



VCMaker

User Manual v1.0

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VCMaker PROJECT

[HTTPS://JULIENENG.GITHUB.IO/VCMaker/](https://julieneng.github.io/VCMaker/)

XXXXX.

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1. General considerations

1.1 How to cite?

There is currently no way of properly citing VCMaker.

1.2 Acknowledgments

J.Eng would like to thank Dr. Conor D. Rankine, Dr. Thomas J. Pope and Clelia Middleton for their involvement in testing VCMaker, correcting the manual and for their amazing feedback.

1.3 Philosophy of VCMaker

VCMaker doesn't aim to be a code for quantum chemistry, but rather a tool that makes the link between quantum mechanics and quantum dynamics. Transparency is key and therefore all efforts are made to explicitly show the unit system in which data is output. In addition, you can find in this manual a complete description of the theory that is used within VCMaker.



2. VConverter

2.1 What is VConverter?

VConverter is a set of utilities that allows for easy conversion of the Hessian and Gradient between outputs generated by quantum chemistry codes and VCMaker format.

Having a separate code to convert calculation output to a format suitable for VCMaker allows us to:

- (1) keep the VCMaker code easy to read and understand
- (2) simplify the extension of compatibility to other codes.

2.2 Compatibility

At the moment, VConverter is able to convert from ORCA output format to VCM format (see below).

2.3 VCM Format

2.3.1 Cartesian Gradient

The Cartesian Gradient is to be provided not mass-weighted and in the following format:

```
[G_1]  
[G_2]  
...  
[G_k]
```

where $k = 3n$ and all elements are given as floating point numbers.

2.3.2 Cartesian coordinates

Cartesian coordinates are to be given in the XYZ format:

```
[n]

[label_1] [x_1] [y_1] [z_1]
[label_2] [x_2] [y_2] [z_2]
...
[label_n] [x_n] [y_n] [z_n]
```

where `[n]` is the number of atoms, `[label_n]` is the atomic symbol of the element and `[x_n]`, `[y_n]` and `[z_n]` are the Cartesian coordinates in floating point format.

2.3.3 Cartesian Hessian

The Cartesian Hessian is to be provided not mass weighted and in the following format:

```
[H_11] [H_12] [H_13] ... [H_1k]
[H_21] [H_22] [H_23] ... [H_2k]
...
[H_k1] [H_k2] [H_k3] ... [H_kk]
```

where $k = 3n$ and all elements are given as floating point numbers.



3. VCMaker

3.1 Job list

At this stage in the development of VCMaker, the following jobs can be requested:

- LVC_GRAD: Determination of the intrastate coupling parameters (κ) from the Cartesian gradients of the potential energy.
- LVC_DISP: Determination of the intrastate coupling parameters (κ) from the excited state displaced geometry.
- LVC_GAP: Analysis of the anharmonicity of one or several states using the Global Anharmonicity Parameter (GAP) and the decomposition in terms of Relative Single Mode Anharmonicity (RSMA).
- LVC_LAMBDA: Determination of the interstate coupling parameters (λ) from the excited states Hessian matrices at Franck-Condon.
- DNC_SCAN: Generation of displaced geometries for the scan along the dimensionless normal coordinates (DNC) of given normal modes.
- DNC_DIAG: (*Requires* DNC_SCAN) Generate geometries along linear combination of two normal modes.
- DNC_GRID: Generate a N-Dimension grid of distorted geometries.
- GEN_XYZ: Generation of a single displaced geometry along a given number of normal modes.

- `GEN_MIN`: (*Requires* `LVC_GRAD`) Build the theoretical minimum of a state from the within the displaced harmonic oscillator approximation at Franck-Condon.
- `OUT_QUANTICS`: (*Requires at least* `LVC_GRAD`, `LVC_DISP` or `LVC_LAMBDA`) Print an operator file for a Quantics[] calculation.

3.2 Worth knowing!

Any job keyword that is not specified is defaulted to FALSE. Job keywords and block specifications can be given in any order.

There can be NO blank line in a block specification but there can be any number of empty lines or any characters outside of them.

If files that are to be read are not contained in the input file directory, relative or full path should be given between double quotes.

3.3 Input architecture

VCMaker is designed with intent to minimise the requisite formatting when constructing input files. This approach ensures that VCMaker is compatible with any quantum chemistry software. For any kind of calculation, you need to provide the ground state geometry and the ground state Cartesian Hessian. This is done by including the following keywords in the input file:

<code>GEOMETRY</code>	<code>filename.xyz.vcm</code>
<code>HESSIAN</code>	<code>filename.hess.vcm</code>

The type of job is defined by setting the appropriate keyword to True:

<code>LVC_Grad</code>	True/False
<code>LVC_Disb</code>	True/False
<code>LVC_Lambda</code>	True/False
<code>LVC_GAP</code>	True/False
<code>DNC_Scan</code>	True/False
<code>DNC_Diag</code>	True/False
<code>DNC_Grid</code>	True/False
<code>GEN_Xyz</code>	True/False
<code>GEN_Min</code>	True/False

Important: There cannot be any empty line within a command block (see hereafter).

Important too: Anything outside of a command block or after the last definition of a line is considered a comment.

3.3.1 LVC_Grad

When `LVC_Grad` is set to True, the following input block needs to be specified:

```
grad [n]
[file_1]
```

```
[file_2]
[file_n]
```

where `[n]` is the number of gradients that need to be projected onto the normal modes, and `[file_1]` to `[file_n]` are the files containing the gradients in the VCM format.

3.3.2 LVC_Disb

When `LVC_Disb` is set to `True`, the following input block needs to be specified:

```
disp [m]
[file_1]
[file_2]
[file_m]
```

where `[m]` is the number of gradients that need to be projected onto the normal modes, and `[file_1]` to `[file_m]` are the files containing the Cartesian coordinates in the XYZ format.

3.3.3 LVC_GAP

If `LVC_Grad` and `LVC_Disb` are set to `TRUE`, the floppiness analysis can be requested by setting `LVC_GAP` to `True`. Then the following input block needs to be specified:

```
gap [m]
[file_grad_1] [file_geo_1]
...
[file_grad_m] [file_geo_m]
```

where `[m]` is the number of gradients-geometry couples for which the floppiness analysis will be done, and `[file_grad_1]` to `[file_grad_m]` and `[file_geo_1]` to `[file_geo_m]` are the index of the gradient and geometries to be considered in the order they appear in the GRAD and DISP blocks, respectively.

3.3.4 LVC_Lambda

When `LVC_Lambda` is set to `True`, the following input block needs to be specified:

```
lambda [k]
[i_1] [j_1]
[i_2] [j_2]
[i_k] [j_k]
es_hessian [1]
[file_1] [e_1] [unit]
[file_2] [e_2] [unit]
[file_1] [e_1] [unit]
```

where `[k]` is the number of pair of electronic states for the computation of the interstate vibronic coupling λ . `[i]` and `[j]` are the indices of the electronic states forming each pair

of states.

`d[1]` is the number of excited-state hessian files and must be equal to the number of excited states involved in the calculation of λ . For example, if λ is estimated between S_1/S_2 , S_1/S_3 and S_2/S_3 , then `[1]` needs to be set to 3.

`[file_1]` and `[e_1]` are the files containing the molecular Hessian matrix in the VCM format and the energy of the electronic state, respectively. `[unit]` can be either eV or Eh.

3.3.5 DNC_Scan

When `DNC_Scan` is requested, the following input block needs to be specified:

```
SCAN [p]
[mode_1] [mode_2] ... [mode_p]
[n_pl_1] [n_pl_2] ... [n_pl_p]
[s_l_1] [s_l_2] ... [s_l_p]
[n_pr_1] [n_pr_2] ... [n_pr_p]
[s_r_1] [s_r_2] ... [s_r_p]
```

where `[p]` is the number of normal modes along which a scan is requested. if `[p]=ALL`, then geometries along all normal modes will be generated. In this case, the second line

```
[mode_1] [mode_2] ... [mode_p]
```

needs to be removed and only `[n_pl_1]`, `[s_l_1]`, `[n_pr_1]`, `[s_r_1]` needs to be specified. `[n_pl_p]` and `[n_pr_p]` are the number of points in each direction (negative and positive, respectively) and `[s_l_p]` and `[s_r_p]` are the dimensionless displacements between each points in each direction.

Geometries will be printed in directories named: `DNC_SCAN_#DNC1` under the name: `DNC#DNC1_#k` (where $\#k = 1, \dots, [n_pl_#DNC1] + [n_pr_#DNC1] + 1$).

3.3.6 DNC_Diag

If `DNC_Scan TRUE`, then an additional 2D scan can be requested by setting `DNC_Diag True`. Doing so requires no additional input. The generated geometries are defined as:

$$Q_i = Q_0 - \left[([n_pl] - (i - 1)) \times [s_r_j] \delta Q^{(j)} \right] - \left[([n_pl] - (i - 1)) \times [s_r_k] \delta Q^{(k)} \right] \quad (3.1)$$

with $i = 1, \dots, [n_pl]$ where $[n_pl] = \text{MAX}([n_pl_j], [n_pl_k])$ and

$$Q_i = Q_0 + \left[i \times [s_r_j] \delta Q^{(j)} \right] - \left[i \times [s_r_k] \delta Q^{(k)} \right] \quad (3.2)$$

with $i = 1, \dots, [n_pr]$ where $[n_pr] = \text{MAX}([n_pr_j], [n_pr_k])$

Geometries will be printed in directories named: `DNC_SCAN_#DNC1_#DNC2` under the name: `DNC#DNC1_DNC#DNC2_#k` (where $\#k = 1, \dots, [n_pl] + [n_pr] + 1$).

3.3.7 DNC_Grid

When `DNC_Grid` is requested, the following input block needs to be specified:

```

Grid [p]
[mode_1] [mode_2] ... [mode_p]
[n_pl_1] [n_pl_2] ... [n_pl_p]
[s_l_1] [s_l_2] ... [s_l_p]
[n_pr_1] [n_pr_2] ... [n_pr_p]
[s_r_1] [s_r_2] ... [s_r_p]

```

See `DNC_SCAN` for details. Geometries will be written in `./DNC_GRID/`. A "distortion" file is written in `./DNC_GRID/DNC_GRID_OUTPUT.vcm`.

3.3.8 GEN_Xyz

When `GEN_Xyz` is set to true, the following input block needs to be specified:

```

gen [m]
[mode_1] [dQ_1]
...
[mode_m] [dQ_m]

```

where `[m]` is the number of normal modes to distort the geometry along, `[mode_1]` to `[mode_m]` are the indices of the normal modes and `[dQ_1]` to `[dQ_m]` are the distortion along modes 1 to m.

3.3.9 GEN_Min

When `GEN_Min` is set to true, the following input block needs to be specified:

```

min [m]
[mode_1] [mode_2] ... [mode_m]

```

where `[m]` is the number of normal modes to distort the geometry along, `[mode_1]` to `[mode_m]` are the indices of the normal modes.

3.3.10 OUT_Quantics

When `OUT_Quantics` is set to true, the following input block needs to be specified:

```

Quantics_mode [n]
[mode_1] [job_1]
...
[mode_n] [job_n]

Quantics_state [j]
[state_1] [de_1] [unit]
...
[state_j] [de_j] [unit]

```

where `[n]` and `[j]` are the numbers of normal modes and electronic states, respectively, to be included in the Hamiltonian.

[mode_1] to [mode_n] are the index of the normal modes and [job_1] to [job_n] can be either 'K': only κ along mode [mode_n] will be printed, 'L': only λ along mode [mode_n] will be printed, or 'KL': both κ and λ along mode [mode_n] will be printed. [state_1] to [state_j] are the index of the electronic states to be included in the Hamiltonian (as specified in LVC_Lambda if LVC_Lambda has been requested). [de_j] and [unit] are the vertical excitation energy and unit ('eV' or 'Eh') of the electronic state. [de_n] can be different from the energy specified in [LVC_Lambda] .

3.4 Output format

VCMaker output may get very long depending on the number of atoms of the system. To make navigating through the output easier, here is an example of the output file for each calculation type for the molecule of water.

Nota Bene: Modes indices are ranging from 1 to $3N-6$ where the mode with index 1 is the mode with the lowest non 0 frequency.

3.4.1 Job Summary

```
Job summary:
-----

LVC_GRAD.....True
  Number of gradients: 2
    1. s1.grad.vcm
    2. s2.grad.vcm

  GEN_MIN.....TRUE
    All modes are considered

LVC_DISP.....True
  Number of geometries: 2
    1. s1.xyz
    2. s2.xyz

LVC_LAMBDA....True
  Number of couplings: 1
    1. s1.hess.vcm and s2.hess.vcm
DNC_SCAN.....True
  Number of modes to scan: 2

      Modes to scan: 1    2
  Number of negative steps: 4    4
  Number of positive steps: 4    4
      Negative increment: 0.50 0.50
      Positive increment: 0.50 0.50
```

```

DNC_DIAG.....TRUE
DNC_GRID.....TRUE
  Number of modes to scan: 2

      Modes considered: 1  2
Number of negative steps: 4  4
Number of positive steps: 2  6
      Negative increment: 0.50 0.50
      Positive increment: 0.50 0.50

OUT_QUANTICS...False

```

3.4.2 Mass weighted normal modes

```

=====
-- Mass-weighted Normal Modes
=====

Mode:           7           8           9
  | x      -0.0000      0.0000     -0.0000
1 | y      -0.0000     -0.0000     -0.0706
  | z      -0.0710     -0.0494      0.0000
  | x       0.0000     -0.0000      0.0000
2 | y       0.4239     -0.5873      0.5600
  | z       0.5637      0.3923     -0.4288
  | x      -0.0000     -0.0000      0.0000
3 | y      -0.4239      0.5873      0.5600
  | z       0.5637      0.3923      0.4288

```

3.4.3 Dimensionless normal coordinates

```

=====
-- Dimensionless Normal Coordinates (DNC)
=====

Cartesian displacements in Bohr associated to each DNC

Mode:           7           8           9
  | x      -0.0000      0.0000     -0.0000
1 | y      -0.0000     -0.0000     -0.0118
  | z      -0.0186     -0.0086      0.0000
  | x       0.0000     -0.0000      0.0000
2 | y       0.1109     -0.1016      0.0939
  | z       0.1475      0.0679     -0.0719
  | x      -0.0000     -0.0000      0.0000
3 | y      -0.1109      0.1016      0.0939
  | z       0.1475      0.0679      0.0719

```

3.4.4 LVC Analysis from Cartesian gradients

```

=====
-- LVC Analysis from Gradients
=====

File: s1.grad.vcm

Mode   Freq / cm-1  Red.Mass | Kappa / meV  dE / meV    dQ
-----
   1    1622.36    0.92 |   -49.841    -0.227     0.248
   2    3850.94    0.96 |  -535.729   -11.045     1.122
   3    3958.57    0.92 |    0.001    -0.000    -0.000
-----
Sum of Energy shifts:                -0.307 eV
   Stokes shift:                       -0.613 eV

```

3.4.5 LVC Analysis from displaced geometries

```

=====
-- LVC Analysis from Displaced Geometries
=====

File: s1.xyz

Mode   Freq / cm-1  Red.Mass | Kappa / meV  dE / meV    dQ
-----
   1    1622.36    0.92 |  -166.686    -2.538     0.829
   2    3850.94    0.96 |   1029.977   -40.826    -2.157
   3    3958.57    0.92 |    0.144    -0.000    -0.000
-----
Sum of Energy shifts:                -1.180 eV
   Stokes shift:                       -2.360 eV

```

3.4.6 Interstate coupling parameter

```

=====
-- Interstate Vibronic Coupling
=====

File: s1.hess.vcm
File: s2.hess.vcm

Mode   Freq / cm-1  Red.Mass | Lambda / meV
-----
   1    1057.96    0.92 |   148.664
   2    3583.56    0.96 |   -90.686
   3    4360.16    0.92 |   421.276

```


3.5 Input Example

Here is an example of a stupidly complete input file. Note that every string preceded by a # is only a comment.

```
##### VCMaker Input #####

Geometry gs.xyz      #Geometry file
Hessian gs.hess.vcm #Formatted Hessian

#=== Job specification ===#
LVC_Grad      True
LVC_Dispatch  True
LVC_GAP       True
LVC_Lambda    True
DNC_Scan      True
GEN_XYZ       True
DNC_Grid      True
DNC_Diag      True
GEN_Min       True
OUT_Quantics  True
#=== End of Job list ===#

### Specification for LVC_Grad #####
Grad 2          #2 States
s1.grad.vcm     #Gradient of State 1
s2.grad.vcm     #Gradient of State 2
### Specification for GEN_Min #####
Min all         #Build the theo. geo. considering all DNC
### Specification for LVC_Dispatch #####
Disp 1          #1Geometry
s1.xyz          #XYZ of Geometry 1
### Specification for LVC_GAP # #####
GAP 1           #2 States
1 1             #First Gradient & 2nd Geometry
### Specification for LVC_Lambda #####
Lambda 1        #1 Coupling
1 2             #Between states 1 and 2
ES_HESSIAN 2    #Number of excited state Hessians
s1.hess.vcm 2.32 ev #Hessian of state 1, Energy and unit
s2.hess.vcm 2.45 ev #Hessian of state 2, Energy and unit
### Specification for DNC_Grid #####
Grid 2          #2 Dimensions
10 11          #Indices of DNC
```

```

5 5 #No of steps to the -ve direction
0.5 0.5 #dQ in the -ve direction
5 5 #No of steps to the +ve direction
0.5 0.5 #dQ in the -ve direction
### Specification for GEN_XYZ #####
Gen 2 #Distortion along 2DNC
8 0.3 #Index of mode 1 and dQ
10 0.5 #Index of mode 2 and dQ
### Specification for DNC_Scan #####
Scan 2 #Scan along two DNC
10 11 #Indices of the two modes
2 2 #No of steps to the -ve direction
0.5 0.5 #dQ in the -ve direction
2 2 #No of steps to the +ve direction
0.5 0.8 #dQ in the -ve direction
### Specification for OUT_Quantics #####
Quantics_mode 3
1 K
6 L
8 KL
Quantics_state 2
1 1.5 ev
2 1.8 ev

```

3.6 Acknowledgements

3.6.1 Credits pictures

- Front cover ??
- *Contents*: Hwangam Daechong, Gyeongju, South Korea: 35°50'20.4"N 129°12'39.2"E
- *General Considerations*: Sluice N°46 Channel Marne-au-Rhin, Wingersheimles-quatre-bancs, Alsace: 48°43'51.8"N 7°39'50.7"E
- *VConverter*: Fisherman's walk, Brodick, Isle of Arran, Scotland: 55°35'27.0"N 5°09'15.5"W
- *VCMaker*: Lamlash Golf Club, Lamlash, Isle of Arran, Scotland: 55°32'29.2"N 5°07'38.5"W