DQΦpac 21 Manual

Chad E. Hoyer, Kelsey A. Parker, Zoltan Varga, Laura Gagliardi, and Donald G. Truhlar

Department of Chemistry, University of Minnesota, Minneapolis, MN 555455-0431

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1. Licensing

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2. Introduction

DQΦpac 21 is a program for computing diabatic states and the diabatic potential energy matrix. Specifically, the program uses the N-electron dipole, quadrupole, electrostatic potential, and/or two-electron orbital angular momentum to compute an adiabatic-to-diabatic transformation matrix by way of the dipole-quadrupole-electrostatic-potential-two-electron-orbital-angular-momentum (DQΦL2) method.[1,2]

The function that is maximized to produce diabatic states is

$$f_{\text{DQΦL2}} = \sum_A \left(\gamma \left| \left\langle \phi_A \middle| \sum_p^{N_{el}+N_{nuc}} q_p \middle| \mathbf{R}_p - \mathbf{R}_0 \middle| \middle| \phi_A \right\rangle \right|^2 \right) +$$
$$\sum_A \left(\sum_j^{N_Q} \alpha_j \left| \left\langle \phi_A \middle| \sum_p^{N_{el}+N_{nuc}} q_p \middle| \mathbf{R}_p - \mathbf{R}_0 \middle|^2 \middle| \phi_A \right\rangle \right|^2 \right) +$$
$$\sum_A \left(\sum_k^{N_\Phi} \beta_k \left| \left\langle \phi_A \middle| \sum_p^{N_{el}} q_p \middle| \mathbf{R}_p - \mathbf{R}_0 \middle|^{-1} \middle| \phi_A \right\rangle \right|^2 \right) + \sum_A \left(\sum_l^{N_{L2}} \lambda_l \middle| \langle \phi_A | L^2 | \phi_A \rangle |^2 \right) \tag{1}$$

where ϕ_A is a diabatic state, γ is a parameter that weights the dipole term, p is an index over particles (a particle is an electron or nucleus), N_{el} is the number of electrons, N_{nuc} is the number of nuclei, q_p is the charge of particle p, α_j is a parameter that weights the quadrupole term for origin j, j is a choice of origin for the quadrupole integrals, N_Q is the number of origins used for the quadrupole integrals, β_k is a parameter that weights the electrostatic potential term for origin k, k is a choice of origin for the electrostatic potential integrals, and N_Φ is the number of origins used for the electrostatic potential integrals, λ_l is a parameter that weights the two-electron orbital angular momentum term for origin l, l is a choice of origin for the two-electron orbital angular momentum integrals, and N_{L2} is the number of origins used for the two-electron orbital angular momentum integrals. Note that when α_j, β_k, and λ_l are set to 0 the DQΦL2 method reduces to Boys localized diabatization.[3]

In addition we developed a weighted version of DQΦL2 diabatization that is analogous to the weighted versions for the diabatization of Werner and Meyer[4] and Boys[5] and uses the same weighting function as in Ref. 5. In weighted DQΦL2 the off-diagonal elements of each adiabatic property are multiplied by a weighting function

$$W_{IJ} = \left\langle \Psi_I \middle| \hat{O} \middle| \Psi_J \right\rangle \tag{2}$$

where W is a weighting function, $\hat{O}$ is a property operator, and Ψ is an adiabatic wavefunction. Then, $f_{\text{DQΦL2}}$ is maximized as normal using the weighted adiabatic properties.

One choice of weighting function for weighted DQΦL2 is the one used in Ref. 5:

$$W_{IJ} = \frac{1}{4} \text{ercf} \left(\frac{E_I - E_{\text{thresh}}}{\alpha_{\text{Weight}}} \right) \text{ercf} \left(\frac{E_J - E_{\text{thresh}}}{\alpha_{\text{Weight}}} \right) \tag{3}$$

where E_I is the energy of adiabatic state I, E_{thresh} is an energy threshold parameter, and α_{Weight} is a parameter (a recommended value is 0.005 a.u.). See the WALPH and ETHRESH keywords in Section 9.

In another choice of weighting function for weighted DQΦL2, the function is only dependent upon the splitting of the adiabatic energies.

$$W_{IJ} = \left(\text{ercf} \left(\frac{|E_I - E_J|}{\sigma_Z} \right) \right)^2 \quad (4)$$

where E_I is the energy of adiabatic state I, E_J is the energy of adiabatic state J, and σ_Z is a parameter that affects the difference in energy at which the weights will become smaller.

Weighting is useful for cases where the highest-energy diabatic state is unimportant in some regions (e.g., very high in energy). The inclusions of such a state in the diabatization may deteriorate the quality of the other diabatic states in a region of unimportance. In such a case one can set a smaller weight on the state, such that the properties of that diabatic state are not as important in the maximization of the DQΦL2 function.

3. Recommended Citations

- Citation for software: Reference 6
- Citation for DQ method: References 1 and 2
- Citation for DQΦ method: Reference 2

4. Version History

4.1. *DQΦpac 2.0* (July 2017)

The following were added in *DQΦpac 2.0*:
- Weighted versions of the Boys localized diabatization, DQ, and DQΦ methods
- The weighting function used in Ref. 5
- The weighting function described in Equation 4
- Optional printing of ".dat" files
- Option for the user to manually create a "qc.out", see GEN option in SOFT
- Printing of weighted adiabatic properties and of diabatic properties

4.2. *DQΦpac 21* (July 2021)
_{5.}

The following were added in *DQΦpac 21:*
- Reading in multiple geometry points from a single qc.out" file and carrying out diabatization for each geometry point if MOLPRO or GEN is used in SOFT keyword. Namely this is a SCAN type calculation.
- Reading in properties calculated by CASSCF, MRCI, and CASPT2 in *Molpro*.
- Reading in two-electron orbital angular momentum properties calculated by CASSC in *Molpro*. This data can be directly taken from a *Molpro* output or from a manually created "qc.out".
- Possibility to read multiple quadrupole origins form "qc.out" if MOLPRO or GEN is used in SOFT keyword. (Originally a single origin was required and addition ones were calculated by *DQΦpac 21*)
- Instead of using MATROP, now it is possible to read electrostatic potentials from the modules of CASSCF, MRCI, and CASPT2 in *Molpro*.
- The properties printed into the ".dat" files now collected from a single run of *DQΦpac 21* if a SCAN type calculation is carried out. The ".dat" files are overwritten if a new *DQΦpac 21* calculation is started.
- The units of γ, α_j, and β_k were changed to be au^{-2}, au^{-4}, au^2, respectively. This modification does not change the values of these parameters as compared with previous versions of *DQΦpac*.

6. Basic Instructions

To use *DQΦpac 21*, run the executable in a directory that also contains two other files "qc.dqv" and "qc.out" (the files must be named as such). The file "qc.dqv" is the *DQΦpac 21* input and contains keywords covered in Section 9. The file "qc.out" contains the output from the electronic structure calculation. It is recommended that the "qc.out" file only contain properties that will be used (e.g., if two origins for the electrostatic potential are needed, do not have three origins in the "qc.out" file).

7. Electronic Structure Packages

This section discusses the electronic structure software that is interfaced with *DQΦpac 21*. Please see the keyword, SOFT, in Section 9.

7.1. *Q-Chem* program
The *DQΦpac 21* software works with REM module (it has been tested using random phase approximation (RPA), time-dependent density functional theory (TDDFT), configuration interaction with singles (CIS), and TDDFT with the Tamm-Dancoff approximation (TDA)) of *Q-Chem* 4.2. Do not include the output of more than one method per "qc.out" to ensure that the correct values are read. The quadrupole moment computed by *Q-Chem* includes only the electronic contribution, but in Equation 1 we see that the DQΦ method (where the two-electron orbital angular momentum term is neglected) also includes the nuclear contribution. In addition, *Q-Chem* calculates the electronic quadrupole moment with the incorrect sign. To add the nuclear contribution to the quadrupole integrals with *DQΦpac 21,* one must use the COORD, NUCL, and QNUC keywords covered in Section 9. The coordinates used with the NUCL keyword of *DQΦpac 21* should be the ones listed under "Standard Nuclear Orientation" in the *Q-Chem* output. *Q-Chem* translates the origin to the center of nuclear charge, which is why one needs to use the Standard Nuclear Orientation geometries. No action is required by the user to fix the sign of the quadrupole moment computed with *Q-Chem*; *DQΦpac 21* fixes the sign automatically.

7.2. Molpro program
In the original *DQΦpac* code, the dipoles and quadrupoles were calculated using the TRANS directive in the CI module; and for the electrostatic potential, the CI module was also used to obtain the transition density matrix. Then this transition density matrix is used in MATROP (more details on this in the next paragraph). This procedure works for both MRCI and CASSCF calculations. For the later case, the NOEXC keyword is required in the CI module to not perform any external excitations.

In the original *DQΦpac* manual it was claimed that, the TRANS module cannot be used to compute the electrostatic potential since it includes the nuclear contribution; however, in Equation 1 we see that the Φ part of the method does not include the nuclear contribution in the electrostatic potential. To compute electrostatic potential integrals in *Molpro*, one can use the density and transition density from TRANS to then compute electrostatic potential integrals in MATROP. One must compute all transition elements of the electrostatic potential. To compute

multiple origins for the electrostatic potential, one has to compute them in the same *Molpro* calculation, which includes calls to MATROP for each choice of origin.

The *DQΦpac 21* code goes beyond some of these limitations. The required properties can be obtained at CASCF, CI, and CASPT2 levels, with some limitations. The *DQΦpac 21* code works with *Molpro* versions 2012, 2015, and 2018.

CASSCF: The TRAN keyword can be used to calculate the dipole, quadrupole, and electrostatic potential one-electron properties. For the quadrupole and electrostatic potential, multiple origins can be chosen. Multiple origins of quadrupole can be also calculated by the *DQΦpac 21*. In this case a single quadrupole origin is enough from *Molpro*, and the calculation requires the dipole moment of the structure as well as the location (geometries) of the other origins.

As mentioned above, the nuclear contribution in the electrostatic potential is added, but this is not a problem. For a given geometry, the nuclear contribution is a single constant and it appears in all the diagonal elements of the transition matrix, i.e., the states. A matrix diagonalization does not changed if all the diagonal elements of the matrix are shifted by a constant, since the differences of the diagonal elements are used in the diagonalization procedure. Therefore, adding or neglecting the nuclear contributions will not change the rotation angle obtained from the matrix diagonalization. Nevertheless, if one decides to use the data by MATROP, the CI module has to be called, the transition density matrix has to be saved and loaded in MATROP to obtain all the data.

The two-electron orbital angular momentums can be obtained by using the TRAN2 keyword. These properties are only available at the CASSCF level. They are only calculated at the origin of the Cartesian space (x = 0.0, y = 0.0, z = 0.0), thus for multiple origins the CASSCF calculation has to be repeated by shifting the geometry and placing the desired geometry point to the origin of the Cartesian space. An example of a *Molpro* input is shown below:

```
geomtyp=xyz
geometry={                        ! Geometry 1, where the Li atom is placed at the origin of the Cartesian space
2
LiH system
Li, 0.0,  0.0, 0.0
H,  1.2,  0.0, 0.0}

text,L2LI                         ! This line is required to tell DQΦL2 that the TRAN2 data are calculated at Li
{multi,maxit=40,maxiti=400
occ,   6,2,2,0
closed, 1,0,0,0
pspace,5.0
wf,4,1,0;state,4
orbital,2140.2
TRAN2,LXX,LYY,LZZ,TRAN2,LXY,LXZ,LYZ}

geomtyp=xyz
geometry={                        ! Geometry 2, where the H atom is placed at the origin of the Cartesian space
2
LiH system
Li, 1.2, 0.0, 0.0
```

```
H, 0.0,  0.0, 0.0}

text,L2H                        ! This line is required to tell DQΦL2 that the TRAN2 data are calculated at H
{multi,maxit=40,maxiti=400
occ,  6,2,2,0
closed, 1,0,0,0
pspace,5.0
wf,4,1,0;state,4
orbital,2140.2
TRAN2,LXX,LYY,LZZ,TRAN2,LXY,LXZ,LYZ}
```

MRCI: With the TRANS keyword, the dipole, quadrupole, and electrostatic potential one-electron properties can be calculated. For the quadrupole and electrostatic potential, multiple origins can be chosen. Multiple origins of quadrupole can be also calculated by the *DQΦpac 21*. In this case a single quadrupole origin is enough from *Molpro*, and the calculation requires the dipole moment of the structure as well as the location (geometries) of the other origins. For the electrostatic potential, the MATROP module can also be used after the transition density matrix is saved in the CI module.

CASPT2: With the TRANS keyword, the dipole, quadrupole, and electrostatic potential one-electron properties can be calculated. For the quadrupole and electrostatic potential, multiple origins can be chosen. Multiple origins of the quadrupole can also be calculated by the *DQΦpac 21*. In this case a single quadrupole origin is enough from *Molpro*, and the calculation requires the dipole moment of the structure as well as the location (geometries) of the other origins. For the electrostatic potential, the MATROP module can be also used after the transition density matrix is saved in the module of CASPT2.

7.3. Gen
The *DQΦpac 21* software is compatible with any electronic structure software that is capable of computing properties of interest. One simply needs to enter the data into "qc.out" using the keywords that are covered in Section 8.

8. GEN Keywords

This section covers keywords for use in "qc.out". See the SOFT keyword in Section 9 and Section 7.3. This section is only needed when using the GEN option for the SOFT keyword. All examples below are for a 3-state case. If "END" is in the example, it is required for that keyword.

AENE

    This keyword specifies adiabatic energies.

    Input example

    AENE

    -2.71114

    -2.12187

    -1.98790

    END

EXDX, EXDY, and EXDZ

    These keywords specify the expectation values of the x, y, and z components of the dipole, respectively.

    Input example

    EXDX

    0.23814

    -4.12187

    -3.28190

    END

TRDX, TRDY, and TRDZ

    These keywords specify the transition values of x, y, and z components of the dipole, respectively. The entries are ordered as if one is reading a matrix from left to right and up to down, but without the diagonal terms, i.e. X_{12}, X_{13}, then X_{23}. Below is an input example for TRDX.

Input example

TRDX

0.33214

-2.92187

-1.21190

END

EXXX, EXYY, and EXZZ

These keywords specify the expectation values of x^2, y^2, and z^2 components of the quadrupole, respectively. For more information on how to read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

EXXX

2.73214

-5.52187

-80.28190

END

TRXX, TRYY, and TRZZ

These keywords specify the transition values of x^2, y^2, and z^2 components of the quadrupole, respectively. The entries are in ordered the same as TRDX. For more information on how to read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

TRXX

0.33224

-4.12287

-2.91290

END

EXEP

This keyword specifies expectation values of the electrostatic potential for a given origin. To read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

EXEP

-1.73214

-2.52187

-6.28190

END

TREP

This keyword specifies transition values of the electrostatic potential. The entries are in ordered the same as TRDX (i.e. the order is, R_{12}^{-1}, R_{13}^{-1}, then R_{23}^{-1} for three states). For more information on how to read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

TREP

0.43224

-2.42287

-1.71290

END

EXLXLX, EXLYLY, and EXLZLZ

These keywords specify the expectation values of x^2, y^2, and z^2 components of the two-electron angular momentum, respectively. For more information on how to read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

EXLXLX

2.73214

-5.52187

-80.28190

END

TRLXLX, TRLYLY, and TRLZLZ

These keywords specify the transition values of x^2, y^2, and z^2 components of the two-electron angular momentum, respectively. The entries are in ordered the same as TRDX (i.e. L_{12}^2, L_{13}^2, then L_{23}^2). For more information on how to read in the electrostatic potential for more than one origin, see Section 8.1.

Input example

TRLXLX

0.33224

-4.12287

-2.91290

END

CUT_HERE

For SCAN type calculation, the text CUT_HERE represents a separator where the data of a new geometry is started. For a given geometry, list all the required data and that section is closed by the CUT_HERE statement in a new line. The data of final geometry point in a scan type calculation is also closed by the CUT_HERE statement for proper usages.

Input example

EXEP

-1.73214

-2.52187

-6.28190

END

TREP

0.43224

-2.42287

-1.71290

END

CUT_HERE

EXEP

-1.69714

-2.13187

-5.73611

END

TREP

0.33224

-1.94857

-1.54893

END

CUT_HERE

8.1. Comment on multiple origins

To read in data for multiple origins, one needs multiple calls of the same keywords. For example, two sets of electrostatic requires the repetition of EXEP and TREP keywords. The ordering of the keywords matters, follow the ordering in the example below.

Input example

EXEP

-1.73214

-2.52187

-6.28190

END

TREP

0.43224

-2.42287

-1.71290

END

EXEP

-1.69714

-2.13187

-5.73611

END

TREP

0.33224

-1.94857

-1.54893

END

9. Keywords

Some input examples contain "END" and some do not. If "END" is in the example, it is required for that keyword.

SOFT

> The keyword SOFT is *mandatory*. It specifies which electronic structure package is used.
>
> a. MOLPRO - The "qc.out" file was generated using *Molpro*
>
> b. QCHEM - The "qc.out" file was generated using *Q-Chem*
>
> c. GEN - The "qc.out" file was generated by the user
>
> *Input example*
>
> SOFT
>
> QCHEM

NSTATE

> The keyword NSTATE is *mandatory*. It specifies how many electronic states are of interest. This defines the size of the NxN property matrices and output NxN diabatic potential energy matrix.
>
> *Input example*
>
> NSTATE
>
> 4

METH

> The keyword METH is *highly recommended*. It specifies which diabatization method is used. The default is to use Boys localized diabatization.
>
> a. DIP – Uses Boys localized diabatization to produce diabatic states (i.e., only the first term in Equation 1 in Section 2 is used).
>
> b. DQUAD – Uses DQ diabatization to produce diabatic states (i.e., only the first and second term in Equation 1 in Section 2 are used).
>
> c. DQV – Uses DQΦ diabatization to produce diabatic states (i.e., all three terms in Equation 1 in Section 2 are used). This is also the keyword for the DΦ method.
>
> d. DQVL2 – Uses Uses DQΦL2 diabatization to produce diabatic states (i.e., all four terms in Equation 1 in Section 2 are used). This is also the keyword for the DΦL2, DL2, QL2, and ΦL2 method. This method only can be used if SOFT is MOLPRO and COMPLEVEL is CASSCF, since the expectation values and transition matrix

elements over the two-electron orbital angular momentum operator is only calculated at SA-CASSCF level.

    e.   L2 – Uses L2 diabatization to produce diabatic states (i.e., only the fourth term in Equation 1 in Section 2 is used).

Input example

METH

DQV

COMPLEVEL

The keyword COMPLEVEL is *highly recommended* if MOLPRO is selected as SOFT. It specifies which electronic structure method is used. The default is to use MRCI calculations.

    a.   CASSCF – The input data for diabatizations is read from the module MULTI. Since multistate calculations are carried out, the calculations correspond to SA(n)-CASSCF or SA(n)-RASSCF.

    b.   MRCI – The input data for diabatizations is read from the CI module. The data can be calculated by either MRCI or CASSCF level if NOEXC keyword is applied.

    c.   CASPT2 – The input data for diabatizations is read from the module RS2. It is highly recommended to do MS-CASPT2 calculations.

Input example

COMPLEVEL

CASSCF

DATA TYPE

The keyword DATA TYPE controls that whether a single geometry point or a set of geometries is read as input. The default is to use SINGLE POINT.

    a.   SINGLE POINT – The diabatization is evaluated on a single geometry point.

    b.   SCAN – The diabatization is carried out on a set of geometries read from a single *qc.out* file. The SCAN option (reading multiple geometries) only works with MOLPRO and it requires a line "text,CUT_HERE"right before the "enddo" statement in the MOLPRO input file.

Input example

DATA TYPE

SINGLE POINT

STATES

The keyword STATES is *optional*. It specifies which electronic states are of interest. This is important when one wishes to exclude certain states in the diabatization (e.g., the ground state). By default, *DQΦpac 21* will assume that the user is interested in states 1 to NSTATE. The value for NSTATE should correspond to the number of entries for STATES (in the example below NSTATE would be 3).

Input example

STATES

2

3

4

END

GAMMA

The keyword GAMMA is *optional*. It specifies the value of the γ parameter in Equation 1 in Section 2. The value entered must be a real number. The default is 1.0.

Input example

GAMMA

2.0

NQOR

The keyword NQOR is *optional*. It specifies the number of origins used for the quadrupole integrals, which is the value of N_Q in Equation 1 in Section 2. The value entered must be an integer. The default is 1.

Input example

NQOR

3

ALPHA

The keyword ALPHA is *optional*. It specifies the α parameter. As a reminder α weights the importance of the quadrupole integrals for each choice of origin, which is the α_j in Equation 1eqn:DQV in Section 2. The values entered must be real numbers. Each line corresponds to each choice of origin, j. If ALPHA is not specified, each value of α_j is assumed to be 0.0. The example below is for a case when NQORitm:nquad is 3.

Input example

ALPHA

1.0

0.5

10.0

END

QORI

The keyword QORI is *optional* and only useful when using more than one quadrupole origin. It specifies the geometry of the origin for the quadrupole integrals. These geometries correspond to the $\mathbf{R}_j$ in Equation 1 in Section 2. The values entered must be real numbers and are given in Cartesians (x,y,z). Each line corresponds to a choice of origin, j.

Only one set of quadrupole integrals at a given origin is needed from "qc.out". The quadrupole integrals at all other origins are computed relative to the integrals read from "qc.out" (the first entry of QORI should correspond to the origin of the quadrupole integrals from "qc.out"). Additionally, the dipole is used to compute new quadrupole integrals. Please make sure the units of the dipole and origin are consistent with the units used for the quadrupole integral read from "qc.out". By default, *DQΦpac 21* will assume that all origins are (0.0,0.0,0.0). The following example corresponds to an QORI of 3.

Input example

QORI

0.0 0.0 0.0

2.0 2.0 2.0

-2.0 0.5 100.0

END

NOQCALC

Besides the QORI keyword, there is another way to get multiple quadrupole origins with the MOLPRO or GEN options of SOFT. This is accomplished with the keyword, NOQCALC.

If the GEN and NOQCALC keywords are used together, the quadrupole cards are read NQOR times, where first the blocks of (EXXX, EXYY, and EXZZ) expectation and (TRXX, TRYY, and TRZZ) transition values for origin 1 have to be listed, then for origin 2, and so on.

If the MOLPRO and NOQCALC keywords are used together, then the keyword QUADSTRINGS is required, where the origin labels are listed.

QUADSTRINGS

This keyword is *mandatory* if NOQCALC is used with a *Molpro* output. Under the keyword QUADSTRINGS, the labels of quadrupole origins have to be listed if MOLPRO is used. Based on the output structure of *Molpro*, we suggest the following conventions: If there are identical atoms in the investigated system, then in the *Molpro* input they can be appended by numbers. For instance, both H1 and H2 mean hydrogen atoms, but they are distinguished. If one would like to obtain the quadrupole at points that are not at positions of the atoms, then those points can be listed in the geometry section of the *Molpro* input with labels Qn or Xn (ghost atoms, with n as an integer). Then these unique identifiers can be used in the TRAN/TRANS modules. The maximum length of these labels is three characters and the characters have to be given the same way in qc.dqv as they appear in the MOLPRO output file (they are usually capitalized versions of the atomic symbol). Each line corresponds to each choice of origin j. After the QUADSTRINGS, NQOR entries are required.

For example, the investigated system is LiF and both atoms are used as origins (NQOR = 2). A corresponding quadrupole output line for Li atom has the following format:

!MRCI trans   <3.1|XX(LI)|2.1>   -0.005386800320

The required QUADSTRINGS from this line is the text "LI".

Input example

QUADSTRINGS

LI

F

END

NEOR

The keyword NEOR is *optional*. It specifies the number of origins used for the electrostatic potential integrals, which is the value, N_Φ in Equation 1 (Section 2). The value entered must be an integer. The default is 1.

Input example

NEOR

3

BETA

The keyword BETA is *optional*. It specifies the β parameter. As a reminder β weights the importance of the electrostatic potential integrals for each choice of origin, which is β_k in Equation 1 (Section 2). The values entered must be real numbers. Each line corresponds to each choice of origin, k. If BETA is not specified, each value of β_k is assumed to be 0.0. The example below is for a case when NEOR is 3.

Input example

BETA

10.0

1.0

0.5

END

NOMATROP

If keyword NOMATROP is used, then, instead of MATROP module, the electrostatic potential data are read from the given electronic structure module directly. For more details see Section 7.2.

Input example

NOMATROP

PHISTRINGS

This keyword is *mandatory* if NOMATROP is used with a *Molpro* output. Under the keyword PHISTRINGS, the labels of electrostatic potential origins should be listed. Due to the output structure of *Molpro*, we suggest the following conventions: If there are identical atoms in the investigated system, then in the *Molpro* input they can be appended by numbers. For instance, both H1 and H2 mean hydrogen atoms, but they are distinguished. If one would like to obtain the electrostatic potential at points not at positions of atoms, then those points can be listed in the geometry section of the *Molpro* input with labels Qn or Xn (ghost atoms where n is an integer). Then these unique identifiers can be used in the TRAN/TRANS modules. The maximum length of such labels is three characters and the characters have to be given the same way in qc.dqv as they appear in the MOLPRO output file. Each line corresponds to each choice of origin k. After the PHISTRINGS, NEOR entries are required.

For example, the investigated system is LiH and both atoms are used as origins (NEOR = 2). As an example, a corresponding electrostatic potential data line for Li atom has the following format:

> !MCSCF trans   <3.1|POT(LI)|1.1>   0.080891186779

The required PHISTRINGS from this line is the text "LI".

Input example

PHISTRINGS

LI

H

END

L2OR

The keyword L2OR is *optional*. It specifies the number of origins used for the two-electron orbital angular momentum integrals, which is the value of N_{L2} in Equation 1 in Section 2. The value entered must be an integer. The default is 1.

Input example

L2OR

3

LAMBDA

The keyword LAMBDA is *optional*. It specifies the λ parameter. As a reminder λ weights the importance of the two-electron orbital angular momentum integrals for each choice of origin, which is λ_l in Equation 1 (Section 2). The values entered must be real numbers. Each line corresponds to each choice of origin, l. If LAMBDA is not specified, each value of λ_l is assumed to be 0.0. The example below is for a case when L2OR is 2.

Input example

LAMBDA

10.0

1.0

END

L2STRINGS

The keyword L2STRINGS is *mandatoy* if more than one L2OR origin is used and the SOFT is MOLPRO. Under the keyword PHISTRINGS, the user defined labels of the origins should be listed. In the MOLPRO input, the card TEXT has to be used before the new origin of two-electron orbital angular momentum is calculated, see Section 7.2. The length of such labels is up to 21 characters and the characters have to be the same in the qc.dqv file as they appear in the MOLPRO output file (i.e. how they are defined in the

Molpro calculation). Each line corresponds to each choice of origin *l*. After the L2STRINGS, L2OR entries are required. The example shown here corresponds to the *Molpro* input example in Section 7.2. Note that the texts written in text card in *Molpro* input can be both small or capital letters, but they will appear with capital letters in the *Molpro* output. Therefore in the qc.dqv file they have to be capitalized too.

Input example

L2STRINGS

L2LI

L2H

END

CHARGE

The keyword CHARGE is *optional*. It specifies the charge of the molecule. This is only used when computing quadrupole integrals at more than one origin (see ALPHA, NQOR, and QORI). The value must be an integer. The default is 0 (neutral molecule).

Input example

CHARGE

1

COORD

The keyword COORD is *mandatory* when using quadrupole integrals that are computed with *Q-Chem* (see Section 7.1). It specifies the number of nuclei. It is used in conjunction with the QNUC and NUCL keywords to add on the nuclear contribution to the quadrupole integrals of *Q-Chem*.

Input example

COORD

3

QNUC

The keyword QNUC is *mandatory* when using quadrupole integrals that are computed with *Q-Chem* (see Section 7.1). The QNUC keyword needs to be specified, along with the COORD and NUCL keywords, to add the nuclear contribution to the quadrupole integrals of *Q-Chem*.

Input example

QNUC

NUCL

The keyword NUCL is *mandatory* when using quadrupole integrals that are computed with *Q-Chem* (see Section 7.1). It specifies the charge and coordinates of the nuclei, which are needed to add the nuclear contribution to the quadrupole integrals of *Q-Chem*. The QNUC and COORD keywords also need to be specified. All values for the charge and coordinates must be real numbers, and the geometries must be in Angstroms. Below is an example for the H_2O molecule and corresponds to the case when COORD is 3. The order of each line is nuclear charge, x, y, then z.

Input example

NUCL

1.0 2.22 3.71 0.22

1.0 1.29 10.71 7.22

8.0 101.29 0.71 11.22

END

ETHRESH

The keyword ETHRESH is *mandatory* for weighted DQΦL2 with the weighting function in Equation 3 in Section 2. It specifies the value of the E_{thresh} parameter (in a.u.) in Equation 3 in Section 2. The value entered must be a real number. There is no default at present. The ETHRESH keyword is mutually exclusive with the ZSIG keyword.

Input example

ETHRESH

-184.203

WALPH

The keyword WALPH is *mandatory* for weighted DQΦL2 with the weighting function in Equation 3 in Section 2. It specifies the value of the α_{Weight} parameter in Equation 3 in Section 2. The value entered must be a real number. There is no default at present, but the 0.005 a.u. value is recommended. The WALPH keyword is mutually exclusive with the ZSIG keyword.

Input example

WALPH

0.005

ZSIG

The keyword ZSIG is *mandatory* for weighted DQΦL2 with the weighting function in Equation 4 of Section 2. It specifies the value of the σ_Z parameter (in kcal/mol) in Equation 4 in Section 2. The value entered must be a real number. There is no default at present. The ZSIG keyword is mutually exclusive with the ETHRESH and WALPH keywords.

Input example

ZSIG

80.0

FPRINT

The keyword FPRINT is *optional*. If entered, *DQΦpac 21* will print out .dat files to the working directory. The .dat files contain data listed in a list format. Many files are printed, and the number of files is dependent on the specific calculation. Files containing weighted properties will only be printed for a weighted calculation and will have a "W" in front of the filename (e.g., "WAdiaX-diag.dat"). Diabatic properties begin with "Dia" instead of "Adia" (e.g., "DiaX-diag.dat"). The entries of the off-diagonal files "-off.dat" are ordered left to right along a row of the matrix as shown symbolically for the *ij* elements of three states: 12, 13, and 23. Below is a list of some .dat files and a brief description:

1. "AdiaE.dat" - adiabatic energies
2. "DiaE-diag.dat" - diabatic energies
3. "DiaE-off.dat" - diabatic couplings
4. "AdiaX-diag.dat" - adiabatic x component of the dipole (diagonal part)
5. "AdiaX-off.dat" - adiabatic x component of the dipole (off-diagonal part)
6. "AdiaY-diag.dat" - adiabatic y component of the dipole (diagonal part)
7. "AdiaY-off.dat" - adiabatic y component of the dipole (off-diagonal part)
8. "AdiaZ-diag.dat" - adiabatic z component of the dipole (diagonal part)
9. "AdiaZ-off.dat" - adiabatic z component of the dipole (off-diagonal part)
10. "AdiaR-diag.dat" - adiabatic magnitude of the dipole (diagonal part)
11. "AdiaR-off.dat" - adiabatic magnitude of the dipole (off-diagonal part)
12. "AdiaXXN-diag.dat" - adiabatic x^2 component of the quadrupole for origin N (diagonal part)

13. "AdiaXX*N*-off.dat" - adiabatic x^2 component of the quadrupole for origin N (off-diagonal part)

14. "AdiaYY*N*-diag.dat" - adiabatic y^2 component of the quadrupole for origin N (diagonal part)

15. "AdiaYY*N*-off.dat" - adiabatic y^2 component of the quadrupole for origin N (off-diagonal part)

16. "AdiaZZ*N*-diag.dat" - adiabatic z^2 component of the quadrupole for origin N (diagonal part)

17. "AdiaZZ*N*-off.dat" - adiabatic z^2 component of the quadrupole for origin N (off-diagonal part)

18. "AdiaRR*N*-diag.dat" - adiabatic quadrupole for origin N (diagonal part)

19. "AdiaRR*N*-off.dat" - adiabatic quadrupole for origin N (off-diagonal part)

20. "AdiaEP*N*-diag.dat" - adiabatic electrostatic potential for origin N (diagonal part)

21. "AdiaEP*N*-off.dat" - adiabatic electrostatic potential for origin N (off-diagonal part)

22. "AdiaLXLX*N*-diag.dat" - adiabatic x^2 component of L^2 for origin N (diagonal part)

23. "AdiaLXLX*N*-off.dat" - adiabatic x^2 component of L^2 for origin N (off-diagonal part)

24. "AdiaLYLY*N*-diag.dat" - adiabatic y^2 component of L^2 for origin N (diagonal part)

25. "AdiaLYLY*N*-off.dat" - adiabatic y^2 component of L^2 for origin N (off-diagonal part)

26. "AdiaLZLZ*N*-diag.dat" - adiabatic z^2 component of L^2 for origin N (diagonal part)

27. "AdiaLZLZ*N*-off.dat" - adiabatic z^2 component of L^2 for origin N (off-diagonal part)

28. "AdiaL2*N*-diag.dat" - adiabatic L^2 for origin N (diagonal part)

29. "AdiaL2*N*-off.dat" - adiabatic L^2 for origin N (off-diagonal part)

30. "DiaP-diag.dat" - diabatic property matrix (diagonal part)

    An element of the property matrix is defined as

    $$P_{12} = \sqrt{\gamma|\boldsymbol{\eta}_{12}|^2 + \sum_j \alpha_j |Q_{12}(j)|^2 + \sum_k \beta_k |\Phi_{12}(k)|^2 + \sum_l \lambda_l |L_{12}^2(l)|^2} \qquad (5)$$

    where $\boldsymbol{\mu}$ is the dipole, Q is the quadrupole, Φ is electrostatic potential, and L^2 is the two-electron orbital angular momentum. Further definitions can be found in Section 2, specifically in the text under Equation 1. The property matrix is useful for labeling the diabatic states correctly.

31. "DiaP-off.dat" - diabatic property matrix (off-diagonal part)

Input example

FPRINT

10. Sample Test Runs

The directory Testruns contains three example runs for LiH with the quantities computed by *Molpro*. These examples are in the following sub-directories:

- LiH_CASSCF: Four states of LiH is calculated by SA-CASSCF and a test DQΦL2 calculation is carried out.

- LiH_MRCI: Four states of LiH is calculated by MRCI and a test DQΦ calculation is carried out.

- LiH_CASPT2: Four states of LiH is calculated by MS-CASPT2 and a test DQΦ calculation is carried out.

All three sub-directories contain the "qc.out" (*Molpro* output file), the "qc.dqv" (input file for *DQΦpac 21*), the "out" file (output of *DQΦpac 21*), and the .dat files generated by FPRINT option. The content of *Molpro* input file is included at the beginning of its output file.

11. Acknowledgements

12. References

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