = epi        EPIC   = epi
  5 ESIG   = esg        EPIS   = epi        EPIC   = epi
  6 ESIG   = esg        EPIS   = epi        EPIC   = epi

     A     = 0           B     = B           C     = C


CALCULATION NO.    1

esg        =   5774.000000
epi        =    484.000000
B          =   1064.000000
C          =   3950.000000
*
zeta       =       .000000

AOM matrix

        xy        xz        yz      x2y2        z2

  8916.091  7489.102      .000      .000      .000
  7489.102 10164.975      .000      .000      .000
      .000      .000 10164.975  7489.102      .000
      .000      .000  7489.102  8916.091      .000
      .000      .000      .000      .000  2289.868

 no.  term     energy       occupation                    character

                            xy    xz    yz  x2y2    z2    C2(X)

  1   4A2         .000     .600  .400  .400  .600 1.000   -1.000  .000
  3   4E     14658.059     .651  .632  .632  .651  .434     .000  .000
  4   4A1    14805.891     .500  .500  .500  .500 1.000    1.000  .000
  6   2E     18897.157     .616  .531  .531  .616  .706     .000  .000
  7   2A2    19597.942     .526  .488  .488  .526  .974   -1.000  .000
  9   2E     20453.126     .641  .405  .405  .641  .908     .000  .000
 11   4E     22009.787     .502  .788  .788  .502  .420     .000  .000
 12   4A2    25831.751     .796  .204  .204  .796 1.000   -1.000  .000
 14   2E     26928.192     .473  .434  .434  .473 1.187     .000  .000
```

```
 15   2A1    28511.408     .710  .403  .403  .710  .774    1.000  .000
 16   2A1    30973.872     .616  .500  .500  .616  .768    1.000  .000
 17   2A1    33553.697     .494  .559  .559  .494  .894    1.000  .000
 19   2E     33746.218     .665  .712  .712  .665  .246     .000  .000
 20   4A2    34545.922     .104  .896  .896  .104 1.000   -1.000  .000
 22   2E     35040.446     .544  .456  .456  .544 1.001     .000  .000
 23   2A2    35148.832     .697  .583  .583  .697  .441   -1.000  .000
 25   2E     37069.375     .572  .573  .573  .572  .709     .000  .000
 27   4E     38211.157     .846  .581  .581  .846  .146     .000  .000
 29   2E     40703.537     .562  .659  .659  .562  .558     .000  .000
 30   2A2    41580.370     .581  .568  .568  .581  .702   -1.000  .000
 31   2A1    47702.370     .555  .698  .698  .555  .494    1.000  .000
 33   2E     47908.197     .538  .712  .712  .538  .500     .000  .000
 34   2A2    48382.162     .313  .766  .766  .313  .842   -1.000  .000
 36   2E     49472.777     .608  .654  .654  .608  .475     .000  .000
 37   2A2    52721.367     .717  .416  .416  .717  .734   -1.000  .000
 39   2E     53687.117     .539  .631  .631  .539  .661     .000  .000
 40   2A1    54848.523     .819  .565  .565  .819  .232    1.000  .000
 42   2E     57738.351     .695  .734  .734  .695  .142     .000  .000
 44   2E     60689.843     .542  .773  .773  .542  .371     .000  .000
 45   2A2    61062.004     .668  .679  .679  .668  .306   -1.000  .000
 47   2E     79206.128     .540  .751  .751  .540  .418     .000  .000
 48   2A1    80830.806     .305  .776  .776  .305  .838    1.000  .000
 50   2E     83586.001     .966  .476  .476  .966  .117     .000  .000
Stop - Program terminated.
```

We obtain the results with assignment and labelling listed in Table S3

8.2. Ligand field parameters from a best fit to energy eigenvalues.

Here we illustrate the derivation of the LF parameters using experimentally reported d-d transitions. We utilize the D_3 symmetry to label the states.

Input:

```
no Spin-Orbit coupling

3 D3

VAR OPT STA
esg = 5917 1000 20000
epi = 412  200  5000
B = 1059 100 2000
C = 3974 400 8000
*
zeta = 0


RTP
1.972  60.81  30.0
1.972  60.81  150.0
1.972  60.81  270.0
1.972  119.19 -30.0
1.972  119.19  90.0
1.972  119.19 210.0

AOM
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi
esg  epi  epi

VEE 0 B C

EXP
2E  14686 1 2E 1
4A1 15700 1 4A1 1
```

```
4E  16800 1 4E  1
2E  21037 1 2E 3
2A1 21037 1 2A1 1
4E  22800 1 4E 2
4A2 24000 1 4A2 2
2A1 30700 1 2A1 3
2E  31650 1 2E  4
2A2 30700 1 2A2 2
2E  31650 1 2E  5
2E  36300 1 2E  7
2A2 37400 1 2A2 3

CTL PLFM

RUN
```

OUTPUT:

```
Program AOMX, 09-Jun-96 Version
        Author Heribert Adamsky, Theoretical Chemistry, HHU Duesseldorf, FRG
        MDET=252, MLIG=150, MVAR=40, MAOP=10, MOCS=10, MEEX=20

no Spin-Orbit coupling

3   electrons

rotation group: D3

esg        = 5917       MIN 1000        MAX 20000
epi        = 412        MIN 200         MAX 5000
B          = 1059       MIN 100         MAX 2000
C          = 3974       MIN 400         MAX 8000
*
zeta       = 0

  1 R      = 1.972      THETA  = 60.81      PHI    = 30.0
  2 R      = 1.972      THETA  = 60.81      PHI    = 150.0
  3 R      = 1.972      THETA  = 60.81      PHI    = 270.0
  4 R      = 1.972      THETA  = 119.19     PHI    = -30.0
  5 R      = 1.972      THETA  = 119.19     PHI    = 90.0
  6 R      = 1.972      THETA  = 119.19     PHI    = 210.0

  1 ESIG   = esg        EPIS   = epi        EPIC   = epi
  2 ESIG   = esg        EPIS   = epi        EPIC   = epi
  3 ESIG   = esg        EPIS   = epi        EPIC   = epi
  4 ESIG   = esg        EPIS   = epi        EPIC   = epi
  5 ESIG   = esg        EPIS   = epi        EPIC   = epi
  6 ESIG   = esg        EPIS   = epi        EPIC   = epi

     A     = 0           B     = B           C     = C

 1   2E        ( Eex =  14686.000 Wt =    1.000) = 1.000 * 2E , 1
 2   4A1       ( Eex =  15700.000 Wt =    1.000) = 1.000 * 4A1, 1
 3   4E        ( Eex =  16800.000 Wt =    1.000) = 1.000 * 4E , 1
 4   2E        ( Eex =  21037.000 Wt =    1.000) = 1.000 * 2E , 3
 5   2A1       ( Eex =  21037.000 Wt =    1.000) = 1.000 * 2A1, 1
 6   4E        ( Eex =  22800.000 Wt =    1.000) = 1.000 * 4E , 2
 7   4A2       ( Eex =  24000.000 Wt =    1.000) = 1.000 * 4A2, 2
 8   2A1       ( Eex =  30700.000 Wt =    1.000) = 1.000 * 2A1, 3
 9   2E        ( Eex =  31650.000 Wt =    1.000) = 1.000 * 2E , 4
10   2A2       ( Eex =  30700.000 Wt =    1.000) = 1.000 * 2A2, 2
11   2E        ( Eex =  31650.000 Wt =    1.000) = 1.000 * 2E , 5
12   2E        ( Eex =  36300.000 Wt =    1.000) = 1.000 * 2E , 7
13   2A2       ( Eex =  37400.000 Wt =    1.000) = 1.000 * 2A2, 3


OPTIMIZATION USING HOGGARDS POWELL-PROGRAM
SIGMA0 = -1.00000       SCALE =  1.00000       VSTART =  .000000       MAXIT =    30

STARTING PARAMETERS:

         esg         epi           B           C

  5917.00000   412.00000  1059.00000  3974.00000

ITERATION    0              1 FUNCTION VALUES          F=   242688643.36
```

```
CURRENT PARAMETER SET:
 5917.000   412.000  1059.000  3974.000

ITERATION    1             16 FUNCTION VALUES          F=    93830018.25
CURRENT PARAMETER SET:
 4908.206   379.559   794.270  3721.324

ITERATION    2             31 FUNCTION VALUES          F=    10649531.18
CURRENT PARAMETER SET:
 6312.008   341.332   552.408  3374.794

ITERATION    3             44 FUNCTION VALUES          F=     9342141.97
CURRENT PARAMETER SET:
 6230.496   286.567   584.818  3347.422

ITERATION    4             56 FUNCTION VALUES          F=     8344394.95
CURRENT PARAMETER SET:
 6061.806   213.528   664.659  3152.613

ITERATION    5             70 FUNCTION VALUES          F=     8300536.96
CURRENT PARAMETER SET:
 6046.530   200.918   671.345  3155.005

ITERATION    6             84 FUNCTION VALUES          F=     8286591.06
CURRENT PARAMETER SET:
 6084.098   232.521   675.012  3158.365

ITERATION    7            102 FUNCTION VALUES          F=     7975487.73
CURRENT PARAMETER SET:
 7103.704   988.219   663.640  3152.325

ITERATION    8            114 FUNCTION VALUES          F=     7958489.62
CURRENT PARAMETER SET:
 7147.382  1036.876   666.488  3156.420

ITERATION    9            125 FUNCTION VALUES          F=     7958488.61
CURRENT PARAMETER SET:
 7148.759  1037.904   666.474  3156.498

ITERATION   10            135 FUNCTION VALUES          F=     7958488.60
CURRENT PARAMETER SET:
 7148.764  1037.904   666.470  3156.512

OPTIMUM VALUE OF FUNCTION:     7958488.60

TOTAL NUMBER OF FUNCTION EVALUATIONS:      136

PARAMETERS:

         esg         epi           B           C

  7148.76418  1037.90444   666.46959  3156.51210

RESIDUAL:
   .79585E+07


NEXT CALCULATION WITH OPTIMIZED PARAMETERS

esg        =   7148.764176
epi        =   1037.904443
B          =    666.469588
C          =   3156.512098
*
zeta       =       .000000

AOM matrix

        xy        xz        yz      x2y2        z2

 12280.517  8418.145      .000      .000      .000
  8418.145 13259.965      .000      .000      .000
      .000      .000 13259.965  8418.145      .000
      .000      .000  8418.145 12280.517      .000
      .000      .000      .000      .000  4266.475

          energy (exp.)   energy(calc.)  difference    weight
```

2E	14686.000	14161.795	-524.205	1.000
4A1	15700.000	16646.159	946.159	1.000
4E	16800.000	16685.756	-114.244	1.000
2E	21037.000	21121.543	84.543	1.000
2A1	21037.000	22622.401	1585.401	1.000
4E	22800.000	22403.286	-396.714	1.000
4A2	24000.000	25043.024	1043.024	1.000
2A1	30700.000	30809.670	109.670	1.000
2E	31650.000	30775.083	-874.917	1.000
2A2	30700.000	31590.826	890.826	1.000
2E	31650.000	31412.617	-237.383	1.000
2E	36300.000	35682.891	-617.109	1.000
2A2	37400.000	36399.373	-1000.627	1.000

Sigma, weighted = 782.427

PARTIAL DERIVATIVE MATRIX

	esg	epi	B	C
2E	.373D-01	.609D-01	.626D+01	.306D+01
4A1	.294D+01	-.404D+01	-.209D+00	-.576D-09
4E	.287D+01	-.354D+01	-.209D+00	-.519D-09
2E	.528D+00	-.945D+00	.810D+01	.410D+01
2A1	.572D+00	-.586D+00	.945D+01	.407D+01
4E	.318D+01	-.417D+01	.601D+01	-.519D-09
4A2	.309D+01	-.401D+01	.107D+02	.231D-09
2A1	.303D+01	-.412D+01	.588D+01	.300D+01
2E	.288D+01	-.347D+01	.652D+01	.300D+01
2A2	.286D+01	-.348D+01	.794D+01	.300D+01
2E	.295D+01	-.405D+01	.760D+01	.301D+01
2E	.306D+01	-.397D+01	.127D+02	.300D+01
2A2	.311D+01	-.410D+01	.134D+02	.300D+01

WEIGHT VECTOR

2E	4A1	4E	2E	2A1	4E	4A2	2A1	2E	2A2
.00100	.00100	.00100	.00100	.00100	.00100	.00100	.00100	.00100	.00100

2E	2E	2A2
.00100	.00100	.00100

(ATRANSPOSE.W.A) MATRIX

	esg	epi	B	C
esg	.905D-01	-.118D+00	.223D+00	.583D-01
epi	-.118D+00	.154D+00	-.290D+00	-.757D-01
B	.223D+00	-.290D+00	.883D+00	.253D+00
C	.583D-01	-.757D-01	.253D+00	.968D-01

VALUE OF DET(ATRANSPOSE.W.A): .2812D-06

(ATRANSPOSE.W.A) INVERSE MATRIX

	esg	epi	B	C
esg	.432D+04	.328D+04	-.152D+02	.498D+01
epi	.328D+04	.251D+04	-.424D+01	-.153D+01
B	-.152D+02	-.424D+01	.759D+01	-.140D+02
C	.498D+01	-.153D+01	-.140D+02	.427D+02

STANDARD DEVIATIONS OF PARAMETERS:

esg	epi	B	C
65.706	50.115	2.755	6.534

CORRELATION COEFFICIENT MATRIX:

	esg	epi	B	C
esg	1.0000	.9965	-.0840	.0116
epi	.9965	1.0000	-.0307	-.0047
B	-.0840	-.0307	1.0000	-.7769
C	.0116	-.0047	-.7769	1.0000

```
EIGENVECTORS OF CORRELATION COEFFICIENT MATRIX

                esg       epi         B         C
esg            .7065    -.7024     .0733     .0455
epi            .0381    -.0808    -.7038    -.7048
B              .1627     .1897     .6786    -.6907
C             -.6877    -.6812     .1969    -.1556

GRADIENT OF SQUARED ERROR:

                esg       epi         B         C
          -.560D-02  .734D-02  .880D-02 -.301D-01

EIGENVALUES OF (APPROXIMATE) HESSIAN MATRIX:

                esg       epi         B         C
           .147D-03  .206D-01  .830D-01  .112D+01

THE HESSIAN IS POSITIVE DEFINITE


EIGENVECTORS OF GAUSS-NEWTON APPROXIMATE HESSIAN

                esg       epi         B         C
esg         .795D+00  .606D+00 -.215D-02  .452D-03
epi         .950D-01 -.127D+00 -.339D+00  .927D+00
B          -.548D+00  .720D+00  .327D+00  .274D+00
C           .241D+00 -.314D+00  .882D+00  .255D+00
Stop - Program terminated.
```

The results are listed in Table S1.

Ligand field parameters computed using direct fit to experimental and computed d-d transitions are listed in Tables S1-S4 along with energies recomputed using the best fit values of the ligand field parameters.

Table S1 Experimental (from Ref.41) vs computed energies of d-d transition of emerald along with best fit ligand field parameters, relative statistical parameter errors and standard deviations (σ) between experimental and computed [a] energies of d-d transitions.[b]

Term $D_3[O(R_3)]$	Exp.	Computed	Computed-Exp
$^4A_2[^4A_2(^4F)]$	0	0	0
$^2E[^2E(^2G)]$	14686	14162	-534
$^4A_1[^4T_2(^4F)]$	15700	16646	946
$^4E[^4T_2(^4F)]$	16800	16686	-114
$^2E[^2T_2(^2G)]$	21037	21122	84
$^2A_1[^2T_2(^2G)]$	21037	22622	1585
$^4E[^4T_1(^4F)]$	22800	22403	-397
$^4A_2[^4T_1(^4F)]$	24000	25043	1043

$^2A_1[^2T_2(^2H)]$	30700	30810	110
$^2E[^2T_2(^2H)]$	31650	30775	-875
$^2A_2[^2T_1(^2P)]$	30700	31591	891
$^2E[^2T_1(^2P)]$	31650	31413	-237
$^2E[^2T_1(^2H)]$	36300	35683	-617
$^2A_2[^2T_1(^2H)]$	37400	36399	-1001
e_σ		7149±66	
e_π		1038±50	
B		666±3	
C		3156±6	
σ		782	

[a] Recomputed using listed best fit ligand field parameter values; [b] all entries are energies are in cm^{-1}.

Table S2 Ab-initio computed state-specific NEVPT2 (active space CAS(3,5)) energies of d-d transition of emerald along with best fit ligand field parameters, relative statistical parameter errors and standard deviations (σ) between NEVPT2 and recomputed using best fit ligand field paramaters energies of d-d transitions.[a]

Term $D_3[O(R_3)]$	NEVPT2 State spec.CAS(3,5)	Computed	Computed-NEVPT2
$^4A_2[^4A_2(^4F)]$	0	0	0
$^2E[^2E(^2G)]$	14257	14500	243
$^2E[^2T_1(^2G)]$	15377	15713	336
$^4A_1[^4T_2(^4F)]$	15552	15667	115
$^4E[^4T_2(^4F)]$	15886	15886	-19
$^2E[^2T_2(^2G)]$	21451	21256	-195
$^2A_1[^2T_2(^2G)]$	22788	23024	236
$^4E[^4T_1(^4F)]$	23079	21969	-1110
$^2A_1[^2A_1(^2G)]$	28367	28096	-271
$^2A_1[^2T_2(^2H)]$	29817	30121	303
$^2E[^2T_2(^2H)]$	30586	30353	-233
$^2E[^2T_1(^2H)]$	36149	35711	-438
$^4A_2[^4T_1(^4P)]$	32933	33366	433

$^4E[^4T_1(^4P)]$	36811	37333	522
e_σ		7297±44	
e_π		1382±32	
B		767±4	
C		3058±7	
σ		428	

[a] all entries are energies are in cm^{-1}.

Table S3 Ab-initio computed state-average CASSCF (active space CAS(3,5)) energies of d-d transition of emerald along with best fit ligand field parameters, relative statistical parameter errors and standard deviations (σ) between CASSCF and recomputed using best fit ligand field paramaters energies of d-d transitions.[a]

Term $D_3[O(R_3)]$	CASSCF State aver.CAS(3,5)	Computed	Computed-CASSCF
$^4A_2[^4A_2(^4F)]$	0	0	0
$^2E[^2E(^2G)]$	19102	18895	-207
$^2A_2[^2T_1(^2G)]$	19694	19596	-98
$^2E[^2T_1(^2G)]$	20452	20451	-1
$^4A_1[^4T_2(^4F)]$	14532	14808	276
$^4E[^4T_2(^4F)]$	15235	14660	-575
$^2E[^2T_2(^2G)]$	26972	26926	-46
$^2A_1[^2T_2(^2G)]$	28520	28509	-10
$^4E[^4T_1(^4F)]$	22894	22011	-883
$^4A_2[^4T_1(^4F)]$	24718	25833	1115
$^2A_1[^2A_1(^2G)]$	30971	30974	3
$^2A_1[^2T_2(^2H)]$	33123	33554	430
$^2E[^2T_2(^2H)]$	34120	33746	-374
$^2A_2[^2T_1(^2P)]$	34415	35148	733
$^2E[^2T_1(^2P)]$	35432	35040	-392
$^2E[^2E(^2H)]$	37363	37068	-294
$^2E[^2T_1(^2H)]$	40750	40703	-47
$^2A_2[^2T_1(^2H)]$	41208	41580	272
$^4A_2[^4T_1(^4P)]$	34526	34547	21
$^4E[^4T_1(^4P)]$	38603	38212	-391

e_σ		5774±32	
e_π		484±24	
B		1064±3	
C		3950±5	
σ		452	

[a] all entries are energies are in cm^{-1}.

Table S4 Ab-initio computed state-average NEVPT2 (active space CAS(3,5)) energies of d-d transition of emerald along with best fit ligand field parameters, relative statistical parameter errors and standard deviations (σ) between CASSCF and recomputed using best fit ligand field paramaters energies of d-d transitions.[a]

Term $D_3[O(R_3)]$	NEVPT2 State-aver.CAS(3,5)	Computed	Computed-NEVPT2
$^4A_2[^4A_2(^4F)]$	0	0	0
$^2E[^2E(^2G)]$	16674	16659	-15
$^2A_2[^2T_1(^2G)]$	17268	17026	-242
$^2E[^2T_1(^2G)]$	17909	17953	44
$^4A_1[^4T_2(^4F)]$	16935	17067	132
$^4E[^4T_2(^4F)]$	17662	17114	-548
$^2E[^2T_2(^2G)]$	24467	24442	-25
$^2A_1[^2T_2(^2G)]$	25925	26152	227
$^4E[^4T_1(^4F)]$	25093	23772	-1321
$^4A_2[^4T_1(^4F)]$	26599	27111	512
$^2A_1[^2A_1(^2G)]$	31228	31420	192
$^2A_1[^2T_2(^2H)]$	33192	33675	483
$^2E[^2T_2(^2H)]$	33876	33744	-132
$^2A_2[^2T_1(^2P)]$	34255	34778	523
$^2E[^2T_1(^2P)]$	35177	34544	-633
$^2E[^2E(^2H)]$	36515	36410	-105
$^2E[^2T_1(^2H)]$	40029	39595	-434
$^2A_2[^2T_1(^2H)]$	40350	40416	66
$^4A_2[^4T_1(^4P)]$	35973	36416	443
$^4E[^4T_1(^4P)]$	39856	40130	274
e_σ		7363±39	

e_π		1082±29	
B		822±3	
C		3654±6	
σ		452	

[a] all entries are energies are in cm^{-1}.

§9. Periodic DFT geometry optimizations

The threshold on the geometry optimization was set to 10^{-7} Ha, a pruned (75,974) p grid was adopted (XLGRID) and the percentage of Hartree-Fock/Kohn-Sham mixing matrices was set to 30 (IPMIX = 30). The values used in the present study for the five tolerances that evaluate Coulomb and exchange integrals were set to 10^{-7} (ITOL1 to ITOL4) and 10^{-14} (ITOL5), respectively. The shrinking factor (Pack-Monkhorst and Gilat net) of the reciprocal space net was set to 8, corresponding to 59 k-points in the irreducible Brillouin zone (IBZ) and for accelerating convergence the Broyden scheme was chosen.

Input files:

d12 input for DFT optimization of undoped crystal(beryl):

```
Beryl-Optimizat_Hiss
CRYSTAL
0 0 0
192
9.208 9.188
5
4    0.50000 0.00000 0.25000
13   0.33333 0.66667 0.25000
14   0.38760 0.11590 0.00000
8    0.31030 0.23690 0.00000
8    0.49850 0.14560 0.14530
OPTGEOM
ENDOPT
END
13  10
0 0 7 2.0 1.0
  37792.5507720      0.00057047888709
  5668.06821650      0.00440930165380
  1289.85828410      0.02263096741100
  364.865960280      0.08802564429500
  118.576315150      0.25223701612000
```

```
  42.0248676050      0.45960547169000
  15.4995016290      0.33277886014000
0 0 3 2.0 1.0
  75.2080265980      0.01925056019000
  23.0314089720      0.08790674395200
  3.63487976490     -0.34246704535000
0 0 2 0.0 1.0
  1.95000627000      1.01062661000000
  0.96103395000      0.38071016000000
0 0 1 0.0 1.0
  0.39881874000      1.00000000000000
0 0 1 0.0 1.0
  0.14940937000      1.00000000000000
0 2 5 6.0 1.0
  452.523031920      0.00231108124660
  107.081950490      0.01856864182300
  34.1310212550      0.08721623703500
  12.5870374280      0.26902101523000
  4.98119197040      0.52128324272000
0 2 1 0.0 1.0
  1.93791887000      1.00000000000000
0 2 1 0.0 1.0
  0.72047185000      1.00000000000000
0 2 1 0.0 1.0
  0.18328583000      1.00000000000000
0 3 1 0.0 1.0
  0.57798580000      1.00000000000000
4 5
0 0 6 2.0 1.0
 4700.2365626        0.00023584389316
 704.82845622        0.00182437910190
 160.43110478        0.00939661482240
 45.425347336        0.03690892415900
 14.798334125        0.10897561281000
 5.3512452537        0.21694284551000
0 0 2 0.0 1.0
 2.1542044819        0.44695408857000
 0.9336374440        0.20866985771000
0 0 1 0.0 1.0
 0.3017450800        1.00000000000000
0 0 1 0.0 1.0
 0.1411145200        1.00000000000000
0 2 1 0.0 1.0
 0.6526215700        1.00000000000000
14 10
0 0 7 2.0 1.0
  44773.358078      0.00055914765868
  6717.1992104      0.00432060401890
  1528.8960325      0.02218709646000
  432.54746585      0.08648924911600
  140.61505226      0.24939889716000
  49.857636724      0.46017197366000
  18.434974885      0.34250236575000
0 0 3 2.0 1.0
  86.533886111      0.02130006300700
  26.624606846      0.09467613931800
```

```
  4.4953057159     -0.32616264859000
0 0 2 0.0 1.0
  2.1035045710      1.39808038500000
  1.3106094922      0.63865786699000
0 0 1 0.0 1.0
  0.5422443800      1.00000000000000
0 0 1 0.0 1.0
  0.1460762500      1.00000000000000
0 2 5 6.0 1.0
  394.47503628      0.00262856939590
  93.137683104      0.02055625774900
  29.519608742      0.09207026280100
  10.781663791      0.25565889739000
  4.1626574778      0.42111707185000
0 2 1 0.0 1.0
  1.4499318500      1.00000000000000
0 2 1 0.0 1.0
  0.4949286700      1.00000000000000
0 2 1 0.0 1.0
  0.1346786100      1.00000000000000
0 3 1 0.0 1.0
  0.3074090300      1.00000000000000
8 8
0 0 6 2.0 1.0
  27032.382631      0.00021726302465
  4052.3871392      0.00168386621990
  922.32722710      0.00873956162650
  261.24070989      0.03523996880800
  85.354641351      0.11153519115000
  31.035035245      0.25588953961000
0 0 2 2.0 1.0
  12.260860728      0.39768730901000
  4.9987076005      0.24627849430000
0 0 1 0.0 1.0
  1.0987136000      1.00000000000000
0 0 1 0.0 1.0
  0.3565870100      1.00000000000000
0 2 4 6.0 1.0
  63.274954801      0.0060685103418
  14.627049379      0.0419125758240
  4.4501223456      0.1615384108800
  1.5275799647      0.3570695131100
0 2 1 0.0 1.0
  0.5489735000      1.0000000000000
0 2 1 0.0 1.0
  0.1858671100      1.0000000000000
0 3 1 0.0 1.0
  0.4534621300      1.0000000000000
99   0
END
DFT
HISS
XLGRID
END
BIPOSIZE
35000000
```

```
EXCHSIZE
35000000
SHRINK
8 8
MAXCYCLE
300
TOLINTEG
7 7 7 7 14
FMIXING
30
BROYDEN
0.0001 50 2
PPAN
END
```

Input for optimization of doped crystal with Cr^{3+} (emerald) :

```
Emerald-Optimizat_Hiss
CRYSTAL
0 0 0
192
9.2378242500  9.2611592600
5
4   0.50000 0.00000 0.25000
13  0.33333 0.66667 0.25000
14  0.27288 0.88284 0.00000
8   0.07342 0.76180 0.00000
8   0.50101 0.14630 0.64610
SUPERCEL
1. 0. 0.  0. 1. 0.  0. 0. 2.
ATOMSUBS
1
13 24
ATOMSYMM
NEIGHBOR
10
OPTGEOM
ENDOPT
END
13  10
0 0 7 2.0 1.0
  37792.5507720      0.00057047888709
  5668.06821650      0.00440930165380
  1289.85828410      0.02263096741100
  364.865960280      0.08802564429500
  118.576315150      0.25223701612000
  42.0248676050      0.45960547169000
  15.4995016290      0.33277886014000
0 0 3 2.0 1.0
  75.2080265980      0.01925056019000
  23.0314089720      0.08790674395200
  3.63487976490     -0.34246704535000
0 0 2 0.0 1.0
  1.95000627000      1.01062661000000
  0.96103395000      0.38071016000000
0 0 1 0.0 1.0
```

```
  0.39881874000      1.00000000000000
0 0 1 0.0 1.0
  0.14940937000      1.00000000000000
0 2 5 6.0 1.0
  452.523031920      0.00231108124660
  107.081950490      0.01856864182300
  34.1310212550      0.08721623703500
  12.5870374280      0.26902101523000
  4.98119197040      0.52128324272000
0 2 1 0.0 1.0
  1.93791887000      1.00000000000000
0 2 1 0.0 1.0
  0.72047185000      1.00000000000000
0 2 1 0.0 1.0
  0.18328583000      1.00000000000000
0 3 1 0.0 1.0
  0.57798580000      1.00000000000000
3  5
0 0 6 2.0 1.0
  6269.2628010      0.00020540968826
  940.31612431      0.00159165540890
  214.22107528      0.00828698297070
  60.759840184      0.03385637424900
  19.915152032      0.11103225876000
  7.3171509797      0.27449383329000
0 0 2 0.0 1.0
  2.9724674216      0.23792456411000
  1.2639852314      0.30765411924000
0 0 1 0.0 1.0
  0.5025516200      1.00000000000000
0 0 1 0.0 1.0
  0.1200746200      1.00000000000000
0 2 1 0.0 1.0
  0.1320350000      1.00000000000000
14 10
0 0 7 2.0 1.0
  44773.358078      0.00055914765868
  6717.1992104      0.00432060401890
  1528.8960325      0.02218709646000
  432.54746585      0.08648924911600
  140.61505226      0.24939889716000
  49.857636724      0.46017197366000
  18.434974885      0.34250236575000
0 0 3 2.0 1.0
  86.533886111      0.02130006300700
  26.624606846      0.09467613931800
  4.4953057159     -0.32616264859000
0 0 2 0.0 1.0
  2.1035045710      1.39808038500000
  1.3106094922      0.63865786699000
0 0 1 0.0 1.0
  0.5422443800      1.00000000000000
0 0 1 0.0 1.0
  0.1460762500      1.00000000000000
0 2 5 6.0 1.0
  394.47503628      0.00262856939590
```

```
  93.137683104      0.02055625774900
  29.519608742      0.09207026280100
  10.781663791      0.25565889739000
  4.1626574778      0.42111707185000
0 2 1 0.0 1.0
  1.4499318500      1.00000000000000
0 2 1 0.0 1.0
  0.4949286700      1.00000000000000
0 2 1 0.0 1.0
  0.1346786100      1.00000000000000
0 3 1 0.0 1.0
  0.3074090300      1.00000000000000
8 8
0 0 6 2.0 1.0
  27032.382631      0.00021726302465
  4052.3871392      0.00168386621990
  922.32722710      0.00873956162650
  261.24070989      0.03523996880800
  85.354641351      0.11153519115000
  31.035035245      0.25588953961000
0 0 2 2.0 1.0
  12.260860728      0.39768730901000
  4.9987076005      0.24627849430000
0 0 1 0.0 1.0
  1.0987136000      1.00000000000000
0 0 1 0.0 1.0
  0.3565870100      1.00000000000000
0 2 4 6.0 1.0
  63.274954801      0.0060685103418
  14.627049379      0.0419125758240
  4.4501223456      0.1615384108800
  1.5275799647      0.3570695131100
0 2 1 0.0 1.0
  0.5489735000      1.0000000000000
0 2 1 0.0 1.0
  0.1858671100      1.0000000000000
0 3 1 0.0 1.0
  0.4534621300      1.0000000000000
24 14
0 0 8 2.0 1.0
  254477.80704      0.00023386945693
  38131.797054      0.00181426018000
  8675.2930607      0.00943639257210
  2455.0099848      0.03834363936700
  799.16217787      0.12459194837000
  286.90021489      0.29489696029000
  111.25413232      0.41846149607000
  43.864152636      0.21633763420000
0 0 4 2.0 1.0
  279.32669173     -0.02345090811100
  86.274732376     -0.11080370027000
  13.555756113      0.53028965842000
  5.6978112751      0.51603516947000
0 0 2 2.0 1.0
  8.5636582615     -0.38109545675000
  1.3988296768      1.19915914360000
```

```
0 0 1 0.0 1.0
  1.5142137900      1.00000000000000
0 0 1 0.0 1.0
  0.5047379300      1.00000000000000
0 0 1 0.0 1.0
  0.1305787700      1.00000000000000
0 2 6 6.0 1.0
  1306.4398864      0.00242773261850
  309.25311441      0.01954404101700
  98.996273963      0.09065179455300
  36.756916451      0.25699279154000
  14.566657077      0.40935504891000
  5.8739937432      0.23729388849000
0 2 3 6.0 1.0
  22.890999695     -0.02816602661300
  3.0855001822      0.56034120148000
  1.2132329118      0.98119019650000
0 2 1 0.0 1.0
  0.4593168100      1.00000000000000
0 2 1 0.0 1.0
  0.2296584050      1.0000000000000
0 3 4 3.0 1.0
  43.720074476      0.01362296402600
  12.391242652      0.07893518013300
  4.2639442006      0.23833840000000
  1.5525221790      0.39526851122000
0 3 1 0.0 1.0
  0.8288617700      1.00000000000000
0 3 1 0.0 1.0
  0.3172623600      1.00000000000000
0 4 1 0.0 1.0
  1.1470000000      1.00000000000000
99   0
END
DFT
SPIN
HISS
XLGRID
END
BIPOSIZE
35000000
EXCHSIZE
35000000
SHRINK
8 8
ATOMSPIN
1
13 1
SPINLOCK
3 100
MAXCYCLE
300
TOLINTEG
7 7 7 7 14
FMIXING
30
```

```
BROYDEN
0.0001 50 2
PPAN
END
```

References

(1) Fairbank Jr., W. M.; Klauminzer, G. K.; Schawlow, A. L. Excited-state absorption in ruby, emerald, and MgO: Cr^{3+}, *Phys. Rev. B* **1975**, 11, 60-76.

(2) Wood, D. L. Absorption, Fluorescence, and Zeeman Effect in Emerald. *Journal of Chemical Physics* **1965**, 42, 3404-3410.

(3) Chen, Z.; Shen, H.; Zhang, G.; Huang, C. Spectrum properties of hydrothermal emerald laser crystals. *Acta Photon. Sin. (in Chinese)* **2004**, 33, 382-384.

(4) Lang, L.; Atanasov, M.; Neese, F. Improvement of Ab Initio Ligand Field Theory by Means of Multistate Perturbation Theory. *J. Phys. Chem. A* **2020**, 124, 1025-1037.

(5) Gellé, A.; Lepetit, M-B. Fast calculation of the electrostatic potential in ionic crystals by direct summation method. *J. Chem. Phys.,* **2008**, 128, 244716.

(6) H.Adamsky, T.Schönherr and M.Atanasov, AOMX: Angular Overlap Model Computation, in Comprehensive Coordination Chemistry II, A.B.P.Lever (Editor), Volume 2, pp 661-664,2003, Elsevier ; the program is freely distributable from one of the authors (MA) upon request.