Operators and the MCTDH Program.

Graham Worth

King's College London

- The ascii representation of an operator
- The machine representation of an operator
- MCTDH - What is so complicated?
- The op.log file

General structure of an operator

$$H = \sum_{\kappa} h_{\kappa} + \sum_{n} c_n h_n^{(1)} \cdots h_n^{(f)} + V(q_1 \ldots q_f)$$

An operator is a sum of *terms*, which are products of *factors*.
Terms and factors are themselves operators.

Distinguish between:
uncorrelated (separable) operators
correlated (non-separable) operators

Distinguish between:
one-dimensional operator
mode operator
multi-dimensional operator

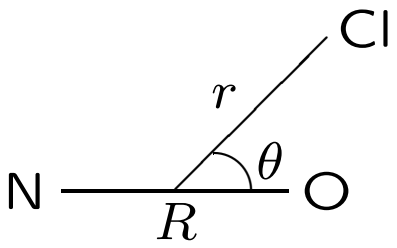
Distinguish between:
grid-based operators (require a representation)
analytic operators (e.g. potentials)

For efficiency:
1. potential operators should be multiplied out where possible
2. matrix operators should be kept 1-D
3. terms summed where possible.

Jacobi Coordinates, $\hat{J} = 0$

$$\hat{H} = -\frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r}\frac{\partial^2}{\partial r^2} - \frac{1}{2I_\theta}\overbrace{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}}^{j^2} + V(R,r,\theta)$$

$$\frac{1}{I_\theta} = \frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2}$$




```
OP_DEFINE-SECTION
title
NOCl S1 surface
end-title
end-op_define-section

PARAMETER-SECTION
mass_rd = 16.1538, AMU
mass_rv =  7.4667, AMU
end-parameter-section

HAMILTONIAN-SECTION
-----------------------------------------
modes          |  rd     |  rv     | theta
-----------------------------------------
0.5/mass_rd    |  q^-2   |  1      |  j^2
0.5/mass_rv    |  1      | q^-2    |  j^2
-0.5/mass_rd   |  dq^2   |  1      |   1
-0.5/mass_rv   |  1      |  dq^2   |   1
1.0            |1&2&3  V
-----------------------------------------
end-hamiltonian-section

LABELS-SECTION
V = nocl1sch
end-labels-section

end-operator
```

For NOCI photodissociation, CAP added in input file

```
OPERATOR-SECTION
opname = nocl1
alter-labels
CAP_rd = CAP [ 5.0 0.3 3 ]   # starting point, strength, order
end-alter-labels
end-operator-section
```

— — NOCI op.log file — —

```
***** Operator details *****

DOF no.    label
    1       rd
    2       rv
    3       theta

Mode no.    DOF no.
    1         1
    2         2
    3         3

Information for Hamiltonian : system

Total no. of terms      :    6
No. of correlated terms :    3

No. of uncorrelated terms for mode   1:    2
No. of uncorrelated terms for mode   2:    1
No. of uncorrelated terms for mode   3:    0

  Parameters
PI                    3.141592653590
mass_rd           29446.600482000000
mass_rv           13610.972763000000
```

— — NOCI op.log file 2 — —

```
  Operator Labels
Label                                 function no.  file no.
1                                            1       302
-1                                          23       302
I                                            1       101
0.5                                          0       301
mass_rd^-1                                   2       301
q^-2                                         3       302
j^2                                          5         3
mass_rv^-1                                   3       301
dqdvr^2                                      4         3
nocl1sch                                     8       201
CAP[1]                                       3       101

Hamiltonian Operator Terms
 No.    f    m   md Typ Sym
   1    1    0    0   1    1    1
   2    2    0    0   1    1    1
   3    3    0    0   1    1    1
   4    K    0    0   1    1    1
   6    1    0    0   2    1    q^-2*0.5*mass_rd^-1
   7    3    0    0   8    1    j^2
   9    2    0    0   2    1    q^-2*0.5*mass_rv^-1
  11    1    0    0   8    1    dqdvr^2*-1*0.5*mass_rd^-1
  13    2    0    0   8    1    dqdvr^2*-1*0.5*mass_rv^-1
  14    0    0    1   2    1    nocl1sch
  15    1    0    0   3   -1    CAP[1]

Arguments for operators
  No.    Arguments
    1       5.000000       0.300000       3.000000       0.000000       0.00

Coordinate sets for multi-dimensional operators
 No.    Size       Dofs
    1  51840  rd        rv        theta
```

— — NOCI op.log file 3 — —

```
Correlated Terms
dof order =  rd, rv, theta,
   k  ki  kf coeff   No.s
   1   1   1    4       6    2    7
   2   1   1    4       1    9    7

Multi-D terms present
   k  ki  kf coeff   No.s
   3   1   1    4      14

Uncorrelated Terms
   k   m   s coeff   No.s
   4   1   1    4      11
   5   1   1    4      15
   6   2   1    4      13

**** Non-hermitian operators ****
     Hermitian      =  1
     Anti-Hermitian = -1

   k  ki  kf coeff   No.s
   5   1   1    1      -1    1    1
```

A 2D - 2 state Model with a conical intersection

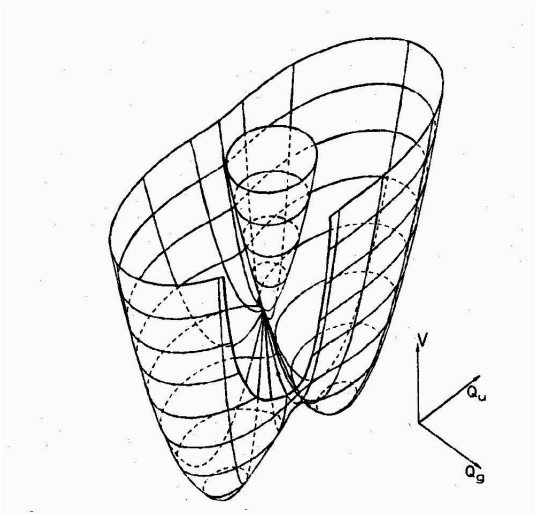
$$\mathbf{H} = \sum_i \frac{\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \begin{pmatrix} \kappa_{6a}^{(1)} & 0 \\ 0 & \kappa_{6a}^{(2)} \end{pmatrix} Q_{6a} + \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} Q_{10a}$$

```
OP_DEFINE-SECTION
title
Pyrazine 2-mode model, linear coupling.
end-title
end-op_define-section

PARAMETER-SECTION
w10a   = 0.09357, ev      w6a    = 0.0740 , ev
delta  = 0.46165, ev      lambda = 0.1825 , ev
k6a1   =-0.0964 , ev      k6a2   = 0.1194 , ev
end-parameter-section

HAMILTONIAN-SECTION
-------------------------------------
    modes       |  el   | v10a | v6a
-------------------------------------
1.0*w10a        | 1     | KE   | 1
0.5*w10a        | 1     | q^2  | 1
1.0*w6a         | 1     | 1    | KE
0.5*w6a         | 1     | 1    | q^2
-delta          | S1&1  | 1    | 1
delta           | S2&2  | 1    | 1
lambda          | S1&2  | q    | 1
k6a1            | S1&1  | 1    | q
k6a2            | S2&2  | 1    | q
-------------------------------------
end-hamiltonian-section

end-operator
```



Multiple electronic states

In MCTDH, 2-possibilities
1. Single-set

$$\Psi = \sum_J A_J \varphi_{j_1}^{(1)} \cdots \varphi_{j_f}^{(f)} \varphi_{j_{el}}^{(el)}$$

f+1 degrees of freedom

$$\varphi_1^{(el)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \varphi_2^{(el)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

In this case, operators on electronic DOF are matrices, e.g.

$$h_n^{(el)} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Simpler, but longer expansion

2. Multi-set

$$\Psi = \sum_\alpha \sum_J A_J^{(\alpha)} \varphi_{j_1}^{(1,\alpha)} \cdots \varphi_{j_f}^{(f,\alpha)}$$

Hamiltonian terms now indexed with $H^{(\alpha\beta)}$ and operate only on relevant parts of wavefunction.

Shorter wavefunction expansion, but more complicated as $\langle \varphi_i^{(\alpha)} \mid h_n^{(\alpha\beta)} \mid \varphi_j^{(\beta)} \rangle$ matrices not square.

2D Pyrazine op.log file : Multiset

```
***** Operator details *****

DOF no.    label
    1       v10a
    2       v6a
    3       el

Mode no.    DOF no.
    1         1
    2         2

Information for Hamiltonian : system

Total no. of terms      :    8
No. of correlated terms :    4

No. of correlated terms :    4

No. of uncorrelated terms for mode   1  state  1:    1
No. of uncorrelated terms for mode   1  state  2:    1
No. of uncorrelated terms for mode   2  state  1:    1
No. of uncorrelated terms for mode   2  state  2:    1

  Parameters
PI                    3.141592653590
w10a                  0.003438632338
w6a                   0.002719448466
delta                 0.016965316007
lambda                0.006706747907
k6a1                 -0.003542632867
k6a2                  0.004387866850
```

— — 2D pyrazine op.log file: Multiset 2 — —

Operator Labels

Label	function no.	file no.
1	1	302
-1	23	302
I	1	101
w10a	2	301
KEdvr	1	3
0.5	0	301
q^2	3	302
w6a	3	301
delta	4	301
S1&1	9	3
S2&2	9	3
lambda	5	301
S1&2	9	3
q	2	302
k6a1	6	301
k6a2	7	301
S2&1	9	3

Hamiltonian Operator Terms

No.	f	m	md	Typ	Sym	
1	1	0	0	1	1	1
2	2	0	0	1	1	1
3	3	0	0	1	1	1
4	K	0	0	1	1	1
13	K	0	0	2	1	-1*delta
15	K	0	0	2	1	delta
17	K	0	0	2	1	lambda
19	1	0	0	2	1	q
24	1	0	0	8	1	KEdvr*1*w10a + q^2*0.5*w10a
25	2	0	0	8	1	q*k6a1 + KEdvr*1*w6a + q^2*0.5*w6a
26	2	0	0	8	1	q*k6a2 + KEdvr*1*w6a + q^2*0.5*w6a

— — 2D pyrazine op.log file: Multiset 3 — —

```
Correlated Terms
dof order =  v10a, v6a,
   k  ki  kf coeff   No.s
   1   1   1   13       1    2
   2   2   2   15       1    2
   3   1   2   17      19    2
   4   2   1   17      19    2

Uncorrelated Terms
   k   m   s coeff   No.s
   5   1   1    4      24
   6   1   2    4      24
   7   2   1    4      25
   8   2   2    4      26

**** Non-hermitian operators ****
     Hermitian      =  1
     Anti-Hermitian = -1

   k  ki  kf coeff   No.s
   3   1   2    1       0    0
   4   2   1    1       0    0
```

2D Pyrazine op.log file : Single-set

```
***** Operator details *****

DOF no.    label
    1       v10a
    2       v6a
    3       el

Mode no.    DOF no.
    1         1
    2         2
    3         3

Information for Hamiltonian : system

Total no. of terms      :    5
No. of correlated terms :    2

No. of correlated terms :    2

No. of uncorrelated terms for mode   1:    1
No. of uncorrelated terms for mode   2:    1
No. of uncorrelated terms for mode   3:    1

  Parameters
PI                    3.141592653590
w10a                  0.003438632338
w6a                   0.002719448466
delta                 0.016965316007
lambda                0.006706747907
k6a1                 -0.003542632867
k6a2                  0.004387866850
```

— — 2D pyrazine op.log file: Single-set 2 — —

```
Hamiltonian Operator Terms
 No.   f   m  md Typ Sym
   1   1   0   0   1   1    1
   2   2   0   0   1   1    1
   3   3   0   0   1   1    1
   4   K   0   0   1   1    1
  18   3   0   0   8   1    S1&2
  19   1   0   0   2   1    q*lambda
  21   2   0   0   2   1    q
  23   1   0   0   8   1    KEdvr*1*w10a + q^2*0.5*w10a
  24   2   0   0   8   1    KEdvr*1*w6a + q^2*0.5*w6a
  25   3   0   0   2   1    S1&1*-1*delta + S2&2*delta
  26   3   0   0   2   1    S1&1*k6a1 + S2&2*k6a2

Correlated Terms
dof order =  v10a, v6a, el,
   k  ki  kf coeff   No.s
   1   1   1    4      19    2   18
   2   1   1    4       1   21   26

Uncorrelated Terms
   k   m   s coeff   No.s
   3   1   1    4      23
   4   2   1    4      24
   5   3   1    4      25
```

2D Pyrazine op.log file : Exact

```
***** Operator details *****

DOF no.    label
    1       v10a
    2       v6a
    3       el

Mode no.    DOF no.
    1         1,    2

Information for Hamiltonian : system

Total no. of terms      :    8
No. of correlated terms :    4

No. of correlated terms :    4

No. of uncorrelated terms for mode   1  state  1:    2
No. of uncorrelated terms for mode   1  state  2:    2

  Parameters
PI                    3.141592653590
w10a                  0.003438632338
w6a                   0.002719448466
delta                 0.016965316007
lambda                0.006706747907
k6a1                 -0.003542632867
k6a2                  0.004387866850
```

— — 2D pyrazine op.log file: Exact 2 — —

Hamiltonian Operator Terms

No.	f	m	md	Typ	Sym	
1	1	0	0	1	1	1
2	2	0	0	1	1	1
3	3	0	0	1	1	1
4	K	0	0	1	1	1
13	K	0	0	2	1	-1*delta
15	K	0	0	2	1	delta
17	K	0	0	2	1	lambda
19	1	0	0	2	0	q
24	1	0	0	8	1	KEdvr*1*w10a + q^2*0.5*w10a
25	2	0	0	8	1	q*k6a1 + KEdvr*1*w6a + q^2*0.5*w6a
26	2	0	0	8	1	q*k6a2 + KEdvr*1*w6a + q^2*0.5*w6a
27	0	1	0	1	1	(1)*(2)
28	0	1	0	2	1	(19)*(2)

Correlated Terms

dof order = v10a, v6a,

k	ki	kf	coeff	No.s
1	1	1	13	27
2	2	2	15	27
3	1	2	17	28
4	2	1	17	28

Terms

k	m	s	coeff	No.s	
5	1	1	4	1	25
6	1	1	4	24	2
7	1	2	4	1	26
8	1	2	4	24	2

Operator representation in the program

3 levels:

hamilton(f,k) = h	Hamiltonian terms
hterm(nh,h) = hl	operators
hoplab(hl)	labels

Associated information with indices k, h, hl

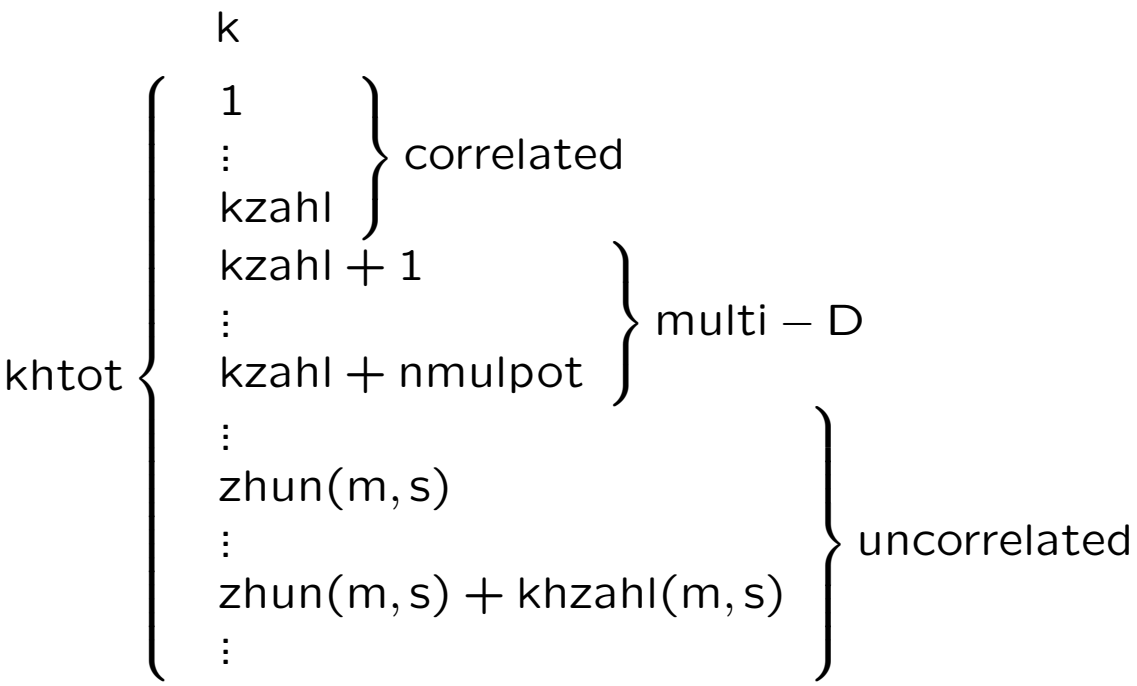
See operdef.inc, arrays dimensioned with maxkoe, maxhtm, maxhop.

Hamilton(f,k)

fkoe, ftime: "DOF" for coefficient and time

ki(k), kf(k)	indices for state labels (multi-set) $\langle \Phi^{(kf)} \mid H_k^{(kf,ki)} \mid \Phi^{(ki)} \rangle$
hsym(m,k)	symmetry flag for operator
diag(m,k)	if .true., unit operator
kact(k)	type of operator (for dissipative operators)

....



Multiple operators add index to kzahl, nmulpot, zhun, khzahl, khtot.
labelled by hamlab(n), n=1,nham
k = zham(n), zham(n)+khtot(n)
hamlab(1) = 'system'
ktot = $\sum$khtot

Hterm(nh,h)

Integers defining operator h, pointing to labels in hoplab
$1 <$ nh $<$ htmfac(h)
htmfac(h) no. of factors in operator.

e.g. for `dqdvr^2*-1*0.5*mass_rd^-1` with

```
hoplab(2) = -1
hoplab(4) = 0.5
hoplab(5) = mass_rd^-1
hoplab(9) = dqdvr^2
```

then

```
htmfac(h) = 4
hterm(1,h) = 9, hterm(2,h) = 2, hterm(3,h) = 4,
     hterm(4,h) = 5
```

If operator is sum of terms, e.g.
`KEdvr*1*w10a + q^2*0.5*w10a`
terms separated in list by 0. Here htmfac(h)=7

htmdof(h), htmmode(h), htmmuld(h)

One of these integers is non-zero and indicates the co-ordinates.

htmdof(h) = f	One-D operator on DOF f
htmmode(h) = m	mode operator on mode m
htmmuld(h) = muld	multi-D operator with coordinates defined in mulddof(n,muld)

htmform(h)

If set to 1, hterm(nh,h) integers point to other hterm operators rather than hoplab.

htmsym(h)

Symmetry of operator.

1 hermitian

-1 anti-hermitian

htmtype(h)

Type of operator. See genoper/asshop.F

```
#######################################################################
C
C ASSIGNHOP
C
C assigns the type of operator
C
C hopz:    operator matrix
C
C hoptype: type of matrix, from folowing list
C 1D types
C 0 = zero
C 1 = unit
C 2 = real vector (diagonal matrix)
C 3 = imaginary vector (imaginary part stored as real)
C 4 = complex vector
C 5 = FFT, real vector
C 6 = FFT, imaginary vector
C 7 = FFT, complex vector
C 8 = real matrix
C 9 = imaginary matrix (imaginary part stored as real)
C 10 = complex matrix
C 2D combined-mode types
C 17 = real 3D tensor (for jm^2)
C 18 = real 3D tensor (for j_p)
C 19 = real 3D tensor (for j_m)
C
C analytic potential
C 101 = multi-dimensional real diagonal analytic
C
C#######################################################################
```

hoplab(hl)

Defines function used to build up operators.

hopilab(hl), hopifile(hl),
define where function is in OPFUNCS library
hopipar(n,hl), hoprpar(n,hl)
associate parameters with function, e.g. CAP[a,b,c]

The OPFUNCS library

File nos.	Description
1-100	Operators defined only on a grid (non-local operators, natural potentials etc.).
101-200	Complex analytic functions.
201-300	Multi-dimensional potential energy surfaces.
301-400	Real analytic functions.

hopifile(hl)	File name	Description
1		diagonal potentials from file
2		non-diagonal potentials from file
3	funcgrd	1D non-local operators
101	funczanl	1D complex analytic functions
201	callsrf	multi-dimensional PES
301		real number
302	funcanl	1D analytic functions
303	func1d	1D potential energy curves

hopilab(hl) defines which operator in file

From opfuncs/funcgrd.f

```
C######################################################################
C ifile = 3
C######################################################################

      subroutine fdefgrd(hopilab,hoplab,hopfile,hlabipar,hlabrpar,
     +           hoppar,maxhpar)
....
C----------------------------------------------------------------------
C assign function number
C----------------------------------------------------------------------
      if (hoplab .eq. 'KEdvr') then
         hopilab=1

....

      else if (hoplab .eq. 'dqdvr^2') then
         hopilab=4

....

C######################################################################

      subroutine funcgrd(hmat,gdim,ifunc,ipar,rpar,mass,d1mat,d2mat,
     +           kinsph,fftp,ort,sphdim)

....
      go to (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17) ifunc

C KEdvr
    1 call kedvrterm(d2mat,hmat,mass,gdim)
      return
....
C dqdvr^2
    4 call cpqxdz(d2mat,hmat,gdim)
      return
```

Overview of Build algorithm

Part I. genoper/heingabe.F (called from mctdh/eingabe.F) reads .op file and makes initial set-up of arrays.

1. reads parameters from .par / .op files, loads into apar(n), rpar(n) arrays (parameters in .inp file already read in einoper).

2. reads HAMILTONIAN-SECTION.
   - breaks up operator keyword to find factors.
   - Stores unique factors in hoplab(hl).
   - Stores unique operator in hterm(nh,h), and associates with coordinates
   - Stores hamilton(f,k)

3. reads any definitions in LABELS-SECTIONS (those in alter-labels already read in einoper)

Now ready for manipulations of operator.
New labels, operators, terms added to arrays.
Redundant terms removed from hamilton.

4. labels substituted / expanded with definitions. Expansions occur for potfit /srf files.

5. alterations made for electronic basis:
   - if multi-set expand 1, mirror S1&2, etc.

6. Labels assigned to functions in library.

Part II. genoper/runoper.F (called from mctdh.F)
After heingabe, memory can be allocated. The operators can then be built, typed, and further sorted.

1. Types hterm operators
   - using information from hoplabs, e.g. product of factors from analytic functions is a "real vector"
   - OR sets up operator matrix and sees what it is

2. Sums up uncorrelated terms of same type. (e.g. DVR and FFT cannot be mixed)
   $$\left.\begin{array}{ccc} k_1 & | & A \\ k_2 & | & B \end{array}\right\} \quad \begin{array}{ccc} 1 & | & 1 \\ k_1 A + k_2 B & | & 1 \end{array}$$
   Types any new operators

3. Sums up (product) correlated terms
   $$\left.\begin{array}{ccc} k_1 & | & A \\ k_2 & | & B \end{array}\right\} \quad \begin{array}{ccc} 1 & | & C \\ k_1 A + k_2 B & | & C \end{array}$$
   Types any new operators

4. Pack coefficients into operators
   $$\left.\begin{array}{ccc} k_1 & | & A \\ k_2 & | & A \end{array}\right\} \quad \begin{array}{ccc} 1 & | & k_1 C \\ k_2 & | & 1 \end{array}$$
   Types any new operators

5. Sets up product mode operators for combined modes
   $$\left.\begin{array}{ccc} k_1 & | & A \\ k_2 & | & B \end{array}\right\} \quad \begin{array}{ccc} k_1 & | & C \\ k_2 & | & D \end{array} \quad \begin{array}{ccc} k_1 & | & AC \\ k_2 & | & BD \end{array} \quad \begin{array}{ccc} | & 1 \\ | & 1 \end{array}$$
   Types any new operators

6. Tries to sum terms again.
$$\left.\begin{array}{ccc} k_1 & | & AC \\ k_2 & | & BD \end{array}\right\} \quad 1 \quad | \quad k_1 AC + k_2 BD \quad | \quad 1$$
Types any new operators

7. Set up operators and write to tmp file

8. Delete any zero terms

9. Order hamilton array

10. Set up pointers for hops array
Write oper file.

End result is oper file.

hamilton(f,k) represents Hamiltonian,

hops(zhop(h)) is representation of operator hterm(h).

Analytic operators (time-dependent, CDVR PES) have no hops representation, but can be calculated on the fly from hterm(h)

From subroutine hop (propwf/hphi.F)

```
      subroutine hop (f,k,hpsi,psi,hops,subdim1,fftfak,hin,rueck,
     +           exphin,exprueck,vec,workc)
....
      real*8     hops(hopsdim)
      complex*16 hpsi(subdim1),psi(subdim1)
....
C-----------------------------------------------------------------------
C Go to selected operator
C-----------------------------------------------------------------------
      h=hamilton(f,k)
      goto (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19) htmtype(h)

      routine='Hop'
      write(message,'(a,i5)')  'Unknown htmtype :',htmtype(h)
      call errormsg

    1 call cpvxz(psi,hpsi,subdim1)
      return

    2 if (htmdof(h) .gt. 0) then
         call dtxxdz(hops(zhop(h)),psi,hpsi,vgdim(f),gdim(f),ngdim(f))
      else
         call dvxxdz(hops(zhop(h)),psi,hpsi,subdim1)
      endif
      return

....
    8 if (htmdof(h) .gt. 0) then
         call qtxxdz(hops(zhop(h)),psi,hpsi,vgdim(f),gdim(f),ngdim(f))
      else
         call qvxxdz(hops(zhop(h)),psi,hpsi,subdim1)
      endif
      return
```