Using Quantum Chemistry to Parameterize the Frenkel/Charge-Transfer Holstein Hamiltonian

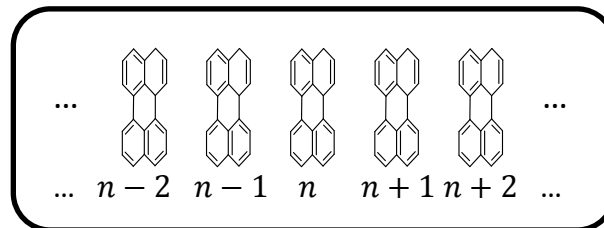Nicholas Hestand

Overview

Frenkel/CT Holstein Hamiltonian:

$$\hat{H} = \hbar\omega_{vib}\sum_n b_n^\dagger b_n + \hbar\omega_{0-0}\sum_n |c_n,a_n\rangle\langle c_n,a_n| + \sum_{n,m} J_{n,m}|c_n,a_n\rangle\langle c_m,a_m|$$

$$+\hbar\omega_{vib}\lambda\sum_n (b_n^\dagger + b_n + \lambda)|c_n,a_n\rangle\langle c_n,a_n| + \sum_{n,s\neq 0}\hbar\omega(s)|c_n,a_{n+s}\rangle\langle c_n,a_{n+s}|$$

$$+t_e\sum_{n,s}(|c_n,a_{n+s}\rangle\langle c_n,a_{n+s+1}| + |c_n,a_{n+s}\rangle\langle c_n,a_{n+s-1}|)$$

$$+t_h\sum_{n,s}(|c_n,a_{n+s}\rangle\langle c_{n+1},a_{n+s}| + |c_n,a_{n+s}\rangle\langle c_{n-1},a_{n+s}|)$$

$$+\hbar\omega_{vib}\lambda_+\sum_{n,s\neq 0}(b_n^\dagger + b_n + \lambda_+)|c_n,a_{n+s}\rangle\langle c_n,a_{n+s}|$$

$$+\hbar\omega_{vib}\lambda_-\sum_{n,s\neq 0}(b_{n+s}^\dagger + b_{n+s} + \lambda_-)|c_n,a_{n+s}\rangle\langle c_n,a_{n+s}|$$

Hole on molecule n,
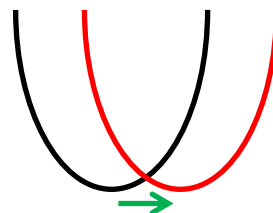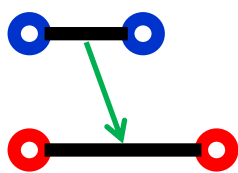Electron on molecule $n+s$

… $n-2$ $n-1$ n $n+1$ $n+2$ …
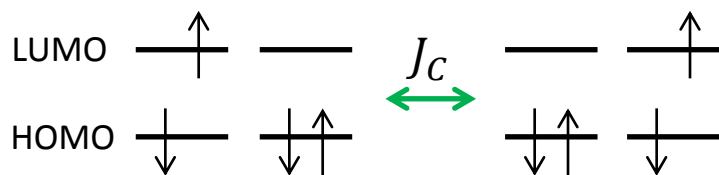
How can we parameterize this Hamiltonian?

Overview

Huang-Rhys Factors
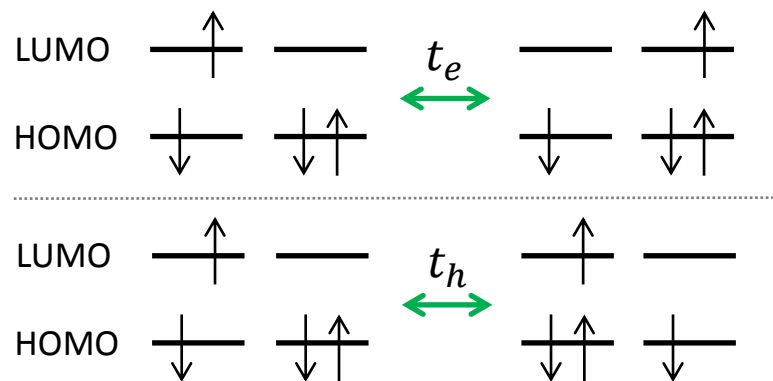$$\lambda^2, \lambda_-^2, \lambda_+^2$$

Ionic factors not easily accessible from experiment.

Coulombic Coupling
(Transition Charges)

LUMO

HOMO

J_C

Point Dipole Approximation breaks down at close intermolecular distances relevant for π-stacked systems.
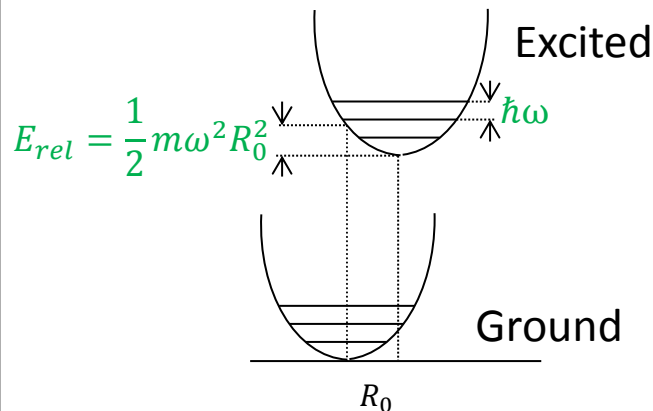
Charge-Transfer Integrals

LUMO

HOMO

t_e

LUMO

HOMO

t_h

Energy splitting method requires symmetry.

3

Huang Rhys Factors

Displaced Harmonic Oscillator:

Excited

$$E_{rel} = \frac{1}{2}m\omega^2 R_0^2$$

$\hbar\omega$

Ground

R_0

- The potential energy surfaces of the ground and excited states have different equilibria.
- λ^2 is related to the relaxation energy via $\lambda^2 = E_{rel}/\hbar\omega$

To calculate the Huang Rhys factor, we need to know:
1. The geometries of the ground and excited states
2. The normal vibrational modes (of the ground state) and their frequencies
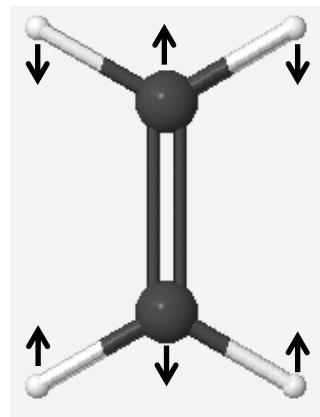
These can be calculated using Gaussian 09.

Example: Ethylene

We can project the displacement onto the normal modes to find the Huang-Rhys Factor for each mode.
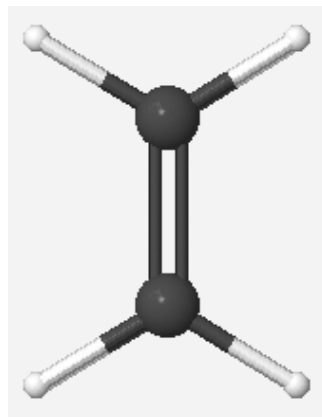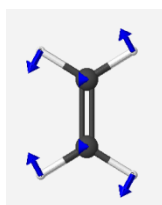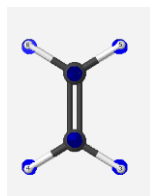

Double Bond Lengthens

Ground State   Excited State

12 Normal Modes (Excluding Translation/Rotation):

Frequency (cm^{-1}): 836   979   984   1067   1247   1382
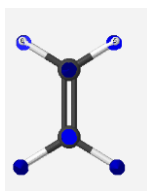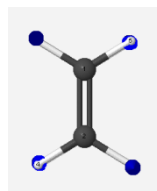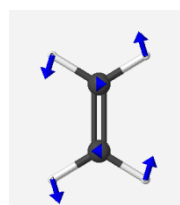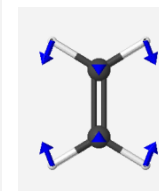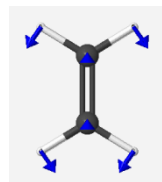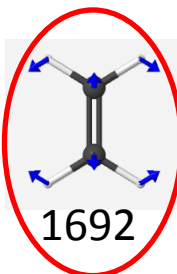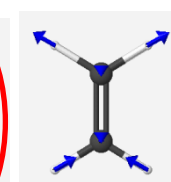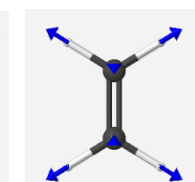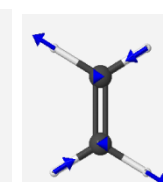
1479   1692   3126   3139   3195   3223
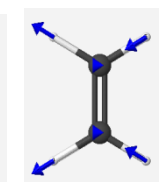
Huang Rhys Factors From Gaussian 09

Steps:

1. Calculate the optimized geometry of the ground and excited state
2. Calculate the normal vibrational modes by diagonalizing the mass weighted Hessian
3. Project the difference of the excited and ground state geometries onto the normal coordinates
4. Calculate the Huang-Rhys factor for each normal mode

$$\lambda_i^2 = \frac{m_i \omega_i}{2\hbar} R_i^2$$

5. Calculate an effective Huang-Rhys factor and Frequency

$$\lambda_{eff}^2 = \sum_i \lambda_i^2 \qquad \omega_{eff} = \frac{1}{\lambda_{eff}^2} \sum_i \lambda_i^2 \omega_i$$

Using the g09_lambda Utility Program

Running `g09_lambda.exe` will calculate the Huang-Rhys parameters for ground to excited (neutral, cation, anion) transformations.

Options:

- `-i in_file`: specify the input file containing the necessary information

- `-o out_file`: specify the file to write the results

- `-m`: make the Gaussian 09 input files

Using the g09_lambda Utility Program

Example Input File:

```
# ethylene.inp input file for making G09 input
# Lines starting with # are ignored
#
# Formatted checkpoint file names
ground_fch  'test_g.fch' # Ground
excited_fch 'test_e.fch' # Neutral Excited
cation_fch  'test_c.fch' # Cation
anion_fch   'test_a.fch' # Anion
#
# Info for effective parameter calculations
lower_bound 1000.d0
upper_bound 1800.d0
#
# Information for setting up Gaussian calculations
# QC method (ground/cation/anion)
method  'B3LYP/cc-pVTZ'
# QC method (neutral excited)
emethod 'TD=(nstates=1,root=1) B3LYP/cc-pVTZ'
# name of G09 input files generated
task ethylene
# xyz file containing coordinates to be optimized
xyz_file ethylene.xyz
```

Example XYZ File:

```
C    0.00000000  0.00000000  0.00000000
C    1.30860442  0.03217880  0.00000000
H    1.87664502 -0.89810604  0.00000000
H    1.83023441  0.98925881  0.00000000
H   -0.52162999 -0.95708001  0.00000000
```

Using the g09_lambda Utility Program

Example Usage:

```
./g09_lambda.exe –m –i ethylene.inp
```

```
(Run Gaussian 09 Calculations)
(Convert chk files to fch files using formchk)
```

```
./g09_lambda.exe –i ethylene.inp –o ethylene.out
```

Using the g09_lambda Utility Program

Results:

ethylene.out
UB3LYP
CC-pVTZ

****

Mode Frequency (cm-1) lambda
****

1 -5.2587794055 -0.0000000000
2 -0.0203707857 -0.0000000000
3 -0.0184218903 -0.0000000000
4 0.0483418898 0.0000000000
5 4.3071018492 -0.0000000000
6 5.0345663643 0.0000000000
7 836.0866449198 -0.0000000013
8 979.0992814061 -0.0000000000
9 983.6754136707 0.0000000000
10 1067.1879585596 -0.0000000000
11 1246.5645659156 0.0000000000
12 1382.1199683765 -0.1245280739
13 1478.8808287271 0.0000000000
14 1692.7685822881 -1.3967306397
15 3125.5667698884 0.0000000000
16 3139.3324582045 0.2790954152
17 3194.7104980596 0.0000000000
18 3223.1612822683 -0.0000000006
****

Effective HR range (cm-1): 1000.0 1800.0
Effective HR Factor: 1.97
Effective HR Frequency: 1690.32
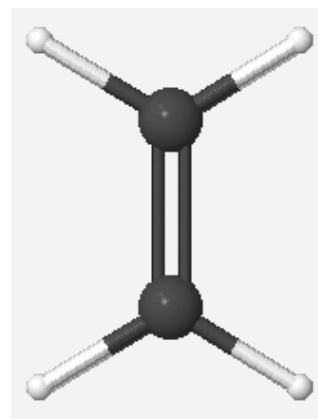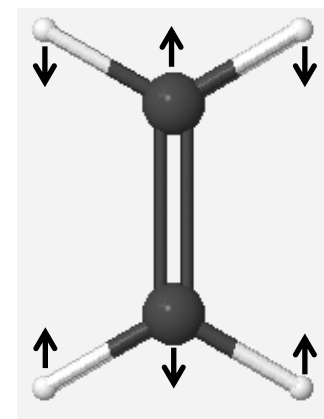
Ground State   Excited State

1692 cm^{-1}

10
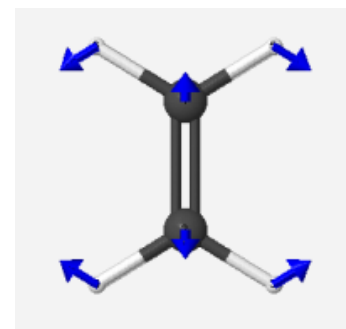
Using the g09_lambda Utility Program

Results (continuted):

```
********************************************************
Mode Frequency (cm-1) lambda-
********************************************************
1 -5.2587794055 -0.0000000000
2 -0.0203707857 -0.0000000000
3 -0.0184218903 -0.0000000000
4 0.0483418898 0.0000000000
5 4.3071018492 -0.0000000000
6 5.0345663643 0.0000000000
7 836.0866449198 -0.0000000021
8 979.0992814061 -0.0000000000
9 983.6754136707 0.0000000000
10 1067.1879585596 -0.0000000000
11 1246.5645659156 0.0000000000
12 1382.1199683765 0.9816962551
13 1478.8808287271 0.0000000000
14 1692.7685822881 -1.0280110470
15 3125.5667698884 -0.0000000000
16 3139.3324582045 -0.0567008341
17 3194.7104980596 -0.0000000000
18 3223.1612822683 -0.0000000004
********************************************************
Effective HR- range (cm-1): 1000.0 1800.0
Effective HR- Factor: 2.02
Effective HR- Frequency: 1544.60
```

```
********************************************************
Mode Frequency (cm-1) lambda+
********************************************************
1 -5.2587794055 -0.0000000000
2 -0.0203707857 -0.0000000000
3 -0.0184218903 -0.0000000000
4 0.0483418898 0.0000000000
5 4.3071018492 -0.0000000000
6 5.0345663643 0.0000000000
7 836.0866449198 -0.0000000016
8 979.0992814061 -0.0000000000
9 983.6754136707 0.0000000000
10 1067.1879585596 -0.0000000000
11 1246.5645659156 0.0000000000
12 1382.1199683765 0.6214830337
13 1478.8808287271 0.0000000000
14 1692.7685822881 -0.9267322291
15 3125.5667698884 -0.0000000000
16 3139.3324582045 -0.0465989385
17 3194.7104980596 -0.0000000000
18 3223.1612822683 -0.0000000004
********************************************************
Effective HR+ range (cm-1): 1000.0 1800.0
Effective HR+ Factor: 1.25
Effective HR+ Frequency: 1596.40
```

Charge Transfer Integrals

Charge Transfer Integrals
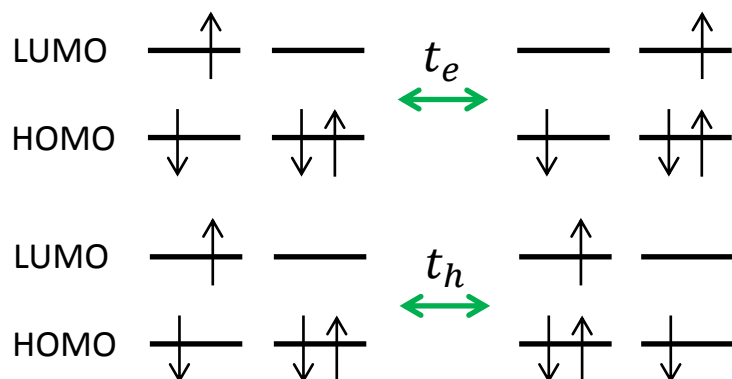
$$t_h = -\langle \phi_1^H | H | \phi_2^H \rangle$$
$$t_e = \langle \phi_1^L | H | \phi_2^L \rangle$$

To calculate the charge transfer integrals, we need to know:

1. The Hamiltonian in the molecular orbital basis
2. The overlap matrix in the molecular orbital basis

These can be calculated with the help of Gaussian 09.

Example: Ethylene

$$t_e = \langle \phi_1^L | H | \phi_2^L \rangle$$

ϕ_2^L

ϕ_1^L

ϕ_2^L

ϕ_1^L
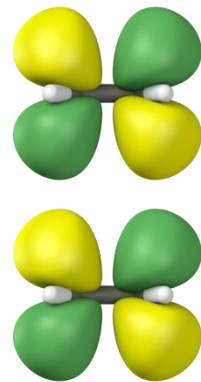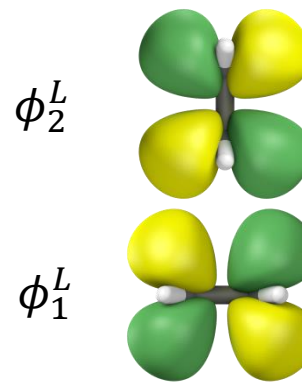
Cofacial

Face to End

- The integrals correspond to the interaction energy between MOs
- Cofacial – Energy splitting method should be fine since both molecules have the same energy
- Face to End – Energy splitting method will not work well since the molecules have different energies (they are not symmetry related)

Charge Transfer Integrals From Gaussian 09

Steps:

1. Calculate the molecular orbitals of the monomers, C_1 and C_2

2. Calculate the supramolecular orbitals of the dimer C, the overlap matrix S, and the eigenvalues E

3. Calculate the dimer Hamiltonian in the atomic orbital basis from the Roothan Equation

$$H_{AO} = SCEC^{-1}$$

4. Project the Hamiltonian and overlap matrix onto the basis of monomer molecular orbitals, $C_{MO} = C_1 \oplus C_2$

$$H_{MO} = C_{MO}^T H_{AO} C_{MO} \qquad S_{MO} = C_{MO}^T S C_{MO}$$

5. Orthogonalize the relevant monomeric wave functions using Lowdin's transformation

$$H'_{MO} = S_{MO}^{-1/2} H_{MO} S_{MO}^{-1/2}$$

Using the g09_ctint Utility Program

Running `g09_ctint.exe` will calculate the Hamiltonian submatrix relevant for charge transfer.

Options:

- `-i in_file`: specify the input file containing the necessary information

- `-o out_file`: specify the file to write the results

- `-m`: make the Gaussian 09 input files

Using the g09_ctint Utility Program

Example Input File:

```
# ct_ethylene.inp input file for making G09 input
# Lines starting with # are ignored
#
# log file and fch file names from G09 output
fch_m1          ethylene_cofacial_m1.fch #mol 1
log_m1          ethylene_cofacial_m1.out
fch_m2          ethylene_cofacial_m2.fch #mol 2
log_m2          ethylene_cofacial_m2.out
fch_d           ethylene_cofacial_d.fch  #dimer
log_d           ethylene_cofacial_d.out
#
# Information for setting up Gaussian calculations
method          'B3LYP/6-31++G**'
# Name of the Gaussian files to create
task ethylene_cofacial
# file with xyz of molecule 1
xyz_file_m1     ethylene_m1.xyz
# file with xyz of molecule 2
xyz_file_m2     ethylene_m2.xyz
```

Example XYZ Files:

```
C  0.672749   0.000000 0.000000
C -0.672749   0.000000 0.000000
H  1.242623   0.934806 0.000000
H  1.242623  -0.934806 0.000000
H -1.242623   0.934806 0.000000
H -1.242623  -0.934806 0.000000
```

ethylene_m1.xyz

```
C  0.672749   0.000000 4.000000
C -0.672749   0.000000 4.000000
H  1.242623   0.934806 4.000000
H  1.242623  -0.934806 4.000000
H -1.242623   0.934806 4.000000
H -1.242623  -0.934806 4.000000
```

ethylene_m2.xyz

Using the g09_ctint Utility Program

Example Usage:

`./g09_ctint.exe -m -i ct_ethylene.inp`

`(Run Gaussian 09 Calculations)`
`(Convert chk files to fch files using formchk)`

`./g09_ctint.exe -i ct_ethylene.inp -o ct_ethylene.out`

Using the g09_ctint Utility Program

Results (Cofacial ethylene):

```
Nonorthogonal Sub Hamiltonian (cm-1)
          |HOMO1>    |HOMO2>    |LUMO1>    |LUMO2>
<HOMO1|    -59949.1   5062.521        0         0
<HOMO2|     5062.521 -59949.1         0         0
<LOMO1|            0         0  -2651.71   2830.339
<LOMO2|            0         0   2830.339  -2651.71

Orthogonalized Sub Hamiltonian (cm-1)
          |HOMO1>    |HOMO2>    |LUMO1>    |LUMO2>
<HOMO1|    -59851.8   1765.845        0         0
<HOMO2|     1765.845 -59851.8         0         0
<LOMO1|            0         0  -2266.34   2477.862
<LOMO2|            0         0   2477.862  -2266.34

Overlap Sub Matrix
          |HOMO1>    |HOMO2>    |LUMO1>    |LUMO2>
<HOMO1|           1  -0.0551         0         0
<HOMO2|     -0.0551        1         0         0
<LOMO1|            0         0         1   -0.1555
<LOMO2|            0         0  -0.1555         1
```
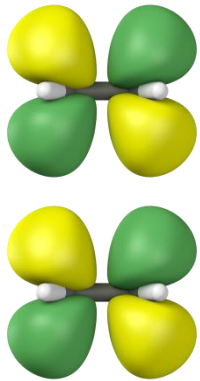
- Failure to orthogonalize results in integrals that are too large and dependent on the reference energy.

- Note that the integrals relevant for singlet fission are also available, although they are zero here for the perfectly eclipsed system.

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Example: Ethylene

ϕ_2^L

ϕ_1^L

Cofacial

ϕ_2^L

ϕ_1^L

Face to End

ϕ_2^H

ϕ_1^H

ϕ_2^H

ϕ_1^H
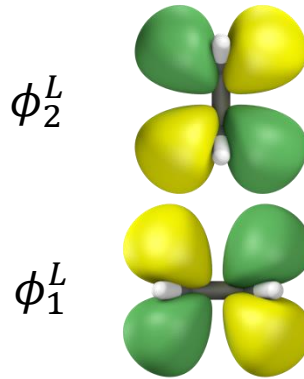
Cofacial

	t_e	t_h
Direct	2478 cm^{-1}	-1766 cm^{-1}
Energy Splitting	2465 cm^{-1}	-1777 cm^{-1}
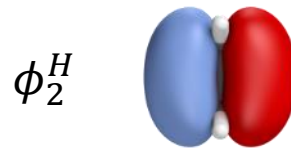
Face to End

	t_e	t_h
Direct	1160 cm^{-1}	0
Energy Splitting	1208 cm^{-1}	446 cm^{-1}

Coulomb Coupling (Transition Charges)

Coulombic Coupling
(Transition Charges)
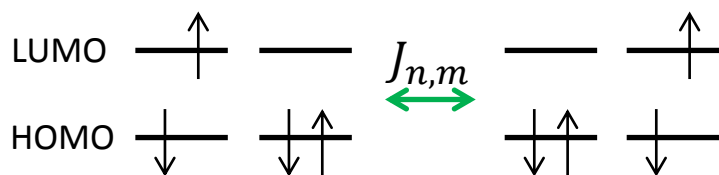
$J_{n,m}$

Point Dipole Approximation breaks down at close intermolecular distances relevant for π-stacked systems.

To calculate the transition charges, we need to know:

1. Overlap Matrix
2. Configuration Interaction Matrix for the excited state
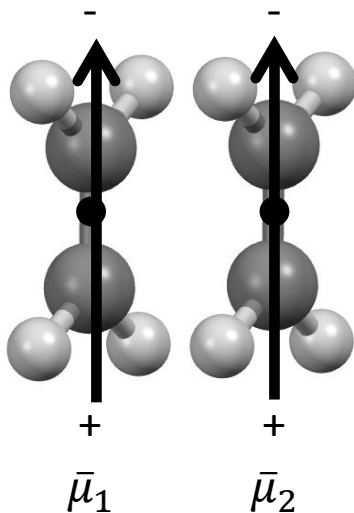3. Molecular Orbital Matrix

These can be calculated with the help of Gaussian 09.

$$J_{n,m} = \frac{1}{4\pi\varepsilon} \sum_{i,j}^{N_n, N_m} \frac{q_i^n q_j^m}{\left| \boldsymbol{R}_i^n - \boldsymbol{R}_j^m \right|}$$

Example: Ethylene

Point Dipole

$$J_{n,m} = \frac{\bar{\mu}_1 \bar{\mu}_2 - 3(\bar{\mu}_1 \cdot \vec{R})(\bar{\mu}_2 \cdot \vec{R})}{4\pi\varepsilon R^3}$$

Transition Charges

$$J_{n,m} = \frac{1}{4\pi\varepsilon} \sum_{i,j}^{N_n, N_m} \frac{q_i^n q_j^m}{\left| \boldsymbol{R}_i^n - \boldsymbol{R}_j^m \right|}$$
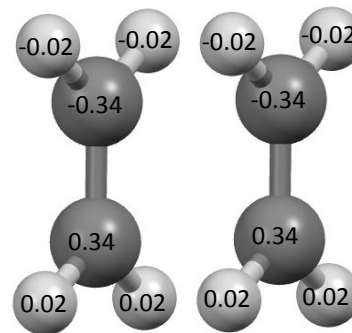
- Using transition charges gives spatial resolution to the transition moments which is necessary for accurate couplings when the molecules are close.
- The difference may not be that significant for ethylene, but can be bigger molecules like perylene.

Transition Charges From Gaussian 09

$$q_P = \sqrt{2} \sum_b^{N_{AO,P}} \sum_c^{N_{AO}} \sum_j^{\text{unocc}} \sum_i^{\text{occ}} A_{i,j} c_i^{Pb} c_j^c S_{bc}$$

$A_{i,j}$ - The CI coefficient from molecular orbital i to molecular orbital j

c_i^{Pb} - The MO expansion coefficient of the bth atomic orbital centered on atom P for the ith MO

c_j^c - The MO expansion coefficient of the cth atomic orbital for the jth MO

S_{bc} - The overlap matrix of atomic orbitals b and c

$N_{AO,P}$ - The number of atomic orbitals centered on atom P

N_{AO} - The total number of atomic orbitals

q_P - The transition charge on atom P

Using the g09_tq Utility Program

Running `g09_tq.exe` will calculate the transition charges of a molecule

Options:

- `-i in_file`: specify the input file containing the necessary information

- `-o out_file`: specify the file to write the results

- -m: make the Gaussian 09 input files

- -c tq_file_m1, tq_file_m2 : calculate the coupling between two molecules after the transition charges have been calculated

Using the g09_tq Utility Program

Example Input File:

```
# ct_ethylene.inp input file for making G09 input
# Lines starting with # are ignored
#
# log file and fch file names from G09 output
fch         tq_ethylene.fch
log         tq_ethylene.out
#
# The excited state of interest
estate      1
# Information for setting up Gaussian calculations
emethod     'CIS(nstates=1,root=1)/cc-pVTZ'
# Name of the Gaussian input files to create
task        tq_ethylene
# file with xyz coordinates
xyz_file    ethylene.xyz
```

Example XYZ Files:

```
C  0.672749  0.000000 0.000000
C -0.672749  0.000000 0.000000
H  1.242623  0.934806 0.000000
H  1.242623 -0.934806 0.000000
H -1.242623  0.934806 0.000000
H -1.242623 -0.934806 0.000000
```

ethylene.xyz

Using the g09_tq Utility Program

Example Usage:

```
./g09_tq.exe –m –i tq_ethylene.inp
```

```
(Run Gaussian 09 Calculations)
(Convert chk files to fch files using formchk)
```

```
./g09_tq.exe –i tq_ethylene.inp –o tq_ethylene_tqs.out
```

```
./g09_tq.exe –c tq_ethylene_tqs.out
                              tq_ethylene_shift_tqs.out
```

Using the g09_tq Utility Program

Results:

Atomic Number	X (bohr)	Y(bohr)	Z(bohr)	TQ (au)
6	0	0	0	0.341555
6	2.472904	0.060809	0	-0.34156
1	3.546345	-1.69717	0	-0.02038
1	3.458642	1.869428	0	-0.02038
1	-0.98574	-1.80862	0	0.020381
1	-1.07344	1.757984	0	0.020381

tq sum	1.04E-09		
tq dipole (au)	-1.02937	-0.02531	0
tq dipole (debye)	-2.61622	-0.06433	0

- The transition charges should sum to zero
- The transition dipole moment calculated from the transition charges should be fairly close to the one calculated by Gaussian, although this is not always the case.
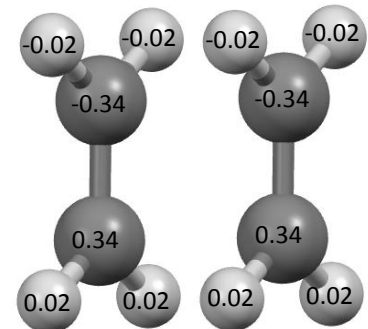- The transition charges can now be used to calculate the couplings (-c)

Example: Ethylene

Unscreened, π-stacked at 8 Bohr (Approx. 4.2 Å)

	J_C
Transition Dipole	454 cm^{-1}
Transition Charge	404 cm^{-1}
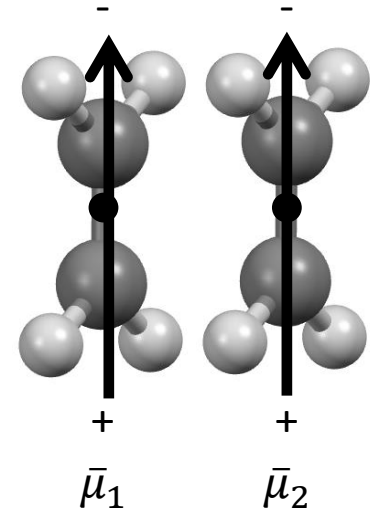
Unscreened, π-stacked at 2 Bohr (Approx. 1 Å) where the spatial resolution becomes more important for ethylene

	J_C
Transition Dipole	29086 cm^{-1}
Transition Charge	11130 cm^{-1}

$\bar{\mu}_1$ $\bar{\mu}_2$

Some References

Huang Rhys Calculation

- Gisslen, L.; Scholz, R. *Phys. Rev. B* **2009**, *80*, 115309. (Sec II B, C, and D.)

Charge-transfer Integrals

- Valeev, E. F.; Coropceanu, V.; da Silva Filho, D. A.; Salman, S.; Bredas, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 9882.
- Senthilkumar, K.; Grozema, F. C.; Bickelhaupt, F. M.; Siebbeles, L. D. A. *J. Chem. Phys.* **2003**, *119*, 9809.

Transition Charges

- Kistler, K. A.; Spano, F. C.; Matsika, S. *J. Phys. Chem. B* **2013**, *117*, 2032.