Long-range exchange interactions in DFT and its significance in chemical reactions

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June 19 - 23, 2017 Interdisciplinary symposium on modern density functional theory (iDFT)@RIKEN, Wako

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1. Long-range exchange interactions in DFT

Density Functional Theory in QC

Fig. Annual variation of the number of papers published in electric journals of chemistry (ISI Web of Science).



Until early 90s:

Ab initio wavefunction theories had occupied QC calculations Since mid-90s:

DFT calculations steadily increase and now occupy ~87% of QC calculations

DFT functionals in Quantum Chemistry



QC field may have produced the most new DFT functionals in science. ←Well-balanced electron correlation should be incorporated in the functionals to provide chemical accuracy (MAE ~1 kcal/mol), which is required to discuss chemical reactions. Formulations: Simple vs Complex Parameters: Minimum vs Many Systems: Specific vs General Target properties: Difficult vs Easy

Long-range correction for DFT

Long-range correction (LC) for general exchange functionals. [likura, Tsuneda, Yanai and Hirao, JCP, <u>115</u>, 3540, 2001.]



For the short-range part, a general exchange functional is adapted $(a_{\sigma} = \mu/(2k_{\sigma}), k_{\sigma} = (9\pi/K_{\sigma})^{1/2} \rho_{\sigma}^{1/3})$. $E_{x}^{sr} \equiv -\frac{1}{2} \sum_{\sigma} \int d^{3}\mathbf{r} \rho_{\sigma}^{4/3} K_{\sigma} \left\{ 1 - \frac{8}{3} a_{\sigma} \right\} \times \left[\sqrt{\pi} \operatorname{erf} \left(\frac{1}{2a_{\sigma}} \right) + \left(2a_{\sigma} - 4a_{\sigma}^{-3} \right) \exp \left(-\frac{1}{4a_{\sigma}^{-2}} \right) - 3a_{\sigma} + 4a_{\sigma}^{-3} \right] \right\}$

For the long-range part, HF exchange integral is used.

$$E_{x}^{lr} = -\frac{1}{2} \sum_{\sigma} \sum_{i}^{\text{occ}} \sum_{j}^{\text{occ}} \int \int d^{3}\mathbf{r}_{1} d^{3}\mathbf{r}_{2} \phi_{i\sigma}^{*}(\mathbf{r}_{1}) \phi_{j\sigma}^{*}(\mathbf{r}_{2}) \frac{\text{erf}(\mu r_{12})}{r_{12}} \phi_{j\sigma}(\mathbf{r}_{1}) \phi_{i\sigma}(\mathbf{r}_{2})$$

LC has innovated the development of various sophisticated functionals:

CAM-B3LYP [T. Yanai, D.P. Tew, & N.C. Handy, CPL, <u>91</u>, 551, 2004.]

LC-@PBE [O. A. Vydrov, J. Heyd, A. V. Krukau, & G. E. Scuseria, JCP, <u>125</u>, 074206, 2006.]

BNL [E. Livshits & R. Baer, PCCP, 9, 2937, 2007.]

00897-series [J.-D. Chai & M. Head-Gordon, JCP, <u>128</u>, 084106, 2008.]

Tuned RSH [R. Baer, E. Livshits, & U. Salzner, ARPC, 61, 85, 2010.]

DFT problems that LC solved or improved



TDDFT calculations of electronic spectra



Charge transfer excitations



Optical properties of long-chain polyenes



Hyperpolarizabilities of radicals

Fig. Diradical y-dependence of hyperpolarizabilities of *p*-quinodimethane model, γ (x10² a.u.)



$$y = 1 - \frac{2T}{1 + T^2}, \quad T = \frac{n_{\text{HOMO}} - n_{\text{LUMO}}}{2}$$

Closed shell $\rightarrow y=0$, diradical $\rightarrow y=1$

[Kishi, Bonness, Yoneda, Takahashi, Nakano, Botek, Champagne, Kubo, Kamada, Ohta, & Tsuneda, J. Chem. Phys. 132, 094107, 2010.]

LC-DFT accurately provides hyperpolarizabilities and 2nd-order hyperpolarizabilities of diradicals



Table. 2nd-order hyperpolarizability of 1,4-bis-imidazol-2-ylidenecyclohexa-2,5-diene (BI2Y) γ (x10² a.u.)

Method	6-31G	6-31G*+ <i>p</i>
UHF	1736	2002
UMP2	9387	9962
UCCSD	4474	-
UCCSD(T)	5244	-
UBLYP	-129	-298
UB3LYP	-377	-472
LC-UBLYP	4310	6019

Weakly-bonded complexes



Benchmark test for weakly-bonded systems

Table. Mean absolute errors of various DFT methods of van der Waals calculations for S22 benchmark set (including 22 weaklybonded systems).

[<u>T. Tsuneda</u> and T. Taketsugu, `` π -Stacking on Density Functional Theory: A review'', in π -Stacked Polymers and Molecules, Ed. T. Nakano, 245 - 270 (Springer, 2013).]

Methods	Corrections	MAE (kcal/mol)	
ωB97X-D	LC + classical vdW	0.22	
BLYP-D3	Classical vdW	0.23	
ωB97X-2	LC + perturbation	0.26	
LC-BOP+LRD	LC + vdW functional	0.27	
B2PLYP-D3	Classical potential + perturbation	0.29	
RSH+RPAx	LC + AC/FDT	0.32	
M06-2x	Classical potential	0.44	
BLYP-D	Classical potential	0.55	
B97-D	Classical potential	0.61	
B3LYP-D	Classical potential	0.70	
MP2/CBS	Perturbation	0.78	
VV09(HF)	vdW functional	0.89	
M05-2x	Classical potential	0.90	
vdW-DF(rPW96)	vdW functional	1.03	
VV09(rPW96)	vdW functional	1.20	
vdW-DF(revPBE)	vdW functional	1.44	
vdW-DF(HF)	vdW functional	2.80	

Orbital energy calculations



Physical meaning of orbital energies

Energy linearity theorem for fractional occupations

[Perdew, Parr, Levy, and Balduz Jr., PRL, 49, 1691, 1982; Yang, Zhang, Ayers, PRL, 84, 5172, 2000.]

$$E\left(n+\frac{p}{q}\right) = \frac{p}{q}E(n+1) + \frac{q-p}{q}E(n)$$

The total electronic energy varies linearly as a function of its fractional occupation number



Janak theorem [Janak, Phys. Rev. B 103, 7165, 1978.]

∂E	= 8
∂n_i	$-\boldsymbol{v}_i$

The derivative of the total electronic energy with respect to the occupation number of an orbital is identical to the orbital energy.

Energy linearity theorem + Janak theorem

= Generalized Koopmans theorem

HOMO energy ε_{HOMO} = –IP LUMO energy ε_{LUMO} = –EA

Sham-Schlüter theorem

[Sham and Schlüter, Phys. Rev. B 32, 3883, 1985.] Outermost orbital energy is independent of occupation number

Energy linearity for fractional occupations



Fig. Total energy dependence of C_2H_4 molecule on occupation number variance toward $C_2H_4^-$ anion.

Only LC-DFT gives an almost linear dependence of the total energy both for increasing and decreasing the occupation number

Other DFTs give concave dependences

[Tsuneda, Song, Suzuki and Hirao, J. Chem. Phys. 133, 174101, 2010.]

Fig. Total energy dependence of C_2H_4 molecule on occupation number variance toward $C_2H_4^+$ cation.



Orbital energy dependence on occupations

Fig. Outermost orbital energy variance of C_2H_4 molecule in terms of the occupation number for $-1 < \Delta n < 0$ (left) and $0 < \Delta n < 1$ (right).



Dependence of Kohn-Sham orbital energy on occupation number [T. Tsuneda, J.-W. Song, S. Suzuki and K. Hirao, J. Chem. Phys. 133, 174101, 2010.]

$$\frac{\delta \varepsilon_i}{\delta n_i} = \iint d^3 \mathbf{r} d^3 \mathbf{r}' \phi_i^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_x \phi_i(\mathbf{r}) \phi_i(\mathbf{r}') \right]$$

Self-interaction error in exchange integral kernel $f_x = \delta^2 E_x / \delta \rho^2$ causes the orbital energy dependence on the occupation number

Exchange integral kernel $f_x = \delta^2 E_x / \delta \rho^2$





Self-interaction correction for LC-DFT

Regional self-interaction correction (RSIC) :

Replacing exchange energy density with exchange self-interaction one only for the region where electrons have no electron-electron interaction.

[Tsuneda, Kamiya, & Hirao, J. Comput. Chem. 24, 1592, 2003.]



Self-interaction region



Exchange self-interaction energy density = Exchange energy of hydrogen-like atoms \rightarrow RSIC

$$\varepsilon_{x\sigma}^{\rm SI}(\mathbf{r}) = -\frac{1}{2r} \Big[1 - (1 + \alpha r) e^{-2\alpha r} \Big] \qquad \alpha = \frac{|\nabla \rho_{\sigma}|}{2\rho_{\sigma}}$$

= Pseudospectral (PS) exchange energy density → PSRSIC (PR) [Nakata, Tsuneda & Hirao, J. Phys. Chem. A 114, 8521, 2010.]

$$\varepsilon_{x}^{\mathrm{SI}}(\mathbf{r}) = -\frac{1}{4} \sum_{\mu\nu\lambda\kappa} P_{\mu\nu} P_{\lambda\kappa} \chi_{\nu}^{*}(\mathbf{r}) \times \chi_{\lambda}(\mathbf{r}) \int d^{3}\mathbf{r}_{2} \frac{\chi_{\kappa}^{*}(\mathbf{r}_{2}) \chi_{\mu}(\mathbf{r}_{2})}{|\mathbf{r}_{2} - \mathbf{r}|}$$

Self-interaction energy correction for exchange energy density:

$$\varepsilon_{x\sigma}^{\text{SIC}}(\mathbf{r}) = (1 - f_{\sigma})\varepsilon_{x\sigma}^{\text{DFT}}(\mathbf{r}) + f_{\sigma}\varepsilon_{x\sigma}^{\text{SI}}(\mathbf{r})$$
$$f_{\sigma} = \begin{cases} 0 \ (t < a) \\ 1 \ (t \ge a) \end{cases} \quad a = -0.0204Z + 1.0728$$

HOMO & LUMO energies of H and rare-gas atoms

[Nakata, Tsuneda & Hirao, J. Chem. Phys. 139, 064102, 2013.]

Fig. Errors in HOMO (left) & LUMO (right) energies of H and rare-gas atoms. Aug-cc-pVTZ basis.



PSRSIC clearly improves HOMO energies of H and rare-gas atoms, which are underestimated by LC-DFT, while it keeps the accuracy of LUMO energies.
Only LUMO energy of H atom cannot be accurately reproduced.
← LUMO of H has no electron correlation.

Core 1s orbital energies

Fig. Errors in the core 1s orbital energies of the second- (left) and third-row (right) atoms of typical molecules. Aug-cc-pVTZ basis.



HOMO & LUMO energies

Fig. Errors in HOMO (left) and LUMO (right) energies of typical molecules. Aug-cc-pVTZ basis.



Core excitation energies

Fig. Errors in calculated core excitation energies of the second-row atoms in typical molecules (eV).

Fig. Errors in calculated core excitation energies of the third-row atoms in typical molecules (eV).



Conclusions of the first part

- Long-range correction (LC) for exchange functionals have solved many problems in DFT: e.g., charge transfer excitations, van der Waals interactions, nonlinear optical properties. In particular, LC-DFT enables us to calculate orbital energies quantitatively for the first time ever.
- 2. Orbital energies are proven to have physical meanings irrespective of the type of theory: HOMO and LUMO energies are identical to the minus ionization potential and electron affinity, respectively. LC-DFT provides accurate orbital energies due to the selfinteraction-free nature of the exchange integral kernel, $\delta^2 E_x / \delta \rho^2$.
- 3. LC-DFT has been reported to have several problems: e.g., overestimation of atomization energies, underestimation of core orbital energies and core excitation energies, poor charge transfer excitation energies in metal complexes, and orbital energies of large systems. However, the underestimation of core orbital energies and core excitation energies are clearly solved by a regional self-interaction correction.

2. Significance of long-range exchange interactions in chemical reactions

Isodesmic reactions of long-chain alkanes

Fig. Errors in calculated isodesmic reaction enthalpies of n-alkanes to ethane for various methods at 0 K. 6-311+G(p,d) basis. [Song, Tsuneda, Sato & Hirao, Org. Lett. 12, 1440, 2010.]

Most functionals overestimate the reaction enthalpies as the chain becomes long

Only LC+vdW(LRD) and LDA provide the correct dependence of the reaction enthalphies on the chain lengths

Semi-empirical functionals (M05-2x, M06-2x, BMK) provide vibrating enthalpies dependent on the number of the chains



Isomerization reactions

[Song, Tsuneda, Sato & Hirao, Theor. Chem. Acc. (Imamura Festschrift), 130, 851, 2011.]



Condensation reactions

[Singh, Tsuneda & Hirao, TCA (Nagase Festschrift) 130, 153, 2011.] Aldol reaction α -Aminoxylation reaction (1) (2) (3) **Isogyric reaction** (4) + 2 CH₄ Mannich reaction + 2 CH₄ (5) N + CH₄ + H₂O _____ (6) (7)

B3LYP does not give

- quantitative enthalpies (8) for condensation
- (9) reactions [Wheeler et al., JPCA, 113, 10376, 2009.]

LC-DFT comprehensively

- provides accurate (11)reaction enthalpies for
- (12) these condensation reactions



Table. MAE of condensation reaction enthalpies (kcal/mol).

(10)

Reaction	LC-BOP	LC-ωPBE	CAM-B3LYP	B3LYP	BMK	M06-2x
Aldol	1.7	1.9	3.0	7.6	3.4	1.7
Mannich	1.1	2.9	1.9	6.3	0.9	1.3
α -Aminoxylation	2.8	1.5	1.4	2.4	3.8	3.9
Isogyric	3.7	4.8	2.0	1.9	2.3	4.0
Total	2.2	2.8	2.2	5.0	2.6	2.6

Diels-Alder reactions



B3LYP also cannot give quantitative Diels-Alder reaction enthalpies [Pieniazek et al., Angew. Chem. Int. Ed. 47, 7746, 2008.]

GGA & B3LYP results are surely poor Semi-empirical functionals, M06-2x & BMK, provide accurate enthalpies LC-DFT also give accurate enthalpies, though these are poorer than semiempirical ones



ППс

IVc

■Vc

■VIc

■VIIc

■ VIIIc

(c)

Th

∎ IIIb

■IVb

∎Vb



Global hardnesses in Diels-Alder reactions



Fig. Calculated global hardnesses (the halves of HOMO-LUMO gaps) of 1,3butadiene+ethylene complex on IRCs and the corresponding reaction energy diagram. [R. K. Singh & T. Tsuneda, J. Comput. Chem., 34, 379, 2013.]

B3LYP: monotonically-increasing

LC-BOP:

almost constant (precursory) rapidly-increasing (successive)

Constant $\eta \rightarrow$ Electron transfer

Conventional theoretical reaction analyses



Frontier orbital theory

Ansatz of Frontier orbital theory



Reactivities are mainly determined by the stabilization energies from electron delocalization in the transition states.

Frontier orbitals (HOMO & LUMO) chiefly contribute to electron delocalization.

Reactivity indicesElectrophilic reactions: $ho_{HOMO}(r)$ Nucleophilic reactions: $ho_{LUMO}(r)$ Radical reactions: $[ho_{HOMO}(r) + ho_{LUMO}(r)]/2$

Conceptual density functional theory

[R. F. Nalewajski & R. G. Parr, J. Chem. Phys. 77, 399, 1982]

Legendre transformation (variable transformation) Hohenberg-Kohn theorem:

Energy functional $E[V: intensive] \rightarrow E[\rho: extensive]$

E : independent of external potential *V* variation in reaction pathways Levy constrained search formulation = Finding optimum chemical potential $\mu = (\partial E / \partial n)$

Maxwell relation (in classical thermodynamics)

$$\frac{\partial}{\partial x_j} \left(\frac{\partial F}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left(\frac{\partial F}{\partial x_j} \right)$$

μ

V

ρ

n

$$f = \left(\frac{\partial \mu}{\partial V}\right)_n = \left(\frac{\partial \rho}{\partial n}\right)_V$$

F: arbitrary thermodynamics potential x_i, x_j : natural variables

$$\mu = (\partial E / \partial n) \& \rho = (\partial E / \partial V)$$

Chemical potential variance wrt structural change with a constant occupation # = Density variance wrt occupation # with no structural change

Conceptual density functional theory

[Tsuneda, Int. J. Quantum Chem.: Special issue on "Theoretical chemistry in Japan", 115, 270, 2014 (Open access).]

Fukui functions

Electrophilic reactions: $f^- = (\partial \rho_{\text{HOMO}} / \partial n)_V \approx \rho_{\text{HOMO}}(\mathbf{r})$ Nucleophilic reactions: $f^+ = (\partial \rho_{\text{LUMO}} / \partial n)_V \approx \rho_{\text{LUMO}}(\mathbf{r})$ Radical reactions: $f^0 = (\partial \rho_{\text{SOMO}} / \partial n)_V$ $\approx [\rho_{\text{HOMO}}(\mathbf{r}) + \rho_{\text{LUMO}}(\mathbf{r})]/2$ Densities are not so sensitive to structural change in reactions

Janak theorem (ϵ : outermost orbital energy)

 $\mu = \frac{\partial E}{\partial n} = \varepsilon \quad \Longrightarrow \quad f = \left(\frac{\partial \varepsilon}{\partial V}\right)_n \quad \text{Orbital energy variance wrt structural change with a constant occupation #}$

Reactivity can be analyzed using orbital energy variance for structural change

Reaction analysis based on orbital energies

[Tsuneda & Singh, J. Comput. Chem., <u>35</u>, 1093, 2014.]



1. Plot LC-DFT valence orbital energies on IRC (the predictor-corrector method).

2. Select the contributing orbital pair: occupied and unoccupied orbitals having the most varied orbital energies.

3. Construct the normalized reaction diagram by plotting the normalized orbital energy gap on the normalized IRC.

4. Calculate the orbital energy gap gradient at the initial reaction stage as a "reactivity index".

Reactions with small index (< 0.25) \Rightarrow Electron transfer-driven Reactions with large index (> 0.25) \Rightarrow Structural change-driven

Reactivity index for forward processes

Fig. Fundamental reactions



Reactivity index for backward processes



Large-index reactions for forward processes



CH₃ reactions

Table. CCSD(T) barrier heights, experimental reaction rates and orbital energy gap gradients of reactions containing CH_3 and giving large reactivity indices.

No	Reactant				Product			Barrier height	k(298K, Exp.	Gradient	
NO.	donor		acceptor					kcal/mol)	data)	of Δ_{gap}	
(4)	CH ₄	+	OH	\rightarrow	CH ₃	+	H ₂ O	6.70	6.77E-15	0.297	
	CH_3	+	H_2O	\rightarrow	CH_4	+	OH	19.60	1.49E-25	-0.068	
(8)	CH_4	+	Cl	\rightarrow	CH_3	+	HCI	7.90	1.07E-13	1.262	
	CH_3	+	HCI	\rightarrow	CH_4	+	Cl	1.70	4.49E-14	-0.020	
(23)	Н	+	FCH ₃	\rightarrow	HF	+	CH ₃	30.38	2.31E-18	0.681	
	HF	+	CH ₃	\rightarrow	н	+	FCH ₃	57.20	-	-0.668	
(31)	C_2H_4	+	CH ₃	\rightarrow	C_3H_7			6.85	1.27E-18	0.410	
	C_3H_7			\rightarrow	C_2H_4	+	CH_3	32.97	7.92E-26	-0.140	



All reactions but (8) simply proceed to lower barrier heights. An experimental study questioning the intrinsic reaction path of $CH_4 + CI \rightarrow CH_3 + HCI$ reaction [Simpson et al., J. Chem. Phys. 103, 7313, 1995].

$CH_4 + CI \rightarrow CH_3 + HCI$ reaction



Experimentally-proposed path: small index in the initial stage of the forward process Minimum energy path: large index

⇒ Experimental path has priority over the MEP due to the initial electron transfer.

$CI^- + CH_3I \rightarrow CH_3CI + I^- S_N^2$ reaction

[Tsuneda, Maeda, Harabuchi & Singh, Computation ``50th Anniversary of the Kohn-Sham Theory – Advances in Density Functional Theory'', 4, 23, 2016.]

Fig. The potential energy curve of the overall $CI^- + CH_3I \rightarrow CH_3CI + I^- S_N2$ reaction, which is calculated by the reaction path search method in the GRRM program with LC-BOP+LRD/D2f2-TZVPD.



Intrinsic reaction coordinate

Reaction path search method using LC+vdW method \rightarrow

There is the IRC of the precursory process called "roundabout path" just before the usual $S_N 2$ process

$Cl^- + CH_3 I \rightarrow CH_3 Cl + l^- S_N^2$ reaction

Fig. The normalized reaction diagrams of the three steps of the Cl⁻ + CH₃I \rightarrow CH₃Cl + l⁻ S_N2 reaction, which is calculated by LC-BOP+LRD/D2f2-TZVPD.



Orbital energy-based reaction analysis \rightarrow Dispersions play a significant role in $S_N 2$ reaction and the roundabout path is driven by structural change, i.e. dynamically, in contrast to the $S_N 2$ process driven by electron transfer



Gas-phase vs solution reactions



Conclusions of the second part

- 1. LC-DFT has solved and improved the reaction enthalpies and reaction barriers in various types of chemical reactions: e.g., isodesmic, isomerization, condensation, and Diels-Alder reactions. In the reaction calculations, dispersion corrections are found to play more significant role than expected.
- 2. In Diels-Alder reactions, it was found that LC-DFT provides almost constant HOMO-LUMO gap for the precursory processes. Based on this finding, we developed an orbital energy-based reaction analysis theory using a new reactivity index, which is the gradient of orbital energy gaps contributing to reactions. This index has revealed that many reactions initially proceed through electron transfers between orbital pairs, which are often not HOMO-LUMO pairs.
- 3. The index using LC-DFT orbital energies also suggested that some reactions may not take the minimum energy paths. For the $CH_4 + CI \rightarrow CH_3 + HCI$ reaction, an experiment indicates another reaction path, which is found to provide a small index. For a $S_N 2$ reaction, it was found that the lack of dispersions may cause the large index and the structural change-driven roundabout path exists just before the usual process.

Acknowledgments

Scientific support:

Prof. Kimihiko Hirao (RIKEN)
Dr. Raman K. Singh (Hokkaido Univ.)
Dr. Ayako Nakata (NIMS)
Prof. Muneaki Kamiya (Gifu Univ.)
Prof. J.-W. Song (Daegu Univ.)
Dr. Satoshi Suzuki (Kyoto Univ.)
Prof. Takeshi Sato (Univ. Tokyo)

Prof. Satoshi Maeda (Hokkaido Univ.) Prof. Yu Harabuchi (Hokkaido Univ.) Takao Tsuneda Density Functional Theory in Quantum Chemistry For details about the discussions on LC-DFT & orbital energies, see <u>"T. Tsuneda, Density</u> <u>Functional Theory in</u> <u>Quantum Chemistry</u> <u>(Springer, 2014)"</u>

Financial support:

Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Grants: 23225001 and 24350005)

Molecular orbitals in experiments

Fig. HOMO image of CO₂ by generalized MO tomography. [Vozzi et al., Nature Phys. 7, 822, 2011]



DFT calculation

Molecular orbital imaging

[Itatani et al., Nature 432, 867, 2004]: Computed tomography scans of molecules that dissociates an electron from orbitals by tuning the laser from all directions to measure the scattering angles of the electron

Fig. Molecular orbitals of PTCDA. [Puschnig et al., Phys. Rev. B 7, 235427, 2011]



Anti-activation energy reactions _

Table. CCSD(T) barrier heights, experimental reaction rates and calculated orbital energy gap gradients for the reactions proceeding to higher barrier heights.

	Reactant				Product			Barrier height	k(298K,	Gradient of
No.								(CCSD(T),	Exp. from	orbital
	donor	or acceptor						kcal/mol)	NIST data)	energy gap
(3)	CH_4	+	Н	\rightarrow	CH_3	+	H_2	15.30	1.64E-19	-0.134
	CH ₃	+	H ₂	\rightarrow	CH_4	+	Н	12.10	8.41E-21	-0.400
(8)	CH_4	+	Cl	\rightarrow	CH ₃	+	HCI	7.90	1.07E-13	1.262
	CH_3	+	HCI	\rightarrow	CH_4	+	Cl	1.70	4.49E-14	-0.020
(15)	OH	+	Cl	\rightarrow	0	+	HCI	10.40	6.62E-16	0.301
	HCI	+	0	\rightarrow	Cl	+	OH	9.80	1.54E-16	1.177
(29)	HCO			\rightarrow	Н	+	CO	22.68	3.30E-22	0.019
	CO	+	Н	\rightarrow	HCO			3.17	1.09E-34	0.294
(32)	HCN			\rightarrow	HNC			48.16	6.93E-22	0.496
	HNC			\rightarrow	HCN			33.11	-	0.561

All reactions but (8) give smaller gradients for forward processes. Initial electron transfers may accelerate the reactions passing higher barriers for anti-activation energy reactions.

Orbital energy gap gradient on IRC

[Tsuneda & Singh, J. Comput. Chem., 35, 1093, 2014.]

