AOMX

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July 1, 1996

AOMX is a FORTRAN program that calculates d^n electron terms in the framework of the *Angular Overlap Model* including electron interaction and spin-orbit coupling. AOMX has been developed by Heribert Adamsky at the local institute on the basis of the AOM1 program which P.E. Hoggard kindly made available to us.[1] Special thanks also belong to Michael Atanasov[2] and Klaus Eifert.[3]

Copying. AOMX may not be redistributed to third parties. Please direct interested persons to the E–mail address of the author or to the AOMX homepage in order that they can obtain a copy of the most recent version. The program may be used only for peaceful purposes; any kind of economical utilization is allowed only if an explicit written agreement with the author about this has been made.

This documentation is valid for versions from February 1995 on. Older versions eventually do not have the full functionality described here.

Bug reports and other corresponence referring to the program are always willingly welcome in Düsseldorf, best as E–mail to heribert@theochem.uni-duesseldorf.de. The AOMX homepage, *http://www.theochem.uni-duesseldorf.de/qc-progs/aomx*, offers up-to-date information on the program.

Disclaimer. This software is distributed without any warranty.

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[1]P.E. Hoggard, formerly at Department of Chemistry, NDSU, Fargo, now working at SCU, Santa Clara.

[2]M. Atanasov, Institute for Inorganic Chemistry, Bulgarian Academy of Science, Sofia 1040. From him stem contributions to the topics phase coupling, magnetic field, delocalization coefficients and orbital reduction factors.

[3]Klaus Eifert, technical assistant at the institute. He took care of the versions AOM1 to AOM3 and undertook the programming of several routines.

Contents

1   About this manual

This manual primarily addresses the user. It ought to help him make himself aquainted with the usage of AOMX and also to serve him later on as a reference-book when putting input files together. The presentation of theory has therefore been restricted to the most important foundations and has been moved into an appendix in order not to hinder the function of this document as a reference-book.

The second section describes the functionality of the AOMX program. The components of the applied Hamiltonian operator are explained concisely without going into details of the underlying theory. Further important features like the treatment of symmetry, parameter optimization and programmable input are also introduced.

Subject of the third section is the structure of an input file: it is explained in detail how the separate program functions can be invoked, examples make the formal descriptions plain. This section is the kernel of the present manual.

Appendix A is designed to be a supplement of the third section. Beneath illustrative input file examples, it also contains a list of questions together with the corresponding answers that can occur during usage of AOMX or already during its installation.

Appendix B presents to the user the theoretical foundations of the *Angular Overlap Model* as well as the concept of holohedry on which the symmetry part of AOMX is based.

2   Program features of AOMX

Model operator

A Hamilton operator of the form

$$\mathbf{H} = \mathbf{V}_{LF} + \mathbf{V}_{ee} + \mathbf{V}_{SO} + \mathbf{V}_{mag} + \mathbf{V}_{Trees}$$

is applied. In the following, the individual terms and their parametrization are explained in short; details can be taken from the given literature.[4]

- $\mathbf{V}_{LF}$ The ligand field is put up in the framework of the *Angular Overlap Model* which is further described in section B.1[5]. For each ligand, the user supplies the AOM parameters e_σ, e_{π_s} and e_{π_c} (eventually e_{δ_s} and

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[4]For a comprehensive representation, see [5] or [1].

[5]In addition, the program can handle a crystal field ansatz with STOs. A description can be ordered from the author

e_{δ_c}) as well as the spatial orientation in form of Eulerian angles Θ, Φ and (optional) Ψ or as a cartesian coordinate triple (x, y, z).[6] The Ψ angle is relevant only in case of anisotropic π-interaction ($e_{\pi_s} \neq e_{\pi_c}$), if required, it can be calculated by the program through a plane to be supplied by the user. Particularly in square planar complexes, the energetic effect of a mixing in of the $(n+1)s$ orbital becomes important and can be covered through a parameter σ_{sd} (see page 27). In chelate ligands with conjugated π-electron system, the possibility exists to allow for the phase coupling between the orbitals of the coordinating atoms of the chelate; the AOM model then works with two e_{π_s} parameters, e_{π_s} und e'_{π_s} (p.26).

- **V_{ee}** The operator of *electron repulsion* is modeled through *Racah parameters* A, B and C. The lowering of d electron interaction which is a consequence of electron delocalization in the complex that generally occurs to a different extent in the individual d orbitals, can be allowed for through orbital reduction factors $\mu_i \leq 1$. The general electron repulsion matrix element then takes the form $\mu_a\mu_b\mu_c\mu_d\langle\phi_a\phi_b|r_{12}^{-1}|\phi_c\phi_d\rangle$ (see [4, 9]).

- **V_{SO}** The spin-orbit coupling operator has the form $\zeta \sum_i \vec{l_i} \cdot \vec{s_i}$ with the parameter ζ. Spatial anisotropy of orbital momentum is introduced by the ansatz $k_x l_x$, $k_y l_y$ and $k_z l_z$ with parameters $k_x, k_y, k_z < 1$.[2]

- **V_{mag}** An external magnetic field is described by the operator $\mu_B \cdot \vec{H}(\Theta_{mag}, \Phi_{mag}) \cdot \sum_i(\vec{l_i} + 2\vec{s_i})$. Here, too, anisotropy can be accounted for through parameters $k_x, k_y, k_z < 1$.

- **V_{Trees}** The *Trees correction* is a two-electron correction of the form $\alpha \cdot \mathbf{L}^2$ (see [5] and [1]) with the Trees parameter α.

Symmetry

AOMX works with a basis of Slater determinants. The advantage is a complete independence of the molecular symmetry of the investigated molecule. On he other hand, the lacking of symmetry blocking in the Hamiltonian matrix means that computational effort will be relatively high and that the symmetry of the calculated eigenstates is not known for the present. The numerical effort in calculations without spin-orbit coupling will be reduced, however, by taking advantage of the M_S blocking of the Hamiltonian matrix which is still present with Slater determinants. In addition, information about spin multiplicity will be gained. AOMX can make available the complete information about term symbols, which is known to be implicitly containded in the eigenvectors, for the effective rotational symmetries $\mathcal{O}$ (cubic), $\mathcal{D}_4$ (tetragonal),$\mathcal{D}_3$ (trigonal), $\mathcal{D}_2$ (orthorhombic) and $\mathcal{C}_2$ (monoclinic) as well as the correspond-

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[6]In doing so, only the direction is the point, not the distance, because the latter is implicitly contained in the AOM parameters e_λ.

ing double groups.[7] [8] The terminus *effective rotational group* here means rotational group of the holoedrized point group of the complex[9] – all more or less frequently occuring symmetries can be reduced to one of the point groups mentioned above. For this purpose, AOMX determines characters with respect to representative symmetry operations from the eigenvectors: in cubic symmetry these are the rotations C_4^z, C_2^z and C_2^x, in case of tetragonal symmetry C_4^z and C_2^z, in the trigonal case C_3^z (simple group) resp. C_2^x (double group), in orthorhombic symmetry C_2^z and C_2^x, in the monoclinic case it is C_2^z.

! → This must be kept in mind when coordinates are supplied since determination of characters will be successful only if the symmetry elements of the input geometry coincide with those mentioned above.

Parameter optimization

One of the most important tasks in spectroscopic research is the fitting of model parameters to experimental data. In AOMX, this is achieved with the *Powell parallel subspace* algorithm. A subsequent error propagation calculation (optional) facilitates the evaluation of optimization results. The appropriate routines POWELL and STATS have been taken from P. E. Hoggard's program [5] .

Flexible input

AOMX has a free-format input syntax at its disposal that allows for flexible control of the calculation. The model parameters and coordinates need not necessarily be supplied directly, but may equally well be associated with freely namable and arithmetically connectable[10] variables for which even variation loops may be defined. This makes it possible to apply many different parametrization schemes (for instance D_q, D_s, D_t instead of e_σ, e_π), and it facilitates the exploitation of symmetry for the construction of coordinates of for optimiziation and variation of parameters.

3 How to build an input file

Introductory remarks. The AOMX input scanner is case sensitive; keywords must be written in capital letters. In this documentation, user input will be denoted by `typescript`. Lower case letters indicate that variable names may be supplied, upper case letters indicate that only constants are allowed. If an input item is optional, this is indicited in the documentation by square brackets.

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[7] At this occasion, also orbital occupations are printed for each state.

[8] The triclinic case is trivial (no symmetry) and will therefore not be treated specially. The one-to-one correspondence of effective rotational symmetries and crystal systems is helpful but nevertheless accidential.

[9] The holoedrized point group is obtained by superposition of the ligand-field potential and its mirror image obtained by inversion (see page 28ff).

[10] Basic arithmetics including exponentiation may be applied.

! → All input is format-free. When AOMX scans input data it distiguishes words, lines and blocks (several lines). Words have to be separated by spaces, blocks must be separated by blank lines.[11]

AOMX treats all energies in units of cm^{-1}.

3.1 Header lines

At the beginning of input file, AOMX expects a block of comment lines, say:

```
OsCl5Br--
This is a first try of a parameter fit...
```

Then, a single line containing some global information must follow:

```
<NEL> [<GROUP> [<NEIG> [<VLOW>]]]
```

- NEL is the number of d-electrons, $1 \leq$ NEL ≤ 9.

- GROUP is an effective symmetry group – more precisely: the rotational group of the holoedrized point group of the complex, see section B.2 on page 28ff and table 2. If you give one of O, D4, D3, D2 or C2 at this place, the program will perform a symmetry analysis and deliver term symbols in addition to term energies. Because this case necessitates the calculation of eigenvectors, computation time will increase remarkably (by a factor of about 5). If you do not want symmetry analysis in order to speed up the calculation, you may enter C1, regardless of the real symmetry (this is also the default).

- Through NEIG, you can fix the number of states to be printed out (default: all states).

- VLOW is relevant only if eigenvectors shall be printed[12] and defines a lower boundary for the absolute value of components that will be printed out (default: 0.1).

3.2 Directives

After the header lines, AOMX expects directives, each consisting of a directive name (which is always composed of three capital letters) followed by data, further keywords or the names of user defined variables. Directives may have line structure or block structure; it is important that those having block structure must be terminated by a blank line. The following directives are known to AOMX:

- VAR: Definition of variables. The additional options OPT and STA induce optimization of some of the variables by fitting them to experimental data resp. an error propagation calculation (statistical analysis of the energy hypersurface in parameter space).

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[11] The maximal word length is 20 characters in general, 13 characters in case of numbers; the maximum line length is 72 characters.

[12] In this case, CVEC has to be set, too, (see the CTL directive).

- XYZ or TPP (or RTP): Input of the angular geometry of the complex in form of cartesian coordinates or Euler angles (or polar coordinates).

- AOM: Input of AOM parameters

- CON: Definition of connected ligands

- VEE: Input of electron repulsion parameters (Racah parameters) and orbital reduction factors

- HSO: Input of the spin-orbit coupling parameter

- HMG: Input of magnetic field parameters

- EXP: Input of experimental data

- CTL: Input of special options for printout or parameter optimization

- RUN: Start a run with actual input data

Normally, the sequence of directives is not important. But there are exceptions that are coherent with the fact that AOMX scans the input file only once and, while doing so, immediately evaluates the directives it encounters:

1. No variable may be used prior to its definition.

2. The CON directive which denotes ligand connectivity may occur only if coordinates and AOM parameters are already defined.

3. Some of the options of the CTL directive have different effects in calculations with and without optimization. Therefore, CTL should not occur before VAR.

3.2.1 VAR Definition and variation of variables (block)

The VAR directive allows the user to define variables, initialize them with numerical values and to induce many calculations with different variable values, in order, for example, to scan the parameter space or to vary the complex geometry. Additional features are offered through the options OPT and STA and will be discussed below.

- VAR **without option.** AOMX distinguishes free and bound variables, the latter being defined through arithmetic expressions which may contain other variables or constants. Thus, bound variables are variables dependend on others or simply constants. First, the definition of free variables in the form

  <vnam> [=] <VARA> [<VARE> [<VARS>]]

  is expected. The new variable <vnam> will be initialized with the value <VARA>. If you also give an end value <VARE> and a step width <VARS>, a loop will be generated, i. e, several calculations with different values ot the variable will be performed. If you define loops for more than one variable, they will be nested in the sequence of their definition.

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If AOMX reads a line consisting of a single *, it switches to the definition of bound variables. Subsequent lines are expected in the form

```
<vnam> = <a1> [<OP1> <a2> [<OPi> <ai>]_n]
```

which directs AOMX to combine the operands `<ai>` with the operators `<OPi>`. Allowable operators are `+`, `-`, `*`, `/` and `**`, during evaluation of arithmetic expressions, the program obeys common priority rules.[13]

Limitations. The number of free variables must be in the range 0 to 10, altogether `MVAR` variables may be defined. A line may contain at most `MAOP` arithmetic operators, and a variable name must not be longer than 10 characters.

Example:

```
VAR
B    = 500 700 50
Dq   = 2000 2200 100
*
C = 4 * B
esig = 10 * Dq / 3
```

B runs from 500 to 700 in steps of 50, Dq from 20000 to 22000 in steps of 1000, it holds `C=4B` and `esig=10Dq/3`.

- VAR **with option** `STA`. The directive `VAR STA` induces causes that derivatives of calculated energies over parameters (free variables) are computed as well as standard deviations of parameters, the correlation matrix of parameters and more. This requires that experimental energies are defined by supplying an EXP block.[14]

  The syntax for the definition of free and bound variables is the same as with `VAR` except that loops cannot be generated.

- VAR **with option** `OPT`. The directive `VAR OPT` induces an optimization of all free variables by fitting them to experimental data. Consequently, an EXP block must also be given. The definition of free variable is done according to the following scheme:

  ```
  <vnam> [=] <VARS> [<VARA> [<VARE>]]
  ```

  The optimization of the variable `<vnam>` will start with the value `<VARS>`. During the optimization process, `<vnam>` may neither fall short of the minimum value `<VARA>` nor pass over the maximum value `<VARE>`. If `<vnam>` leaves the allowable range during optimization, a penalty function will be invoked that artificially deteriorates the least squares function.

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[13]Brackets and mathematical functions are not supported. If necessary, you have to expand a function in a power series.

[14]Even if you are only interested in the partial derivative matrix, you must enter en EXP block in order to define the states that shall be examined.

Example:

```
VAR OPT
esig     = 5000
epi/esig = 0.20 0.18 0.22
*
epi = epi/esig * esig
```

esig and epi shall be optimized, starting with 5000 resp. 1000 cm^{-1}, but under the boundary condition that the ratio epi/esig may not deviate more than 10% from the starting value. To achieve this under free variation of esig, not epi itself is varied, but the ratio epi/esig – retricted, however, to the interval $[0.18, 0.22]$ which corresponds to the requirement of a maximal deviation of 10% from the starting value.

- VAR **with both options** OPT **and** STA. The directive VAR OPT STA causes an optimization of all free variables followed by an error propagation calculation.

Example:

```
VAR OPT STA
esig = 5000
epi  = 1000
B    =  400
*
C    = 5 * B
```

esig and epi shall be optimized with the same starting values as in the preceding example, but this time without restriction of the epi/esigma ratio; as a third fittable variable, B is added. C, on the contrary, is not optimized but bound to B. After settlement of the optimization, an error propagation calculation for esig und epi shall be performed.

Even if the options OPT and/or STA are applied, bound variables can be defined after insertion of a * line as the example for VAR OPT demonstrates.

3.2.2 XYZ Cartesian coordinates (block)

Read cartesian coordinates x, y, z of the ligands in the form

```
<x> <y> <z>
```

Because they serve only to determine the angular geometry, the choose of units is without significance.

Example: Coordinates of a regular tetrahedron

```
XYZ
  1   1   1
 -1  -1   1
  1  -1  -1
 -1   1  -1
```

3.2.3 TPP Euler angles (block)

Read Euler angles Θ, Φ, Ψ of the ligands in the form

`<theta> <phi> [<psi>]`

The optional angle Ψ is relevant only in the case of anisotropic π interaction, default value is zero.

Example: Coordinates of a tetragonally distorted tetrahedron with variation of the distortion.

```
VAR
theta+ = 50 60 5
theta- = 180 - theta+

XYZ
theta+    45
theta+   135
theta-   -45
theta-  -135
```

theta+ and theta- will take the values 50, 55 and 60 resp. 130, 125 and 120 . The ligands are placed such that the C_2 symmetry axes coincide with the coordinate axes. Under these premises, AOMX can correctly evaluate the term symbols in the effective rotational symmetry $\mathcal{D}_4$ that is obtaeind by holoedrization of the potential (see section B.2) and has to be given in the head lines (see page 6).

3.2.4 RTP Polar coordinates (block)

Read polar coordinates R, Θ, Φ of the ligands in the form

`<r> <theta> <phi>`

The R coordinate has no significance for the AOM ligand field because the distance dependance is implicitly contained in the AOM parameters. Θ and Ψ are identical with the namesake Euler angles.[15]

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[15] At first sight, the input directive RTP is superfluous. Yet, it is useful if the coordinates are present as R, Θ, Φ triples (for instance, after a conversion cartesian $\rightarrow$ polar as it, e. g., can be taken from the output of AOMX) and is mandatory in crystal field calculations (not documented here).

3.2.5 AOM AOM parameters (block)

- AOM **without extra option.** The directive AOM induces the program to read one, three or five AOM parameters e_λ in the form

  <esigma> [<epis> <epic> [<edeltas> <edeltac>]]

- AOM **with the option SDM.** After the directive AOM SDM, the program reads (in addition to the AOM parameters) an *sd* mixing parameter which (taking pattern from e_σ) is mostly termed σ_{sd}. The syntax then reads:

  <esigma> [<epis> <epic> [<edeltas> <edeltac>]] <sigmasd>

! $\rightarrow$ *Note:* e_σ must, e_{π_s} and e_{π_c} can be given, but the latter always only joint, this correspondingly applies also to the e_δ parameters. Hence, after the directive AOM, the program expects one, three or five numbers or variables, and after the directive AOM SDM two, four or six.

3.2.6 CON Connected ligands (block)

This directive serves to fix the Ψ angles in the case of anisotropic π interaction and to define the two e_{π_s} parameters of the phase coupling model and has the form

<ILA> <ILB> [<episd(ILA)> <episd(ILB)>].

<ILA> and <ILB> are the sequence numbers of two ligands whose coordinates and AOM parameters must already be defined. AOMX then calculates the two appropriate Ψ angles such that the ligand y axes will be placed perpendicular to the plain containing the metal and the two ligands.

The specifications <episd(ILA)> <episd(ILB)> are necessary if phase coupling shall be included in the calculation; by these two items, the difference of *in phase* and *out of phase* e_{π_s} parameters will be fixed:

$$\text{<episd(ILA)>} = e_{\pi_s,A} - e'_{\pi_s,A}$$
$$\text{<episd(ILB)>} = e_{\pi_s,B} - e'_{\pi_s,B}$$

In the AOM-Block where usual e_λ parameters are read in, the avarage value must have been given before:

$$\text{<epis0(ILA)>} = (e_{\pi_s,A} + e'_{\pi_s,A})/2$$
$$\text{<epis0(ILB)>} = (e_{\pi_s,B} + e'_{\pi_s,B})/2$$

AOMX then computes the *in phase* and *out of phase* e_{π_s}-parameters according to

$$e_{\pi_s,A} = \text{<epis0(ILA)>} + \text{<episd(ILA)>}\ /2$$
$$e'_{\pi_s,A} = \text{<epis0(ILA)>} - \text{<episd(ILA)>}\ /2$$
$$e_{\pi_s,B} = \text{<epis0(ILB)>} + \text{<episd(ILB)>}\ /2$$
$$e'_{\pi_s,B} = \text{<epis0(ILB)>} - \text{<episd(ILB)>}\ /2\ .$$

The unusual parametrization through an avarage e_{π_s} parameter and the e_{π_s} splitting instead of the *in phase* and *out of phase* parameters themselves has technical reasons since this way phase coupling could be implemented more easily as an additional perturbation. How you can, nevertheless, work with e_{π_s} und e'_{π_s} by using variables, is demonstrated by the first of the following examples:

Example 1:

```
TPP
 65    40
 65   140
115   -40
115  -140

VAR OPT
epis   1000
epis'  700
*
epis_0 = epis / 2 + epis' / 2
epis_d = epis - epis'

AOM
7000 900 200
7000 900 200
6000 epis_0 0
6000 epis_0 0

CON
1 2
3 4 epis_d epis_d
```

A distorted tetrahedron is defined with two symmetrical chelate ligands that both exhibit anisotropic π interaction. Ligands no. 1 and 2 form the first chelate, no. 3 and 4 the second; for all ligands, the Ψ angle will be calculated. On the second chelate, moreover, phase coupling is present, e_{π_s} and e'_{π_s} shall be optimized.

Example 2:

```
XYZ
x    y    z
xdum ydum zdum

AOM
esig epis epic
0    0    0

CON
1 2
```

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In this example, not a chelate is defined but a unidentate ligand with anisotropic π interaction. The second ligand is a *dummy* since its contributions to the ligand field are equal to zero; it solely serves for the calculation of the Ψ angle by spanning a plane together with the central ion and the coordinating atom of the ligand which fixes the orientation of that orbital which is π antibonding with respect to the metal-ligand interaction. Regarding this π^* orbital in an idealizing way as a nonbonding p orbital, the plane defined by the aid of the *dummy* has to be its nodal plane. Examples: in the H_2O ligand, one of the hydrogen atoms may act as the *dummy*, in the pyridine ligand one of the carbon atoms in *ortho* or *meta* position.

3.2.7   VEE   Electron repulsion parameters (line)

The input line has the form

VEE <a> <b> <c> [<mue1> <mue2> <mue3> <mue4> <mue5>]

<a>, <b> and <c> are the Racah parameters A,B and C, and mue1 to mue5 are orbital reduction factors (see p. 4) for the d orbitals in the standard sequence $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$ of the AOMX program. Dafault value for the μ coefficients is 1.

3.2.8   HSO   Spin-orbit parameters (line)

Read the parameter ζ and the reduction factors k_i (see p. 4) in the form

HSO <zeta> [<kx> <ky> <kz>].

3.2.9   HMG   Magnetic field parameters (line)

Read the strenth and direction of a homogeneous extenal magnetic field and of reduction factors (see p. 4) in the form

HMG <hmag> <thmag> <phmag> [<kx> <ky> <kz>].

<hmag> is the magnetic field strength H in Tesla, the polar coordinates <thmag> and <phmag> define the direction (Θ, Φ) of the magnetic field.

3.2.10   TRE   Trees parameter (line)

Read the parameter α of the *Trees correction* (see p. 4) in der form

TRE <alpha>

3.2.11 EXP Experimental data (block)

Here, the connexion (assignment) between experimental energies and the eigenvalues of the AOM calculation can be given. In doing so, an experimental energy corrsponds to an eigenvalue or a linear combination (average, splitting) of eigenvalues of an AOM calculation.

Assignment with symmetry. In case it is calculated with symmetry, the following syntax is valid:

$$\texttt{<NAMEX> <EEX> <WT>} \ \big[\texttt{<TERMEX> <ICTEX>}\big]_n \ \big[\texttt{-} \ \big[\texttt{<TERMEX> <ICTEX>}\big]_m\big]$$

`<NAMEX>` is a freely choosable denotation for the experimental energy, `<EEX>` the numerical value of the experimental energy in cm^{-1} and `<WT>` the weight by which EEX shall enter into the least squares function.[16] `<TERMEX>` must be a term symbol known to the program through which the state being searched for can be identified by AOMX. A term symbol consists of one of the irreducible representation symbols listed below which in case of calculation without spin-orbit coupling must be prefixed with the spin multiplicity. The following irreducible representation symbols are known to the program:

A1	A2	E	T1	T2	G6	G7	G8	$\mathcal{O}, \mathcal{O}^*$
A1	A2	B1	B2	E	G6	G7		$\mathcal{D}_4, \mathcal{D}_4^*$
A1	A2	E	G4	G56				$\mathcal{D}_3, \mathcal{D}_3^*$
A	B1	B2	B3	G5				$\mathcal{D}_2, \mathcal{D}_2^*$
A	B	G3						$\mathcal{C}_2, \mathcal{C}_2^*$

Valid specifications of `<TERMEX>` are, for example: 4T2, 6A1, 3B2 (without SOC) or T2, A1, G6 (with SOC). Through `<ICTEX>` you must specifiy which occurence (sequence number) of `<TERMEX>` AOMX shall look for.

If you give several `<TERMEX>` `<ICTEX>` pairs, the program will calculate average values of theoretical energies. If a minus sign is inserted between two `<TERMEX>` `<ICTEX>` specifications, AOMX will first average to the left and right of the minus sign and then form the difference. In this way, splittings can be declared.

Assignment without symmetry. In some cases, an assigment between experimental and calculated energies solely based on state degeneracies is possible. You may then work without symmetry and save a considerable part of computing time since eigenvectors need not be calculated. The input syntax for experimental energies is nearly the same as with symmetry – you merely have to give term degeneracies instead of term symbols: in a calculation with SOC the total degeneracy, in a calculation without SOC a two-digit number whose first cypher specifies the spin multiplicity and whose second cypher specfies orbital degenaracy.

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[16]WT should be choosen the larger the exacter the experimental energy could be determined.

Hint: Doing the calculation without SOC will further reduce the consumption of CPU time distinctly due to M_S blocking.

Restrictions: <NAMEX> may be maximal 10 characters long, and at most 10 <TERMEX> <ICTEX> pairs may be given.

Example 1:

```
EXP
4E(T2g)     18700     10    4E  1
4B2(T2g)    21500     10    4B2 1
a4T1g       27000      1    4E  2    4A2 1
2Eg-split     183   1000    2B1 1 - 2A1 2
```

The 4E(T2g) band has the experimental value 18700 cm^{-1}, gets a weight of 10 and is identified with the first ^4E from the calculation. The second band, 4E(T2g), was determined experimentally at 21500 cm^{-1}. The third band, a^4T_{1g}, could not be resolved, hence it gets a smaller weight factor and is identified with the mean value of the second ^4E and the first $^4A_2$ being calculated. The ^2E_g splitting has been determined experimentally to a particularly exact degree and corresponds to the difference between the first $^2B_1$ and the first $^2A_1$ from the calculation.

Example 2:

```
EXP
4B2(T2g)    21000     10    41 2
b4T1g       40000      1    41 4    42 3
2Eg-split     183   1000    21 1 - 21 2
```

This corresponds to the preceding example, but for a calculation without symmetry which runs considerably faster.[17] The term $^4B_2(T_{2g})$ ist idendified with the second orbitally nondegenerate quartet and so on.

3.2.12   BAS   Basis set restriction (block)

Normally, the basis of an AOMX calculation consists of all possible Slater determinants for a given number of d electrons. Sometimes, howewer, it may be desirable to make the basis smaller, for instance in order to speed up the calculation, to suppress uninteresting output or for the purpose of studying CI effects.

With the BAS directive you can influence the basis set size in two different ways: by giving a minimal spin multiplicity and by giving minimal and maximal orbital occupations.

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[17]It should be noted, however, that renunciation of symmetry determination brings about that terms of different symmetry but equal degeneray cannot be distinguished any longer which can lead to misinterpretations. If in doubt, you should perform control calculations with symmetry determination.

Minimal spin multiplicity. An input of the form

    BAS <MINSM>

induces that only terms eith at least <MINSM>-fold spin degeneracy are computed.[18] Giving a <MINSM> is optional and makes only sense in a run without spin-orbit coulping and without external magnetic field.

Minimal and maximal orbital occupations. The BAS directive may contain a sequence of lines of the form

    <MINOC> <MAXOC>,

where <MINOC> and <MAXOC> are occupation vectors, each consisting of five digits 0, 1 or 2. The first up to the fifth digit stand for the minimal resp. maximal occupation of the orbitals $d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{z^2}$. AOMX will then select all Slater determinants for which $MINOC(1) \leq n(d_{xy}) \leq MAXOC(1)$ and $MINOC(2) \leq n(d_{xz}) \leq MAXOC(2)$ etc. holds. Several <MINOC> <MAXOC> lines will be logically *or*-combined by AOMX.

Example:

    BAS 3
    00010 22210
    00001 22201

The spin multiplicity shall be at least three, exactly one e_g-Orbital shall be occupied. For a two-electron system this means " all triplets of the configuration $t_{2g}^1 e_g^1$ ", for a four-electron system " all triplets und quintets of the configuration $t_{2g}^3 e_g^1$ ".

3.2.13 CTL Control options (line)

In a line of the form

    CTL <OPTION1> [<OPTION2> ...]

you may give print options or optimization options.

Print options induce the AOMX program to print additional information.[19]

Normally, AOMX gives out the result of a calculation as follows:

- In a run without symmetry: eigenvalues and multiplicities.

---

[18] The cause hat only a minimal and not a maximal or some intermediate spin multiplicity may be given is that AOMX must diagonalize all matrices up to the maximal M_S in order to determine $2S + 1$, so that higher spin multiplicities are also calculated in any case.

[19] or to suppress them, if the option is preceded by a '-'. The CTL directive is the only directive that does not completely overwrite the old values if it is called once more. Hence, through CTL directives between two runs, you can selectively switch print options on and off.

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- In a run with symmetry: terms, orbital occupations and characters.

- In case of given experimental data: calculated vs. experimental data, no printing of additional terms.

This standard presentation of results can be extended through the print options PGRD, PTRM, PEIG and PVEC:[20]

- PGRD *Print the ground state energy.*

- PTRM *Print terms.* Forces printout of term symbols, energies and orbital occupations for all states in a run with experimental data and symmetry.

- PEIG *Print eigenvalues and multiplicities.* Forces printout of energies and multiplicities for all states in a run with experimental data without symmetry.

- PVEC *Print eigenvectors.* Beyond that, orbital occupations that eventually should be given out, will be printed seperately for α and β spins.

Matrix elements of operators can be obtained by the following print options:

- PLFM *Print the ligand field matrix.*

- PEII *Print electron interaction integrals.*

- PHSO *Print the spin-orbit matrix.*

- PHMG *Print the magnetic field matrix.*

The options PPAR and PSTD are provided for debugging purposes:

- PPAR *Printout of internal parameters.* The program always transforms the input parameters to the internal parameters SIG(), PIS(), PIC(), X(), Y(), Z(), R(), THE(), PHI(), PSI(), A, B, C, TAU(), ZET etc. Their printout should be induced only in case of suspicion of errors in the definition or usage of variables.

- PSTD *Do not reduce printout during optimization.* In an optimization run, printout is normally reduced to a minimum, print options are ignored. If PSTD is set, printout will occur to the same extent as in a normal run, print options are recognized. *Attention:* Since an optimization run often requires hundreds of calculations, the size of output may increase enormously.

The sole **optimization option** is

---

[20]See also NEIG and VLOW in the global information line in the header lines.

- MAXIT <N>

  Hereby, breaking off of the optimization will be forced after N iterations (default: 30).

3.2.14 RUN Start a run (line)

The keyword RUN induces the start of a run with the data read in so far.

A Practical matter

A.1 Input examples

Optimization: trans $- [\mathrm{Cr(en)_2Cl_2}]^+$

In this example, the AOM parameters and the Racah parameter B are fitted to experimental data. The parameters Dq, Ds, Dt are not relevant for the calculation, but they are printed out together with the others since Dubicki and Day had applied this parametrization. Only quartets are calculated (BAS 4). CTL TERM has been set in order that all quartet states are printed out, not only those specified in EXP.

```
**************************************
tr-Cr(en)2Cl2+                       *
Lit: Dubicki, Day, IC 9, 2043 (1971) *
**************************************

3 D4

VAR OPT
esig(N)  = 7000
esig(Cl) = 5000
epi(Cl)  = 1000
B        =  600
*
C        = 5 * B
Dq = 3 * esig(N) / 10
Ds = -2 / 7  * esig(N) + 2 / 7  * esig(Cl) + 2 / 7  * epi(Cl)
Dt = -6 / 35 * esig(N) + 6 / 35 * esig(Cl) - 8 / 35 * epi(Cl)

TPP
 90   0
 90  90
 90 180
 90 -90
  0   0
180   0

AOM
esig(N) 0 0
esig(N) 0 0
```

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```
esig(N) 0 0
esig(N) 0 0
esig(Cl) epi(Cl) epi(Cl)
esig(Cl) epi(Cl) epi(Cl)

VEE 0 B C

EXP
4Eg(T2g)    17700   1   4E   1
4B2g(T2g)   22800   1   4B2  1
4A2g(aT1g)  25400   1   4A2  1
4Eg(aT1g)   26000   1   4E   2

BAS 4

CTL PTRM

RUN
```

Trigonally distorted octahedron and phase coupling: $Cr(acac)_3$

This is a single-point calculation without optimization. By the aid of two geometric parameters, a trigonally distorted octahedron is defined: theta+ controls compression, phi torsion along the trigonal axis. In the CON block, chelate connectivity as well as phase coupling parameters are specified (see section 3.2.6). The line '3 D3 14' defines: 3 electrons, trigonal symmetry, printout of the first 14 states (resp. 7 Kramers doublets since it is a calculation with spin-orbit coupling on a system with odd electron number).

```
Cr(acac)3
Lit: Atanasov, Schoenherr, IC 29,4545 (1990), Fig. 4

3 D3 14

VAR
*
10Dq          = 18700
epis          =  1000
epis´         =     0
pic/2pis0     =     0.6
B             =   500
C             =  3400
zeta          =   245
theta+   =     53.8
phi      =     60.8
epis0    = epis / 2 + epis´ / 2
epic     = 2 * epis0 * pic/2pis0
episdiff = epis - epis´
esig     = 10Dq / 3 + 2 * epis0 / 3 + 2 * epic / 3
theta-   = 180 - theta+
phi1     = phi /    2
```

```
phi2      = phi1 + 120
phi3      = phi1 + 240
phi4      = phi  /  -2
phi5      = phi4 + 120
phi6      = phi4 + 240

AOM
esig epis0 epic
esig epis0 epic
esig epis0 epic
esig epis0 epic
esig epis0 epic
esig epis0 epic

TPP
theta+ phi1
theta+ phi2
theta+ phi3
theta- phi4
theta- phi5
theta- phi6

CON
1 4 episdiff episdiff
2 5 episdiff episdiff
3 6 episdiff episdiff

VEE 0 B C

HSO zeta

RUN
```

Tetragonally distorted tetrahedron: FeS_4^{5-}

Here, a tetragonally distorted fourfold coordinated d^5-System is concerned, alpha controls the axial compression of the tetrahedron. Beneath the sextet ground state, only quartets are calculated, but no doublets (BAS 4). It is typical for a relatively weak distorted tetrahedron that e_σ und e_π cannot be determined independently. Therefore, e_π has been arbitrarily set to zero, and additionaly the 'classical' Dq parameter is printed out.

```
FeS4(5-), Lit: Inorg. Chem. 32, 654 (1993), Table XI

5 D4

VAR
esig    = 4260
B       =  460
C       = 1800
alpha   =  102.4
```

```
*
epi     =     0
theta+ = alpha / 2
theta- = 180 - theta+
Dq      = 3 * esig / 10

TPP
theta+    45
theta+  -135
theta-   135
theta-   -45

AOM
esig epi epi
esig epi epi
esig epi epi
esig epi epi

VEE 0 B C

BAS 4

RUN
```

A.2   Questions and Answers

A.2.1   Question: Which requirements does AOMX demand concerning hardware?

> **Answer:** During installation, about 4 MB of disk memory should be available. At runtime, AOMX needs about 3 MB of main memory[21] and usually not more than a few hundred kB of disk space. CPU-time consumption depends heavily on the problem to be solved. It varies (on a PC with DX2/66 processor) between milliseconds for d^1 systems and several minutes for computations on d^5 systems including spin-orbit coupling and symmetry analysis.

A.2.2   Question: Can AOMX be configured at compile-time?

> **Answer:** Yes, the index boundaries MDET, MLIG, MVAR, MAOP, MOCS and MEEX can be adapted if necessary, they have the following meanings:
>
> - MDET: maximal number of Slater determinants
> - MLIG: maximal number of ligands
> - MVAR: maximal number of variables
> - MAOP: maximal number of arithmetic operators
> - MOCS: maximal number of orbital occupation schemes
> - MEEX: maximal number of experimental data

---

[21]configurable, see next question

Adaptation is done by changing all `PARAMETER` statements in the source code that contain one of these constants. `MDET` is of special importance since the two-dimensional arrays `HR`, `HI`, `VR` und `VI` that are declared in routine `calc.f` cause with `MDET*MDET*32` Byte the largest part of the memory requirements of AOMX. Dependent on the number of electrons, the following `MDET` values are required at minimum:

	with SOC	without SOC
d^1, d^9	10	5
d^2, d^8	45	15
d^3, d^7	120	50
d^4, d^6	210	100
d^5	252	100

A.2.3 **Question:** Does AOMX presuppose any external libraries?

Answer: No. It is true that AOMX needs some subroutines from the EIS-PACK library but they are added to the source code as a file `eispsub.f`. In case that a particularly efficient implementation of the NAG library is available on the computer on which AOMX shall be installed, it may be worth to use the NAG routines instead of the EISPACK routines for matrix diagonalization. For this purpose, the lines marked `NAG` in cols. 73ff must be activated and those marked `EISPACK` must be deactivated in routine `calc.f`.

A.2.4 **Question:** Can I compile AOMX with a compiler that does not support double precision complex numbers?

Answer: Yes, but it is not recommended because of the loss of exactness and reliability of the results. For FORTRAN compilers that do not support COMPLEX*16 arithmetics, all lines with `C16` in cols. 73ff must be commented out and all lines with `NO C16` must be activated. Moreover, the replacement library `noc16.f` must be compiled and linked.

A.2.5 **Question:** Under which presuppositions can AOMX determine term symbols?

Antwort: Two presuppositions must be fulfilled (see also page 4 and appendix B.2):

1. The rotational group of the holoedrized point group of the molecule must be one of the groups $\mathcal{O}$, $\mathcal{D}_4$, $\mathcal{D}_3$, $\mathcal{D}_2$ or $\mathcal{C}_2$. The holoedrized point group can be found out by inversion of the molecule at the origin of the coordinate system and superpositioning with its original. The required rotation group is the subgroup of all pure rotations of the holoedrized point group.

2. The molecule must be oriented in space such that the main rotational axis coincides with the z axis and that, if present, a two-fold axis perpendicular to the former coincides with the x axis of the metal coordinate system.

B Theoretisches

B.1 Das *Angular Overlap Model*

Der Ansatz des AOM

Das *Angular Overlap Model*[22] ist ein moderner ligandenfeldtheoretischer Ansatz zur Beschreibung der offenen d-Schale von Übergangsmetallkomplexen. Anders als in der elektrostatischen ("'klassischen"') LFT wird hier vom MO-Bild ausgegangen: setzt man einen effektiven Einelektronenoperator und eine Basis aus der äußeren d-Schale des Zentralatoms M und den Valenzschalen der Liganden L an, dann bestehen die höchsten fünf Orbitale eines solchen Systems im Allgemeinen aus Metall-d-Orbitalen mit kleinen Einmischungen von Ligandenfunktionen. Man kann nun in einer Art Störungsrechnung zweiter Ordnung zeigen, daß die Eigenwerte der AOM-Matrix mit den Elementen

$$H_{ij}^{\mathrm{AOM}} = \sum_{k=1}^{n_L} \langle \phi_{M_i} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{M_j} \rangle + \sum_{\lambda} \sum_{k=1}^{n_L} \frac{\langle \phi_{M_i} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{L_{k\lambda}} \rangle \langle \phi_{L_{k\lambda}} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{M_j} \rangle}{\epsilon_M - \epsilon_{L_{k\lambda}}} \tag{1}$$

eine gute Näherung für die Antibindungsenergien der atomaren d-Orbitale im molekularen System darstellen, wobei λ den Wechselwirkungstyp bezeichnet (siehe unten). Kennt man die Antibindungsenergien, dann hat man den Schlüssel zur Berechnung spektraler Übergänge innerhalb der offenen Schale von Übergangsmetallkomplexen in der Hand. Allerdings muß zuvor noch eine Hürde überwunden werden, nämlich die Berechnung bzw. Parametrisierung der Matrixelemente Gl. 1. Hierzu ist die Einführung einer Standardorientierung erforderlich, mittels derer es gelingt, Komplexgeometrie und Stärke einzelner Metall-Ligand-Wechselwirkungen rechnerisch voneinander zu trennen.

Standardorientierung

In einem einzelnen linearen Metall-Ligand-System kann die Wechselwirkung vom σ-, π- oder δ-Typ sein, wie Abb. 1 zeigt. Dieses Bild setzt allerdings voraus, daß Metall-d- und Ligandenorbitale in entsprechender Weise zueinander orientiert sind. Bei Verwendung orthoaxial ausgerichteter Orbitale ist dies gleichbedeutend mit der Forderung, daß die lokalen Koordinatensysteme des Zentralatoms und des Liganden eine gemeinsame z-Achse haben und daß die x- und y-Achsen jeweils parallel zueinander sind. Im Allgemeinen ist dies jedoch nicht der Fall (Abb. 2 links). Man hat jedoch innerhalb des entarteten d-Satzes eine Basistransformation "'frei"', so daß man durch Drehungen des Metallkoordinatensystems um drei Winkel Θ, Φ und Ψ (Euler-Winkel) die oben beschriebene Standardorientierung immer erreichen kann. Die einzelnen Schritte sind in Abb. 2 gezeigt: Drehungen um Θ und Φ (die Winkel sind mit den Polarkoordinaten des Liganden identisch) führen zur Koinzidenz der z-Achsen, die abschließende Drehung um Ψ richtet die x- und y-Achsen

---

[22]das Ende der sechziger Jahre von Jørgensen, Pappalardo und Schmidtke sowie von Schäffer entwickelt worden ist

parallel aus. Die Ψ-Drehung ist nur bei Liganden mit anisotroper π- Wechselwirkung $(e_{\pi_s} \neq e_{\pi_c})$ erforderlich – zum Beispiel beim H_2O-Molekül, das nur ein π-ständiges *lone pair* hat.

Figure 1: Symmetrie der Metall-Ligand-Wechselwirkungen

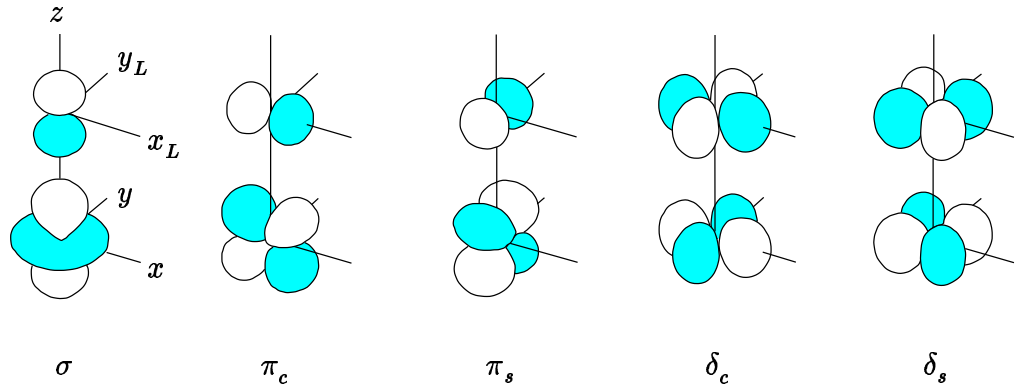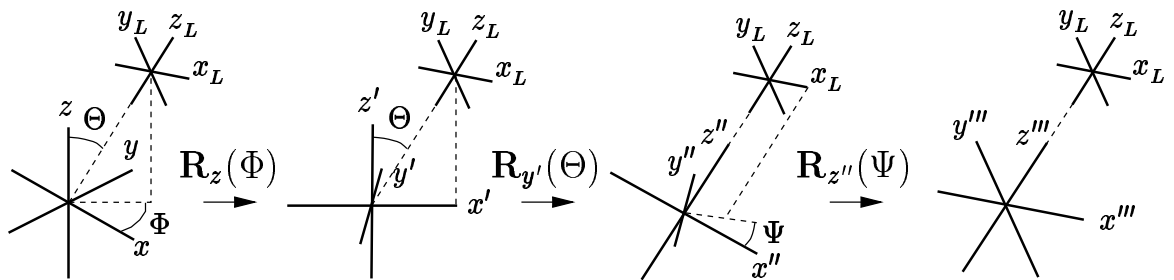$$\sigma \qquad \pi_c \qquad \pi_s \qquad \delta_c \qquad \delta_s$$

Figure 2: Drehung des Metallkoordinatensystems um drei Euler-Winkel

Der mit den Drehungen verbundenen Koordinatentransformation entspricht eine Zerlegung der d-Orbitale in Symmetriekomponenten bezüglich des neuen Koordinatensystems. Die alten Orbitale $\phi_{M_i}(x, y, z)$ sind mit den neuen, im gedrehten System symmetrieadaptierten Orbitalen $\phi_{M_\lambda}(x''', y''', z''')$ über eine orthogonale Transformation $\boldsymbol{F}(\Theta_k, \Phi_k, \Psi_k)$ verknüpft:

$$
\begin{aligned}
|\phi_{M_i}(x, y, z)\rangle &= \sum_\lambda |\phi_{M_\lambda}(x''', y''', z''')\rangle \langle \phi_{M_\lambda}(x''', y''', z''')|\phi_{M_i}(x, y, z)\rangle \\
&= \sum_\lambda |\phi_{M_\lambda}(x''', y''', z''')\rangle \cdot F_{\lambda i}(\Phi_k, \Theta_k, \Psi_k) \qquad (2)
\end{aligned}
$$

Ersetzt man die d-Orbitale Gl. (1), die ja im alten Koordinatensystem definiert sind, gemäß vorstehender Gleichung durch ihre Komponentenzerlegung in Richtung der Liganden und beachtet, daß Symmetriefunktionen zu unterschiedlichen Darstellungen λ und λ' nicht kombinieren, dann resultiert:

$$
\begin{aligned}
H_{ij}^{\mathrm{AOM}} &= \sum_{\lambda} \sum_{k=1}^{n_L} F_{\lambda i}(\Phi_k, \Theta_k, \Psi_k) F_{\lambda j}(\Phi_k, \Theta_k, \Psi_k) \times \\
&\underbrace{\left(\langle \phi_{M\lambda} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{M\lambda} \rangle + \frac{\langle \phi_{M\lambda} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{L_k\lambda} \rangle \langle \phi_{L_k\lambda} | \mathbf{V}_{L_k}^{\mathrm{eff}} | \phi_{M\lambda} \rangle}{\epsilon_M - \epsilon_{L_k\lambda}} \right)}_{e_\lambda(k)} \\
&= \sum_{\lambda} \sum_{k=1}^{n_L} F_{\lambda i}(\Phi_k, \Theta_k, \Psi_k) F_{\lambda j}(\Phi_k, \Theta_k, \Psi_k) \cdot e_\lambda(k).
\end{aligned}
\tag{3}
$$

Das AOM-Matrixelement ist nun für jeden Liganden k und für jeden Bindungstyp λ additiv zerlegt in einen Winkelgeometriefaktor $F_{\lambda i}(k) F_{\lambda j}(k)$ und ein Standard-Matrixelement $e_\lambda(k)$, das von der Orientierung des Liganden unabhängig ist, aber noch vom Metall/Ligand-Abstand abhängt. Wegen ihrer Additivität und ihrer Unabhängigkeit von der Winkelgeometrie sind die AOM-Parameter $e_\lambda(k)$ übertragbar, solange der Metall/Ligand-Abstand sich nicht allzusehr ändert (Ausnahmen sind zum Beispiel stark Jahn-Teller-verzerrte Systeme), und die Aufteilung nach σ-, π- und δ-Anteilen kommt der geläufigen Vorstellung von chemischer Bindung entgegen. Aus diesen Gründen ist das AOM als semiempirisches Modell für die spektroskopische Praxis sehr gut geeignet.

Zweidimensionale spektrochemische Serien. Der Begriff "'spektrochemische Serie"' steht bekanntlich für eine Reihung von Liganden nach ihrer Ligandenfeldstärke $\Delta = 10Dq_{\mathrm{okt.}}$ relativ zu einem gegebenen Zentralion. Im AOM gibt es zwei solcher Reihen: je eine für die e_σ- und die e_π-Parameter.[23] Solche zweidimensionalen spektrochemische Serien enthalten Informationen über die Bindungsverhältnisse im Komplex, die aus dem Vergleich der Dq-Parameter allein nicht erhältlich sind. Allerdings benötigt man zu ihrer Aufstellung mehr experimentelle Information: Während Dq-Parameter allein aus den Spektren oktaedrischer Komplexe gewonnen werden können, braucht man zur Bestimmung von zwei Parametern e_σ und e_π auch die Daten niedersymmetrischer Verbindungen.

Spektrochemische Serien von e_δ-Parametern werden nicht geführt, weil e_δ in AOM-Anwendungen normalerweise nicht berücksichtigt wird – warum, sei kurz erläutert: Zwar sind kovalente δ-Wechselwirkungen vernachlässigbar, was in der Wolfberg-Helmholtz-Näherung[1] an den praktisch verschwindend kleinen Überlappungsintegralen $S_{M_\delta L_{k\delta}}$ deutlich wird. Aber das erlaubt noch nicht, den Parameter zu Null zu setzen, denn die elektrostatische Energie

---

[23]für Liganden mit isotroper π-Wechselwirkung, $e_{\pi_s} = e_{\pi_c}$

eines d_{δ_s}- oder d_{δ_c}-Elektrons im effektiven Potential eines Liganden auf der z-Achse kann immer noch beträchtlich groß sein. Man kann jedoch die e_δ-Parameter formal eliminieren, ohne sie gleich Null zu setzen, indem man die AOM-Parameter in der Form

$$e'_\lambda = e_\lambda - e_\delta \tag{4}$$

definiert. Setzt man dies in Gl. (3) ein und berücksichtigt die Orthogonalität der $F_{\lambda i}$-Matrix, findet man, daß die Definition Gl. (4) nur zu einer Verschiebung der potentiellen Energie führt, die aber auf zu berechnende Energiedifferenzen keine Auswirkung hat.[24]

$$
\begin{aligned}
H_{ij}^{\mathrm{AOM}'} &= \sum_\lambda \sum_{k=1}^{n_L} F_{\lambda i}(k) F_{\lambda j}(k) \cdot [e_\lambda(k) - e_\delta(k)] \\
&= \sum_\lambda \sum_{k=1}^{n_L} F_{\lambda i}(k) F_{\lambda j}(k) \cdot e_\lambda(k) - \sum_{k=1}^{n_L} e_\delta(k) \cdot \sum_\lambda F_{\lambda i}(k) F_{\lambda j}(k) \\
&= H_{ij}^{\mathrm{AOM}} - \sum_{k=1}^{n_L} e_\delta(k) \cdot \delta_{i,j}
\end{aligned}
\tag{5}
$$

Phasenkopplung

Die oben gegebene Ableitung additiver AOM-Parameter e_λ gilt nicht bzw. muß modifiziert werden, wenn zwischen den Orbitalen der koordinierenden Atome eines zweizähnigen Liganden, welche die koordinative Bindung betätigen, eine feste Phasenbeziehung besteht, d. h. wenn sie im MO-Bild zu ein und demselben delokalisierten *frontier orbital* gehören. Sind sie in Phase, spricht man von *in phase* oder *ψ type coupling*, im anderen Fall von *out of phase* oder *χ type coupling*. Phasenkopplung tritt bei Chelaten mit konjugierten π-Elektronensystemen auf, zum Beispiel Acetylacetonat oder Bipyridin. Das AOM ist dann nicht mehr additiv bezüglich der einzelnen Liganden (Koordinationszentren); vielmehr muß der Chelat als Einheit betrachtet werden mit der Winkelhalbierenden zwischen den beiden Koordinationszentren als Symmetrieachse. In der Darstellung nach Atanasov, Schönherr und Schmidtke[3] wird eine Standardorientierung eingeführt, bei der die Chelatachse mit der Winkelhalbierenden der xy-Ebene des Metall-Koordinatensystems zur Deckung gebracht wird. Die d_π-Orbitale müssen an die Symmetrie der Ligandenorbitale adaptiert werden:

$$
\begin{aligned}
d_\psi &= \frac{1}{\sqrt{2}}\left(d_{xz} + d_{yz}\right) \\
d_\chi &= \frac{1}{\sqrt{2}}\left(d_{xz} - d_{yz}\right),
\end{aligned}
\tag{6}
$$

Rücktransformation auf die alte Basis führt zu einer "'Aufspaltung"' des e_{π_s}-Parameters in e_{π_s} (in phase) und e'_{π_s} (out of phase).

---

[24]Falls allerdings die π-Wechselwirkung anisotrop und die Symmetrie $\mathcal{C}_{2v}$ oder niedriger ist, ist auch $e_{\delta_s} \neq e_{\delta_c}$ zu erwarten. Dann ist diese Schlußfolgerung nur noch eine Näherung, da man nicht beide e_δ-Parameter gleichzeitig beseitigen kann. Hinzu kommt noch eine mögliche Mischung zwischen den Orbitalen d_σ und d_{δ_s}, da diese in $\mathcal{C}_{2v}$-Symmetrie beide totalsymmetrisch sind.

Bei ausreichend niedriger Komplexsymmetrie kann unter Energiegewinn eine $nd, (n+1)s$–Hybridisierung auftreten, nämlich genau dann, wenn eine der d–Funktionen, meist das d_{z^2}–Orbital, totalsymmetrisch wird und damit zur gleichen Symmetrierasse gehört wie das nächsthöhere s–Orbital des Zentralions (siehe [7, 1]). Auch Mischungen mit p–Funktionen sind möglich, wegen des größeren energetischen Abstands allerdings nur von untergeordneter Bedeutung.

Die weitaus größte Bedeutung hat sd–Mischung bei quadratisch planaren Komplexen, denn die Einmischung von s ermöglicht eine Ausdehnung des d_{z^2}–Orbitals in axialer Richtung bei gleichzeitigem Schrumpfen in der äquatorialen Ebene, was einer Verschiebung von antibindender Elektronendichte in Richtung auf die unbesetzten axialen Koordinationsstellen entspricht und hier einen besonders großen Energiegewinn bedeutet.

Die sd–Mischung kann über eine Störungsrechnung zweiter Ordnung eingeführt werden, nachdem man die AOM–Basis um eine s–Funktion am Zentralion erweitert hat. Dieses wird formal ähnlich wie eines der Ligandenorbitale behandelt, und man gelangt schließlich zu folgender Erweiterung der Gleichung (3):

$$
\begin{aligned}
H_{ij}^{\mathrm{AOM,sd}} &= H_{ij}^{\mathrm{AOM}} + H_{ij}^{sd} \qquad\qquad (7)\\
&= H_{ij}^{\mathrm{AOM}} + \\
&\quad \frac{\displaystyle\sum_{k=1}^{n_L}\left[F_{\sigma i}(k)\langle\phi_{M_{d\sigma}}|\mathbf{V}_{L_k}^{\mathrm{eff}}|\phi_{M_s}\rangle\right]\cdot\sum_{k'=1}^{n_L}\left[F_{\sigma j}(k')\langle\phi_{M_s}|\mathbf{V}_{L_k'}^{\mathrm{eff}}|\phi_{M_{d\sigma}}\rangle\right]}{\epsilon_{M_d}-\epsilon_{M_s}}
\end{aligned}
$$

Der neue Störterm ist ein Produkt zweier Summen über alle Liganden, während der entsprechende Ausdruck zweiter Ordnung in Gl. (3) als Einfachsumme geschrieben werden konnte. Letzteres war nur möglich durch Vernachlässigung von Dreizentrenintegralen. Da in den Matrixelementen mit Metall-s-Orbitalen eine solche Vereinfachung nicht möglich ist (alle Integrale sind Zweizentrenintegrale und nicht vernachlässigbar), behalten die sd–Störmatrixelemente die Doppelsummengestalt, was eine additive Parametrisierung erschwert, aber dennoch nicht unmöglich macht. Gl. (7) kann nämlich in der folgenden Form geschrieben werden:

$$H_{ij}^{\text{AOM,sd}} = H_{ij}^{\text{AOM}} + H_{ij}^{sd}$$

$$= H_{ij}^{\text{AOM}} -$$

$$\sum_{k=1}^{n_L} \left[F_{\sigma i}(k) \sqrt{\sigma_{sd}(k)} \right] \cdot \sum_{k'=1}^{n_L} \left[F_{\sigma j}(k') \sqrt{\sigma_{sd}(k')} \right]$$

mit

$$\sigma_{sd}(k) = \frac{\langle \phi_{M_{d\sigma}} | \mathbf{V}_{L_k}^{\text{eff}} | \phi_{M_s} \rangle^2}{\epsilon_s - \epsilon_d} \tag{8}$$

σ_{sd} ist also analog zum kovalenten Anteil des AOM–Parameters e_σ definiert. Nimmt man an, daß in einem quadratisch planaren Komplex das d_{z^2}–Orbital gerade nichtbindend wird, dann ergibt sich, daß σ_{sd} mit ungefähr einem Viertel von e_σ anzusetzen ist. Diese Größenordnungsabschätzung ist allerdings nicht mehr als ein grober Anhaltspunkt, in der Praxis muß σ_{sd} tatsächlich als unabhängiger Parameter behandelt werden.

B.2 Holoedrische Symmetrie im AOM

Die weitaus meisten Chromophore von Übergangsmetallkomplexen haben die Koordinationszahl 6 oder 4, und ihre Symmetrie kann vom regulären Oktaeder, vom regulären Tetraeder oder vom Quadrat abgeleitet werden. Substitution (MA_6, MA_5B ...), Isomerie (*cis/trans, fac/mer*) oder Verzerrung (tetragonal, trigonal ...) erzeugen aus diesen drei Stammformen zahlreiche Strukturvarianten, die in der Ligandenfeldnäherung wegen der geraden Parität der d-Orbitale auf einige wenige Punktgruppen zurückgeführt werden können. Nach Jørgensen [6] bleibt nämlich die Energie eines d-Orbitals erhalten, wenn man das Potential $\mathbf{V}_{\text{LF}}^{\text{eff}}$ *holoedrisiert*, das heißt, durch Punktspiegelung am Zentralion invertiert und anschließend mittelt:

$$\mathbf{V}_{\text{LF}}^{\text{eff}}[+\mathcal{C}_i] = \frac{\mathbf{V}_{\text{LF}}^{\text{eff}}(x, y, z) + \mathbf{V}_{\text{LF}}^{\text{eff}}(-x, -y, -z)}{2}. \tag{9}$$

Dieser Übergang zu holoedrischen Punktgruppen entspricht der aus der Kristallographie bekannten Abbildung der 32 Kristallklassen auf die 11 Lauegruppen. Da fünf- und höherzählige Drehachsen hier nicht betrachtet werden[25], fallen die beiden hexagonalen Lauegruppen heraus. Die Erfahrung hat außerdem gezeigt, daß von den verbleibenden nur die sechs Gruppen $\mathcal{O}_h$, $\mathcal{D}_{4h}$, $\mathcal{D}_{3d}$, $\mathcal{D}_{2h}$, $\mathcal{C}_{2h}$ und $\mathcal{C}_i$ in der Praxis eine bedeutsame Rolle spielen (siehe die Beispiele in Tabelle 2 am Ende dieses Abschnitts). Damit hat man zufällig genau je einen Repräsentanten aus dem kubischen, tetragonalen, trigonalen, orthorhombischen, monoklinen und triklinen Kristallsystem. Von den irreduziblen Darstellungen der genannten Gruppen sind wegen der Parität der d-

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[25]Es sei aber erwähnt, daß auch fünfzählige Symmetrie in der LFT eine Rolle spielen kann, zum Beispiel in Cyclopentadienyl- und in ikosaedrisch koordinierten f-Element-Komplexen.

Orbitale nur die geraden Darstellungen zu berücksichtigen. Deren Charakterensystem wiederum zerfällt bezüglich der Klassen in zwei Blöcke: Der erste gehört zu den eigentlichen Drehungen, die eine Untergruppe bilden, der zweite zu den uneigentlichen Drehungen, die aus ersteren durch Verknüpfung mit Inversion hervorgehen. Da beide Blöcke identisch sind, reicht es aus, wenn man nur den betrachtet, der aus der Untergruppe der eigentlichen Drehungen besteht. Daraus ergibt sich: Eine Charakterisierung von Wellenfunktionen, die aus d-Orbitalen bestehen, ist auch dann noch eindeutig, wenn man statt der oben aufgeführten holoedrischen Punktgruppen die aus nur halb sovielen Elementen bestehenden reinen Drehgruppen $\mathcal{O}$, $\mathcal{D}_4$, $\mathcal{D}_3$, $\mathcal{D}_2$, $\mathcal{C}_2$ und $\mathcal{C}_1$ heranzieht; bei einem Hamiltonoperator mit Spin-Bahn-Kopplung sind die entsprechenden Doppelgruppen heranzuhiehen. Betrachtet man die Charakterentafeln dieser Gruppen, dann erkennt man, daß zur eindeutigen Bestimmung einer irreduziblen Darstellung über die Charaktere gar nicht alle Drehungen benötigt werden, sondern daß die Kenntnis der Charaktere zu höchstens zwei Klassen bzw. repräsentativen Drehoperatoren aus diesen Klassen genügt. Wählt man das Koordinatensystem so, daß die Hauptdrehachse mit der z-Achse und von eventuell vorhandenen $\mathbf{C}_2'$-Achsen eine mit der x-Achse zusammenfällt, dann wird das auf den vier Drehungen $\mathbf{C}_4^z$, $\mathbf{C}_3^z$, $\mathbf{C}_2^z$ und $\mathbf{C}_2^x$ basierende Schema der Tabelle 1 anwendbar.

Table 1: Repräsentative Drehungen zur Identifizierung irreduzibler Darstellungen

	$\mathcal{O}$	$\mathcal{D}_4$	$\mathcal{D}_3$	$\mathcal{D}_2$	$\mathcal{C}_2$	$\mathcal{C}_1$
gewöhnliche Gruppe oder eindeutige Darstellungen der Doppelgruppe	$\mathbf{C}_4^z, \mathbf{C}_2^x$	$\mathbf{C}_4^z, \mathbf{C}_2^x$	$\mathbf{C}_2^x$	$\mathbf{C}_2^z, \mathbf{C}_2^x$	$\mathbf{C}_2^z$	$-^a$
zweideutige Darstellungen der Doppelgruppe	$\mathbf{C}_4^z$	$\mathbf{C}_4^z$	$\mathbf{C}_3^z$	$-^a$	$-^a$	$-^a$

^{a}Keine Unterscheidung erforderlich

Anwendungen des Konzepts der holoedrischen Symmetrie von Übergangsmetallkomplexen auf Strukturtypen, die besonders häufig vorkommen oder auffällige Symmetrieeigenschaften haben, sind in Tabelle 2 zusammengestellt. Sie enthält mehrere Beispiele, die zeigen, daß Strukturen, die zur gleichen Punktgruppe gehören, unterschiedliche holoedrische Symmetrien aufweisen können. So haben ein facial trisubstituierter Oktaeder und ein trigonal verzerrter Tetraeder zwar beide $\mathcal{C}_{3v}$-Symmetrie, führen aber dennoch zu verschiedenen holoedrischen Punktgruppen ($\mathcal{O}_h$ bzw. $\mathcal{D}_{3d}$). Um dies zu verstehen, muß man beachten, daß man die holoedrische Symmetrie nicht durch Direktproduktbildung der Punktgruppe des Moleküls mit $\mathcal{C}_i$ erhält (dies würde in beiden Fällen $\mathcal{D}_{3d}$ ergeben), sondern durch Mittelung des Potentials mit seinem punktsymmetrischen Spiegelbild gemäß Gl. (9), was beim facial trisubstituierten Oktaeder wegen der Orthoaxialität zu $\mathcal{O}_h$ führt. Wie dieser Fall zeigt, kann der Prozeß der Holoedrisierung also eine

versteckte höhere Symmetrie (Pseudosymmetrie) zum Vorschein bringen. Ein weiteres, häufig vorkommendes Beispiel hierfür ist der *cis*-disubstituierte Oktaeder mit $\mathcal{C}_{2v}$-Symmetrie. Holoedrisierung, die im allgemeinen von $\mathcal{C}_{2v}$ nur nach $\mathcal{D}_{2h}$ führt, ergibt hier $\mathcal{D}_{4h}$, wiederum als Folge der orthoaxialen Koordination. Im Molekülorbitalbild ist das Holoedrie-Konzept nicht mehr streng gültig, doch folgt aus Hartree-Fock-Rechnungen, zum Beispiel an mono- und disubstituierten $Co(CN, OH)$-Verbindungen, daß die holoedrische Symmetrie bei der Berechnung der Energie elektronischer Übergänge eine recht gute Näherung darstellt. Ein bekanntes Beispiel für den Erfolg dieser Näherung ist die (unter anderem) auf dem Holoedriekonzept basierende Aussage Perumareddis, daß die Differenz zwischen axialem und äquatorialem Ligandenfeldpotential sich vom monosubstituierten über den *cis*- zum *trans*-disubstituierten Oktaeder im Verhältnis $1 : -1 : 2$ ändern sollte [8]. Unter dieser Prämisse von Perumareddi, *loc. cit.*, berechnete Anregungsenergien sind in gutem Einklang mit den optischen Spektren zahlreicher $Cr(III)$-Verbindungen.[26] Recht interessant sind die Verhältnisse bei tris-Chelatkomplexen: Handelt es sich beim Chelatliganden um ein konjugiertes π-System, zum Beispiel Oxalat oder Acetylacetonat, dann ist die Elektronenstruktur der koordinierenden Atome stark anisotrop, eventuell sogar auch phasengekoppelt. Die holoedrische Symmetrie kann in einem solchen Fall nicht höher sein als $\mathcal{D}_{3d}$. Anders hingegen ist die Situation bei tris-Chelaten mit rein σ-bindenden, isotropen Liganden wie Ethylendiamin. Solche Komplexe können oft in guter Näherung als pseudooktaedrisch angesehen werden.

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[26]Das Holoedriekonzept erlaubt jedoch keine Aussagen zur Intensität von *dd*-Übergängen, denn es sind ja gerade die Abweichungen von der Inversionssymmetrie, die durch Aufhebung des Paritätsverbotes solche Übergänge ermöglichen.

Table 2: Holoedrische Symmetrieen von Komplexstrukturen

	Punktgruppe	holoedrische Punktgruppe	Drehgruppe
Oktaederstrukturen			
MA_6, kubisch	$\mathcal{O}_h$	$\mathcal{O}_h$	$\mathcal{O}$
MA_6, entlang $\mathbf{C}_3$ verzerrt	$\mathcal{D}_{3d}$	$\mathcal{D}_{3d}$	$\mathcal{D}_3$
MA_6, um $\mathbf{C}_3$ verdrillt	$\mathcal{D}_3$	$\mathcal{D}_{3d}$	$\mathcal{D}_3$
$M(A-A)_3$	$\mathcal{D}_3$	$\mathcal{D}_{3d}$, $\mathcal{O}_h$	$\mathcal{D}_3$, $\mathcal{O}$
MA_5B, orthoaxial	$\mathcal{C}_{4v}$	$\mathcal{D}_{4h}$	$\mathcal{D}_4$
MA_4B_2, orthoaxial, *cis*	$\mathcal{C}_{2v}$	$\mathcal{D}_{4h}$	$\mathcal{D}_4$
MA_4B_2, orthoaxial, *trans*	$\mathcal{D}_{4h}$	$\mathcal{D}_{4h}$	$\mathcal{D}_4$
MA_3B_3, orthoaxial, *fac*	$\mathcal{C}_{3v}$	$\mathcal{O}_h$	$\mathcal{O}$
MA_3B_3, orthoaxial, *mer*	$\mathcal{C}_{2v}$	$\mathcal{D}_{2h}$	$\mathcal{D}_2$
Tetraederstrukturen			
MA_4, kubisch	$\mathcal{T}_d$	$\mathcal{O}_h$	$\mathcal{O}$
MA_4, entlang $\mathbf{S}_4$ verzerrt	$\mathcal{D}_{2d}$	$\mathcal{D}_{4h}$	$\mathcal{D}_4$
MA_4, um $\mathbf{S}_4$ verdrillt	$\mathcal{C}_{2v}$	$\mathcal{D}_{2h}$	$\mathcal{D}_2$
MA_4, entlang $\mathbf{C}_3$ verzerrt	$\mathcal{C}_{3v}$	$\mathcal{D}_{3d}$	$\mathcal{D}_3$
planare Strukturen			
MA_4, quadratisch	$\mathcal{D}_{4h}$	$\mathcal{D}_{4h}$	$\mathcal{D}_4$
MA_4, rechteckig	$\mathcal{D}_{2h}$	$\mathcal{D}_{2h}$	$\mathcal{D}_2$
MA_2B_2, rechteckig, *cis*	$\mathcal{C}_{2v}$	$\mathcal{D}_{2h}$	$\mathcal{D}_2$
MA_2B_2, rechteckig, *trans*	$\mathcal{C}_{2h}$	$\mathcal{C}_{2h}$	$\mathcal{C}_2$

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