



DFTB Parameter Development and Implementation in Gaussian Development Version Program

Guishan Zheng^{a*}, Michael Frisch^b, Keiji Morokuma^a

^aCherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322

^bGaussian Inc, 340 Quinnipiac St Bldg 40 Wallingford, CT 06492

*Present address: University of Illinois at Urbana-Champaign, Department of Chemistry, Urbana, IL, 61801

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I. Parameterization of DFTB method for first-row transition metal elements

**Coauthors: Henryk Witek, Petia Bobadova-Parvanova,
Stephan Irle, Djamaladdin G. Musaev, Rajeev
Prabhakar, Keiji Morokuma, Marcus Elstner, Christof
Köhler and Thomas Frauenheim**

Motivation

- Extend DFTB applicability to large compounds (inorganic clusters, metalloenzymes) containing Transition Metal (TM) atoms; no reliable semiempirical methods for TM elements.
- An appropriate methodology candidate as a low-level/medium-level method in the ONIOM scheme.

DFTB Energy expression

$$\begin{aligned}
 E_{DFTB} &= \sum_{\sigma=\alpha,\beta} \sum_i^{occ} \langle \psi_{i\sigma} | \vec{H}_0 | \psi_{i\sigma} \rangle + \frac{1}{2} \sum_{A,B}^{atoms} E_{AB}^{rep} + \frac{1}{2} \sum_{A,B}^{atoms} \Delta q_A \gamma_{AB} \Delta q_B + \frac{1}{2} \sum_A \sum_{l \in A} \sum_{l' \in A} Q_{Al}^s Q_{Al'}^s W_{All'} \\
 &= \sum_{\sigma=\alpha,\beta} \sum_{\mu\nu} P_{\mu\nu} \underline{H_{\mu\nu}} + \frac{1}{2} \sum_{A,B}^{atoms} \underline{E_{AB}^{rep}} + \frac{1}{2} \sum_{A,B}^{atoms} \Delta q_A \underline{\gamma_{AB}} \Delta q_B + \frac{1}{2} \sum_A \sum_{l \in A} \sum_{l' \in A} Q_{Al}^s Q_{Al'}^s \underline{W_{All'}}
 \end{aligned}$$

where,

E_{AB}^{rep} : is the diatomic repulsive potential between atom A and B

$\Delta q_A / \Delta q_B$: Mulliken charge on atom A/B

$Q_{Al}^s / Q_{Al'}^s$: Spin density in orbital l/l' on atom A

γ_{AB} : charge interaction parameter

$W_{All'}$: spin density interaction parameter

$$H_{\mu\nu} = \begin{cases} \varepsilon_{\mu}^{\text{neutral free atom}} & \text{if } \mu = \nu \\ \langle \varphi_{\mu(A)} | \hat{T} + V_{0(A)} + V_{0(B)} | \varphi_{\nu(B)} \rangle & \text{if } A \neq B \\ 0 & \text{otherwise} \end{cases}$$

Parameterization scheme

1. Atomic (DFT) calculations:

- Obtain atomic orbitals φ_μ
- Determine atomic Hubbard value $U_A, U_B, \gamma_{AB} = \gamma_{AB}(U_A, U_B, R_{AB})$
- Determine spin interaction parameters $W_{All'}$

$$W_{All'} = \frac{\partial^2 E_{total}}{\partial Q_{Al}^s \partial Q_{Al'}^s} = \frac{1}{2} \left(\frac{\partial \varepsilon_l^\alpha}{\partial n_{l'}^\alpha} - \frac{\partial \varepsilon_l^\beta}{\partial n_{l'}^\beta} \right),$$

$\varepsilon_l^\alpha, \varepsilon_l^\beta$: atomic orbital energy; $n_{l'}^\alpha, n_{l'}^\beta$: orbital occupancy

2. Diatomic (DFT) calculations:

$$H_{\mu\nu} = \langle \varphi_\mu | H | \varphi_\nu \rangle, S_{\mu\nu} = \langle \varphi_\mu | \varphi_\nu \rangle$$

3. Fitting repulsion potential to B3LYP binding energies (trial-and-error method):

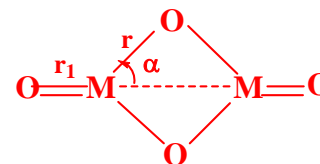
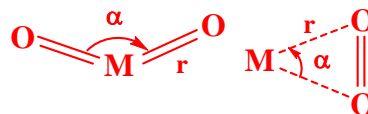
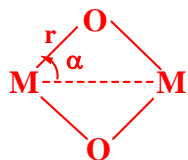
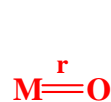
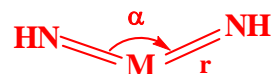
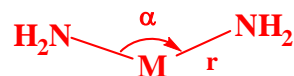
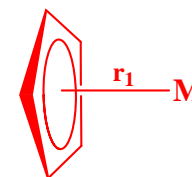
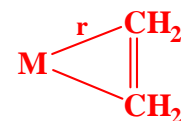
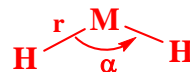
$$E_{rep}^{AB}(R) = \left\{ E_{DFT}^{SCF}(R) - \left[\sum_i^{occ} \langle \psi_i | \bar{H}_0 | \psi_i \rangle - \frac{1}{2} \sum_{A,B}^{atoms} \Delta q_A \gamma_{AB} \Delta q_B - \frac{1}{2} \sum_A \sum_{l \in A} \sum_{l' \in A} Q_{Al}^s Q_{Al'}^s W_{All'} \right]_{DFTB} \right\} \Big|_{reference\ systems}$$

Parameterized atom pairs

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
H	✓	✓			✓	✓	✓	✓	✓	✓
C	✓	✓			✓	✓	✓	✓	✓	✓
N	✓	✓			✓	✓	✓	✓	✓	✓
O	✓	✓			✓	✓	✓	✓	✓	✓

✓ = done ■ : our work ■ : Prof. Elstner and Prof. Cui's work

Test Molecule Structure Scheme



Different bond types are represented

Geometry Benchmark Results

---comparison between DFTB and B3LYP/SDD results



Average absolute bond length difference (Å)
between DFTB and B3LYP/SDD results

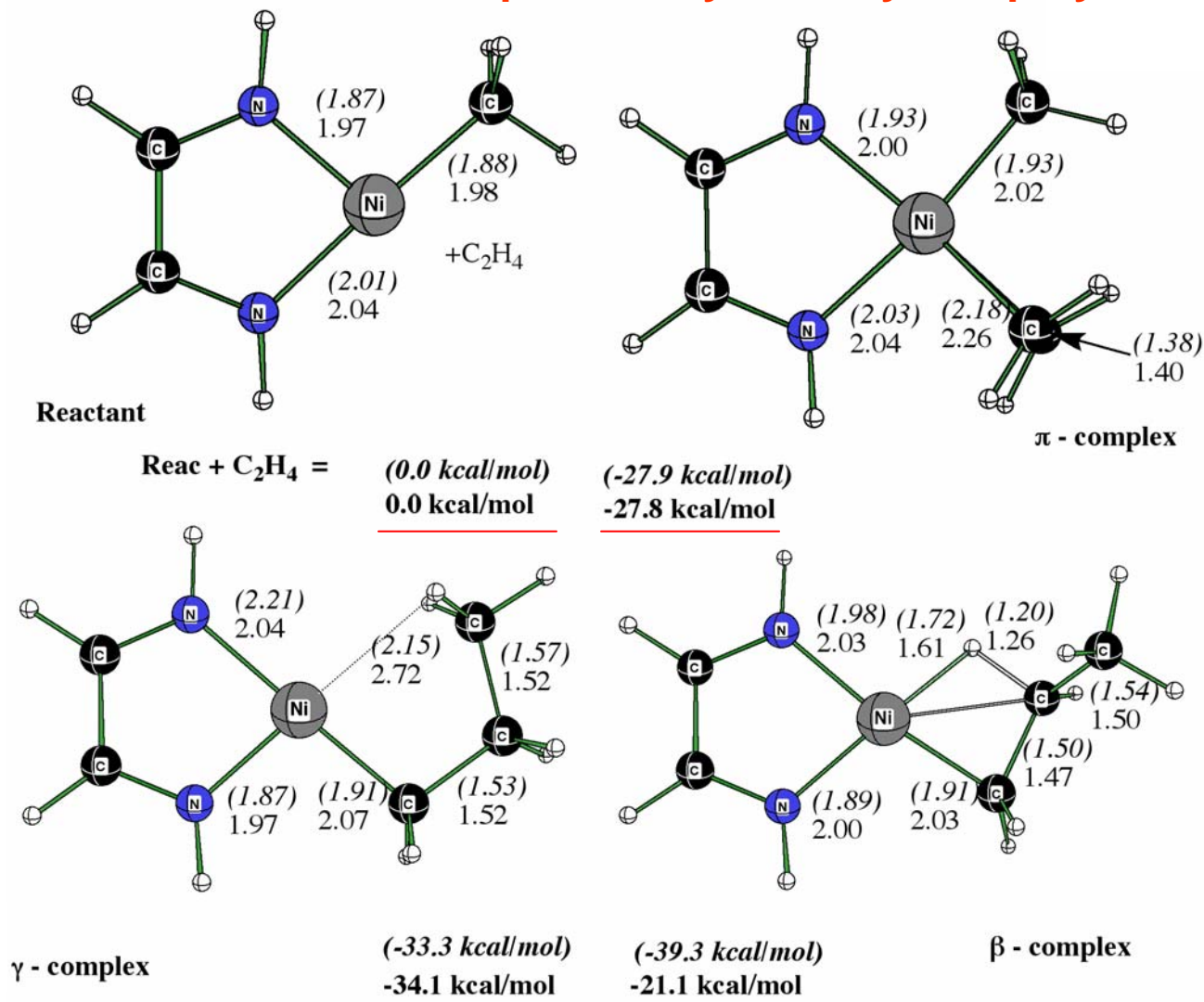
	H	C	N	O
Ti	0.06	0.06	0.01	0.02
Fe	0.04	0.10	0.06	0.05
Co	0.03	0.12	0.03	0.03
Ni	0.04	0.16	0.08	0.02

Average absolute bond angle difference
(degree) between DFTB and B3LYP/SDD
results

	H	C	N	O
Ti	7.2	6.7	3.2	4.8
Fe	10.1	2.8	15.6	7.8
Co	2.1	5.4	2.9	3.8
Ni	3.6	1.7	16.0	9.4

Energetics Benchmark Results

Compounds in diimine Ni complex catalyzed ethylene polymerization reaction

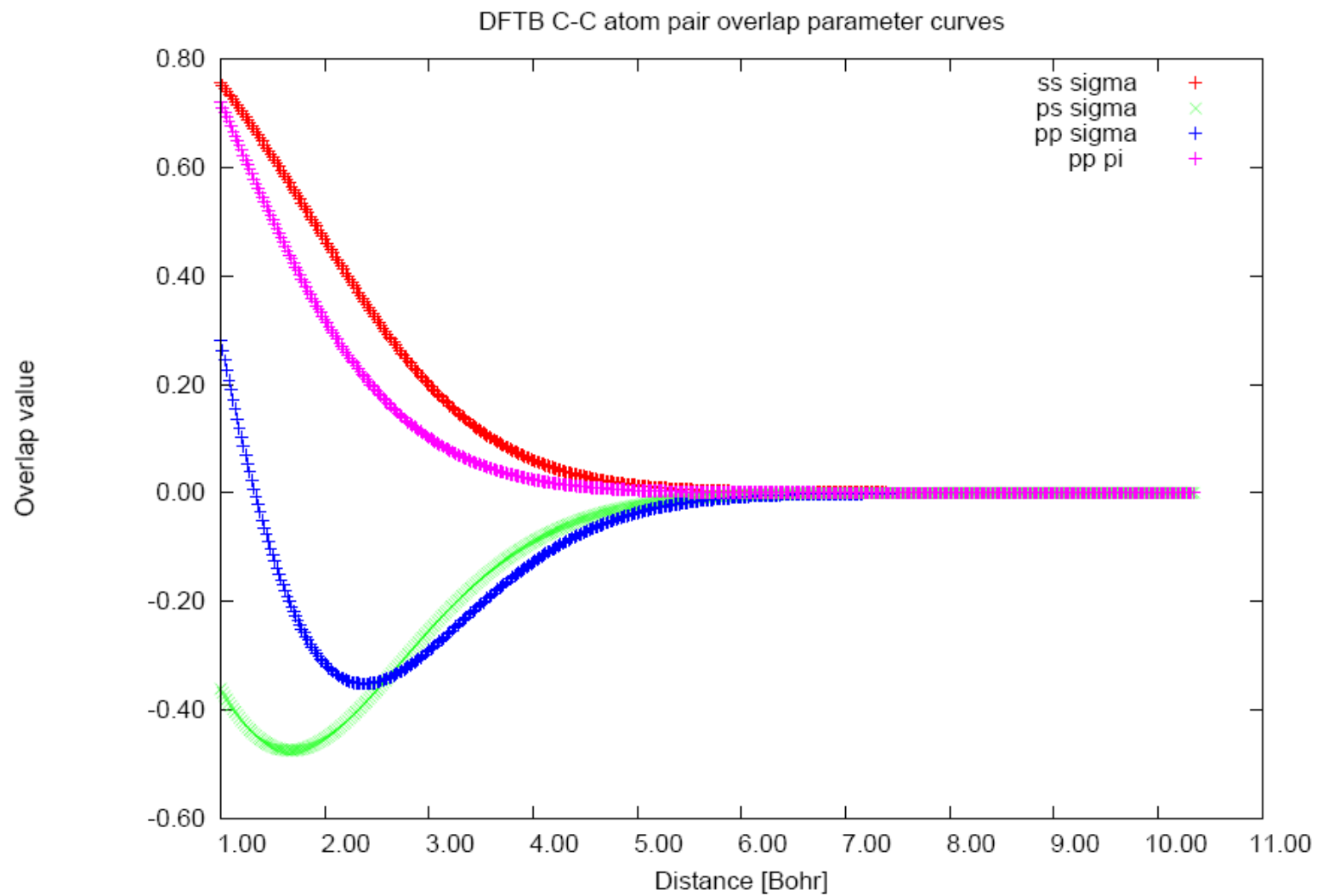


II. Development of analytical functions for DFTB parameters

Motivation

- Smooth functions, important for high order energy derivative
- Small parameter data base

C-C parameter curves



Functional Forms

$$E = \sum_{i=1}^{10} C_i \exp(-\alpha \beta^i R)$$

C_i , α and β are coefficients to be fitted

R : distance

E : fitted value

Fitting Details

- Hamiltonian/Overlap values on grids with $R=1.0$ — 10.4 Bohr are fit
- About 480 points with energy less than 0.3 Hartree of repulsion potential are fitted
- Levenberg-Marquardt Method is used for nonlinear fitting

Fitting Results

RMS and maximum deviation between fitted values and original grid values of Hamiltonian and Overlap matrix elements for the C-C atom pair.

Orbital pair		Bond type	RMS [a.u.]	MAX [a.u.]
pp	Hamiltonian	σ	6.09E-06	1.32E-04
pp	Hamiltonian	π	4.24E-06	9.18E-05
ps	Hamiltonian	σ	7.29E-06	1.86E-04
ss	Hamiltonian	σ	4.78E-06	1.14E-04
pp	overlap	σ	2.03E-05	5.34E-04
pp	overlap	π	4.75E-07	7.55E-05
ps	overlap	σ	1.17E-05	3.14E-04
ss	overlap	σ	6.28E-06	1.36E-04

Other Hamiltonian and overlap parameters fit quality is similar to the above C-C parameter fitting result.

Fitting Results

RMS and maximum deviation between fitted values and original grid values of repulsion curves.

RMS [a.u.]	H	C	N	O
H	3.3E-05	1.8E-04	8.8E-05	1.5E-04
C	1.8E-04	7.0E-04	2.4E-04	1.2E-04
N	8.8E-05	2.4E-04	4.7E-04	6.6E-04
O	1.5E-04	1.2E-04	6.6E-04	1.4E-04

MAX [a.u.]	H	C	N	O
H	2.44E-04	1.2E-03	7.3E-04	1.3E-03
C	1.19E-03	4.76E-03	1.2E-03	6.1E-04
N	7.27E-04	1.19E-03	1.71E-03	4.1E-03
O	1.27E-03	6.08E-04	4.07E-03	3.38E-04

Test Optimization calculations for 264 molecules



- All 264 molecules consist of H, C, N and O atoms.
- Geometry optimization starting from the same point using the original parameter and the fitted function forms
- All calculations are done in C_1 symmetry.
- The optimized geometries are superimposed in order to compare how close they are.
- The average RMS deviation of 264 molecules is **0.007Å!**

III. Implementation of DFTB method in Gaussian program

Motivation

- Extend the applicability of DFTB to a wider range of chemistry problems, e.g. transition states.
- Take advantage of existing Gaussian functionalities, e.g. SCF convergence techniques, partial geometry optimization
- A smooth combination with ONIOM method
- Numerically efficient and stable implementation for dealing with large molecular systems

DFTB Energy

$$\begin{aligned}
 E^{DFTB} = & \sum_{\mu\nu}^{orb.} P_{\mu\nu} h_{\mu\nu}^0 + \frac{1}{2} \sum_{AB}^{atoms} Q^A \gamma^{AB} Q^B + \frac{1}{2} \sum_A^{atoms} \sum_{l,l' \in A} Q^{Al} (U_{ll'}^A - \gamma^{AA}) Q^{Al'} \\
 & + \frac{1}{2} \sum_A^{atoms} \sum_{l,l' \in A} Q_s^{Al} W_{ll'}^A Q_s^{Al'} + \frac{1}{2} \sum_{AB}^{atoms} E_{rep}^{AB}
 \end{aligned}$$

P : density matrix;

h^0 : diatomic Hamiltonian matrix;

Q^A/Q^B : Mulliken charge on atom A/B;

γ^{AB} : charge interaction parameter between atom A and B;

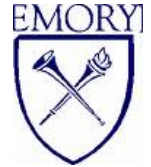
Q^{Al} : Mulliken charge charge of orbital l on atom A;

$U_{ll'}^A$: On site charge interaction parameter;

$W_{ll'}^A$: Spin interaction parameter between orbital l and l' ;

E_{rep}^{AB} : Repulsion interaction potential between atom A and B.

an alternative energy expression



$$E = \langle Ph \rangle + \frac{1}{2} \langle PG(P) \rangle + V \longleftarrow \text{Exactly the same form as SCF/KS-DFT}$$

1e matrix term:

$$h_{uv} = h_{uv}^0 - \frac{1}{2} S_{uv} \left[\sum_C^{\text{atoms}} (\gamma^{AC} + \gamma^{BC}) Z^C + \sum_{l' \in A(u)} (U_{ll'}^A - \gamma^{AA}) Z^{Al'} + \sum_{l' \in B(v)} (U_{ll'}^B - \gamma^{BB}) Z^{Bl'} \right]$$

2e matrix term:

$$G_{uv}^\sigma = \frac{1}{2} S_{uv} \left[\sum_C^{\text{atoms}} (\gamma^{AC} + \gamma^{BC}) q^C + \sum_{l' \in A(u)} (U_{ll'}^A - \gamma^{AA}) q^{Al'} + \sum_{l' \in B(v)} (U_{ll'}^B - \gamma^{BB}) q^{Bl'} \right. \\ \left. + \delta_\sigma \left[\sum_{l' \in A(u)} W_{ll'}^A Q_s^{Al'} + \sum_{l' \in B(v)} W_{ll'}^A Q_s^{Bl'} \right] \right]$$

Repulsion term

$$V = \sum_{A>B} (E_{rep}^{AB} + Z^A \gamma^{AB} Z^B)$$

DFTB Gradient

$$E^x = \sum_{A>B} (E_{rep}^{AB^x} + Q^A \gamma^{AB^x} Q^B) + 2 \sum_{\mu>\nu} (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) h_{\mu\nu}^{0^x} + 2 \sum_{\mu>\nu} W'_{\mu\nu} S_{\mu\nu}^x$$

$$W'_{\mu\nu} = -W_{\mu\nu} + \frac{1}{2} (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) \left\{ \left[\begin{aligned} &\sum_C^{atoms} (\gamma^{AC} + \gamma^{BC}) Q^C + \\ &\sum_{l' \in A(u)} (U_{ll'}^A - \gamma^{AA}) Q^{Al'} + \sum_{l' \in B(v)} (U_{ll'}^B - \gamma^{BB}) Q^{Bl'} \end{aligned} \right] \right. \\ \left. + \left[(P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta) \left(\sum_{l' \in A(u)} W_{ll'}^A Q_s^{Al'} + \sum_{l' \in B(v)} W_{ll'}^B Q_s^{Bl'} \right) \right] \right\}$$

where W is energy weighed density matrix, it is defined

$$W = PFP$$

$$F = h + G(P)$$

Analytical 2nd Derivative

$$\begin{aligned}
 E^{xy} &= \langle Ph^{xy} \rangle + \frac{1}{2} \langle PG^{xy}(P) \rangle - \langle S^{xy}W \rangle + V^{xy} - \langle S^x W^y \rangle - \langle P^x \tilde{F}^y \rangle \\
 &= \sum_{A>B}^{atoms} Q^A \gamma^{AB^{xy}} Q^B + \sum_{A>B}^{atoms} E_{rep}^{AB^{xy}} + 2 \sum_{\mu>\nu}^{orbs} S_{\mu\nu}^{xy} W'_{\mu\nu} + 2 \sum_{\mu>\nu}^{orbs} (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) h_{\mu\nu}^{0^{xy}} \\
 &\quad + \sum_{AB}^{atoms} \left(\tilde{Q}^{A^x} \gamma^{AB^y} Q^B + \tilde{Q}^{A^y} \gamma^{AB^x} Q^B + \tilde{Q}^{A^x} \gamma^{AB} \tilde{Q}^{B^y} \right) \\
 &\quad + \sum_A^{atoms} \sum_{l,l' \in A} \left(\tilde{Q}^{Al^x} \tilde{U}^{All'} \tilde{Q}^{Al'^y} + \tilde{Q}_s^{Al^x} W^{All'} \tilde{Q}_s^{Al'^y} \right) \\
 &\quad - \langle S^x W^y \rangle - \langle P^x \tilde{F}^y \rangle
 \end{aligned}$$

$$\tilde{Q}^{A^x} = \sum_{\mu} \sum_{v \in A} (P_{\mu v}^\alpha + P_{\mu v}^\beta) S_{\mu v}^x, \tilde{Q}_s^{Al^x} = \sum_{\mu} \sum_{v \in Al} (P_{\mu v}^\alpha - P_{\mu v}^\beta) S_{\mu v}^x, \tilde{U}^{All'} = U^{All'} - \gamma^{AA}$$

Analytical 2nd Derivative

$$\tilde{F}^y = h^y + G^y(P)$$

The "y" at the right up corner represents the derivative w.r.t. the coordinate.

Density matrix derivative embedded in \tilde{F}^y and W^y can be obtained by solving the following CPHF equation via DIIS algorithm.

$$F^0 P_{ov}^y + F^0 S_{ov}^y = P_{ov}^y F^0 + F_{ov}^y$$

where McWeeny notation is adopted. The subscript "o" and "v" represent occupied and virtual space, respectively. And

$$F_{ov}^y = h^y + G(P^y) + G^y(P^0)$$

New Features

- Integral occupancy of orbitals
- Extended to open shell-molecules including energy, gradient, frequency and spectrum calculations
- Support both analytical function forms and the original parameter forms
- All Gaussian features including SCF and geometry optimization techniques can be applied.

Gaussian DFTB calculation Examples

---ONIOM calculation of Ethane



Input File:

```
#p oniom(b3lyp/3-21g:dftba=read) opt  
  
Ethylane ONIOM job using B3LYP:DFTB  
  
0 1 0 1 0 1  
C      0 -3.744589  1.450216  0.000000 L H  5  
H      0 -3.387916  1.954615  0.873652 L  
H      0 -3.387916  1.954615 -0.873652 L  
H      0 -4.814589  1.450230  0.000000 L  
C      0 -3.231273 -0.001716  0.000000 H  
H      0 -2.161273 -0.001728 -0.000001 H  
H      0 -3.587945 -0.506114  0.873652 H  
H      0 -3.587946 -0.506115 -0.873651 L H  5
```

@../all_ch_para.txt

@../all_ch_para.txt

(Part of) output file:

```
ONIOM: saving gridpoint 1  
ONIOM: restoring gridpoint 3  
ONIOM: calculating energy.  
ONIOM: gridpoint 1 method: low system: model energy: -3.221606349599  
ONIOM: gridpoint 2 method: high system: model energy: -40.301310546382  
ONIOM: gridpoint 3 method: low system: real energy: -5.702210847049  
ONIOM: extrapolated energy = -42.781915043832  
ONIOM: calculating first derivatives.  
ONIOM: calculating electric field derivatives.  
ONIOM: Integrating ONIOM file 5 number 695  
.  
.  
1\1\GINC-MARS\FOpt\ONIOM(B3LYP/3-  
21G:DFTBA)\Mixed\C2H6\GUISHAN\07-Sep-  
2006\0\#p oniom(b3lyp/3-21g:dftba=read) opt\Ethylane ONIOM job using  
B3LYP:DFTB\0,1\C,-3.7364771235,1.4272785779,0.0000028846\H,-3.378871  
9455,1.9676063577,0.8935190967\H,-3.380834151,1.9669006335,-0.89472249  
05\H,-4.8399452403,1.4510407232,0.0012013114\C,-3.238675661,0.01923059  
68,0.0000002407\H,-2.1396794588,-0.0031457709,0.0012096267\H,-3.595462  
3792,-0.5178058816,0.8902795307\H,-3.5935010408,-0.5171022367,-0.89149  
02005\Version=AM64L-GDVRRevE.X4\State=1-A\HF=-  
3.2216063\RMSD=3.064e-09  
\RMSF=8.169e-06\PG=C01 [X(C2H6)]\@
```

Gaussian DFTB calculation Examples

---Geometry optimization of CH₂



Input File:

```
#p dftba=read opt  
  
CH2 molecule geometry optimization  
  
0 3  
C 0.0 0.0 0.0  
H 1.0 0.0 0.0  
H 0.0 1.0 0.0  
  
@../all_ch_para.txt
```

(Part of) output file:

```
Orbital symmetries:  
Alpha Orbitals:  
  Occupied (A1) (B2) (A1) (B1)  
  Virtual (A1) (B2)  
Beta Orbitals:  
  Occupied (A1) (B2)  
  Virtual (A1) (B1) (A1) (B2)  
The electronic state is 3-B1.  
Alpha occ. eigenvalues -- -0.58334 -0.37028 -0.24743 -0.21978  
Alpha virt. eigenvalues -- 0.30831 0.41798  
Beta occ. eigenvalues -- -0.50789 -0.32934  
Beta virt. eigenvalues -- -0.15808 -0.12139 0.34087 0.46635  
  
. . .  
1\1\GINC-MARS\FOpt\UDFTBA\ZDO\C1H2(3)\GUISHAN\07-Sep-2006\0\#p dftba=  
read opt\Gaussian Test Job: CH2 molecule geometry optimization\0,3\C  
,0.1282399937,0.1282399937,0.\H,1.1501549125,-0.2783949061,0.\H,-0.278  
3949061,1.1501549125,0.\Version=AM64L-GDVRvE.X4\State=3-B1\HF=-2.291  
9205\S2=2.013125\S2-1=0.\S2A=2.000064\RMSD=1.888e-10\RMSF=1.566e-04\Di  
pole=0.,0.,-0.3304982\Quadrupole=-0.4364781,0.6359741,-0.1994961,0.,0.  
,0.\PG=C02V [C2(C1),SGV(H2)]\@
```

Gaussian DFTB calculation Examples

---spectrum calculation of C₂



Input File:

```
#p dftba=read freq IOP33(11=3,7=3) nosymm  
scf=noincore cphf=separate
```

Gaussian Test Job: C2 molecule frequency

```
0 1  
C -0.036013 -0.036013 -0.036013  
C 0.680735 0.680735 0.680735
```

```
@../all_ch_para.txt
```

(Part of) output file:

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (A⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

```
1  
A  
Frequencies -- 2140.7294  
Red. masses -- 12.0000  
Frc consts -- 32.4007  
IR Inten -- 0.2061  
Atom AN X Y Z  
1 6 0.41 0.41 0.41  
2 6 -0.41 -0.41 -0.41
```

Conclusion

- Sc, Ti, Fe, Co and Ni parameters can reasonably predict geometries and reaction energetics
- Fitted analytical forms of DFTB parameters can reproduce results from the original parameters
- DFTB method including the analytical second derivative has been implemented in Gaussian development version



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