Nuclear Orbital plus Molecular Orbital (NOMO) Theory: Overview and Recent Progress

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Comment & Reply @ JCP

Comment on "Elimination of translational and rotational motions in nuclear orbital plus molecular orbital theory" [J. Chem. Phys. 122, 164101 (2005)]

Brian Sutcliffe[a)]
Department of Theoretical Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest 112, Hungary

"…It is suggested that the chosen rotational term is not unique and is not valid over all regions of space."

Reply to "Comment on 'Elimination of translational and rotational motions in nuclear orbital plus molecular orbital theory' " [J. Chem. Phys. 123, 237101 (2005)]

Hiromi Nakai,[a)] Minoru Hoshino, and Kaito Miyamoto
Department of Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Shi-aki Hyodo
Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

"…We have focused on the locality of the Gaussian functions, of which the orbital centers can approximately define the rigid-body rotator. It is possible to define the center of mass c.m., angular, and internal coordinates uniquely for the rigid-body rotator, …. Thus, the rotational operator has been expanded in Taylor series with respect to the displacement **x** based on the rigid-body rotator,…."

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Seminar @ Waseda University

- The 14th Quantum Chemistry Seminar

- Waseda University, October 24, 2007

- Title: "The Born-Oppenheimer Approximation

  - Foundations and Limitations"

- Lecturer: Prof. Brian Sutcliffe
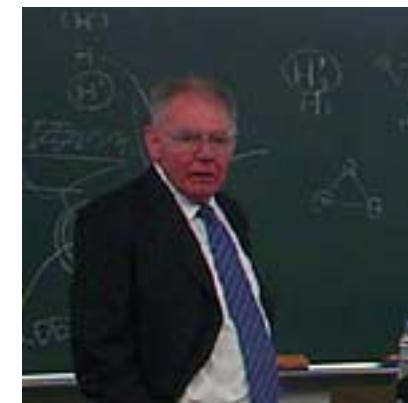
Congress @ Waseda University
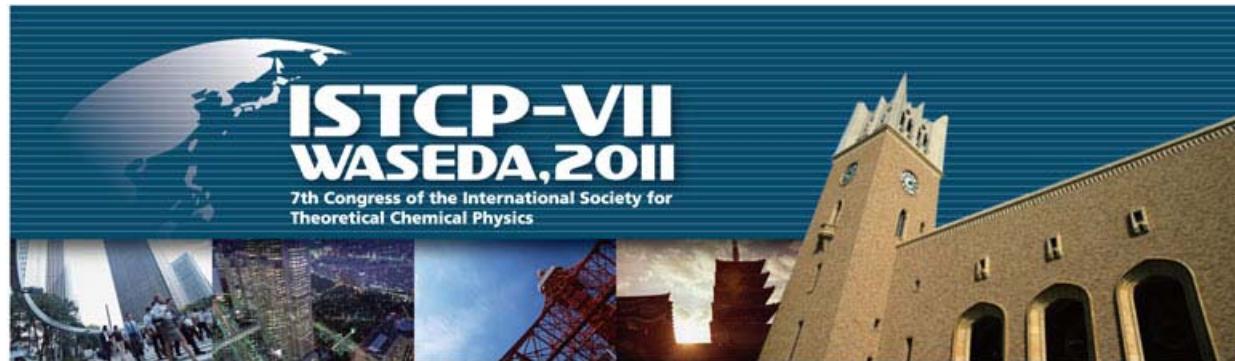
- The 7th Congress of the International Society of Theoretical Chemical Physics (ISTCP-VII)
- Waseda University, September 2-8, 2011
- Chair: Hiromi Nakai
- Participants: 431 scientists from 32 countries/regions
- One-day participation: 1 scientist ⇒ Prof. Brian Sutcliffe

80-Year-Old Celebration

- 8 ⇒ 八

- 10 ⇒ 十

- 80 ⇒ 八十 ⇒ 仐

- 仐 ⇒ 傘（Umbrella）

- 80-Year-Old Celebration ⇒ 傘寿(San-Ju)

- Celebration of Umbrella

- Present to Prof. Sutcliffe

  （Waseda Univ. Original)

88-Year-Old Celebration

- 8　⇒　八

- 10 ⇒　十

- 88 ⇒　八十八　⇒ 米

- 米　⇒　米（Rice）

- 88-Year-Old Celebration　⇒　米寿(Bei-Ju)

- Celebration of Rice

99-Year-Old Celebration

- １００　⇒　百

- １ ⇒　一

- ９９ （＝１００－1）⇒　「百」－「一」　⇒　百

- 白（White）

- 99-Year-Old Celebration　⇒　白寿(Haku-Ju)

- Celebration of White

Contents

- **Introduction: Born-Oppenheimer Approximation**

- What is NOMO?

- How to use NOMO?

- Summary and Perspective

Development of Quantum Theory

- Quantum Mechanics
  - 1925 Heisenberg; matrix formula
  - 1926 Schrödinger; wave formula
    - $\Rightarrow$ Schrödinger equation

- Quantum Chemistry
  - 1927 Born-Oppenheimer;
    - $\Rightarrow$ BO approximation
  - 1927 Heitler-London;
    - $\Rightarrow$ valence bond (VB) method
  - 1927 Hund-Mulliken;
    - $\Rightarrow$ molecular orbital (MO) method
  - 1930 Hartree-Fock equation
  - 1931 Hückel method
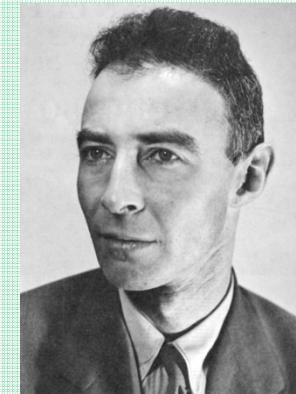
1927   № 20

ANNALEN DER PHYSIK
VIERTE FOLGE. BAND 84

1. Zur Quantentheorie der Molekeln;
von M. Born und R. Oppenheimer

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

Adiabatic Approximation

- *Time-dependent* Schrödinger eq. (SE) $\quad i\dfrac{\partial}{\partial t}\Psi(\boldsymbol{x},\boldsymbol{X},t)=\hat{H}\Psi(\boldsymbol{x},\boldsymbol{X},t)$

  - Total Hamiltonian $\quad \hat{H}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{T}^{\mathrm{e}}(\boldsymbol{r})+\hat{V}^{\mathrm{nn}}(\boldsymbol{R})+\hat{V}^{\mathrm{ee}}(\boldsymbol{r})+\hat{V}^{\mathrm{ne}}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{H}^{\mathrm{e}}(\boldsymbol{r},\boldsymbol{R})$

- *Time-independent* electronic SE $\quad \hat{H}^{\mathrm{e}}(\boldsymbol{r};\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})=E_m^{\mathrm{e}}(\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})$

  - Expanding total wave function $\Psi(\boldsymbol{r},\boldsymbol{R},t)$ in terms of eigen functions of $\hat{H}^{\mathrm{e}}$

  $$\Psi(\boldsymbol{x},\boldsymbol{X},t)=\sum_m \Phi_m^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$$

- A set of couple differential eqs. $i\dfrac{\partial}{\partial t}\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)=\left[\hat{T}^{\mathrm{n}}(\boldsymbol{R})+E_m^{\mathrm{e}}(\boldsymbol{R})\right]\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)+\sum_n c_{mn}\Phi_n^{\mathrm{n}}(\boldsymbol{X},t)$

  - Coupling constant $\quad c_{mn}\equiv\left\langle\Phi_m^{\mathrm{e}}\middle|\hat{T}^{\mathrm{n}}(\boldsymbol{R})\middle|\Phi_n^{\mathrm{e}}\right\rangle-2\sum_P\dfrac{1}{M_A}\left\langle\Phi_m^{\mathrm{e}}\middle|\hat{\tau}_P^{\mathrm{n}}\middle|\Phi_n^{\mathrm{e}}\right\rangle\cdot\hat{\tau}_P^{\mathrm{n}}$

- Adiabatic approximation $\quad \underline{c_{mn}=0\quad(m\neq n)\qquad c_{mm}=\left\langle\Phi_m^{\mathrm{e}}\middle|\hat{T}^{\mathrm{n}}(\boldsymbol{R})\middle|\Phi_m^{\mathrm{e}}\right\rangle\equiv U_m^{\mathrm{n}}(\boldsymbol{R})}$

  - *Time-dependent* nuclear SE $\quad i\dfrac{\partial}{\partial t}\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)=\left[\hat{T}^{\mathrm{n}}(\boldsymbol{R})+E_m^{\mathrm{e}}(\boldsymbol{R})+\underline{U_m^{\mathrm{n}}(\boldsymbol{R})}\right]\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$

  - Total wave function $\quad \Psi(\boldsymbol{x},\boldsymbol{X},t)=\Phi_m^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$ **Diagonal Born-Oppenheimer Correction (DBOC)**

Born-Oppenheimer Approximation

- *Time-dependent* Schrödinger eq. (SE) $i\dfrac{\partial}{\partial t}\Psi(\boldsymbol{x},\boldsymbol{X},t)=\hat{H}\Psi(\boldsymbol{x},\boldsymbol{X},t)$

  - Total Hamiltonian $\hat{H}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{T}^{\mathrm{e}}(\boldsymbol{r})+\hat{V}^{\mathrm{nn}}(\boldsymbol{R})+\hat{V}^{\mathrm{ee}}(\boldsymbol{r})+\hat{V}^{\mathrm{ne}}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{H}^{\mathrm{e}}(\boldsymbol{r},\boldsymbol{R})$

    WFT/DFT

- *Time-independent* electronic SE $\quad \hat{H}^{\mathrm{e}}(\boldsymbol{r};\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})=E_m^{\mathrm{e}}(\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})$

  - Expanding total wave function $\Psi(\boldsymbol{r},\boldsymbol{R},t)$ in terms of eigen functions of $\hat{H}^{\mathrm{e}}$

    $E_l^{e}(\boldsymbol{R})$: PES
    $\{\boldsymbol{R}_1,\ \boldsymbol{R}_2,\ \boldsymbol{R}_3,\ \dots,\ \boldsymbol{R}_N\}$

    $$\Psi(\boldsymbol{x},\boldsymbol{X},t)=\sum_m \Phi_m^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$$

- A set of couple differential eqs $i\dfrac{\partial}{\partial t}\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)=\left[\hat{T}^{\mathrm{n}}(\boldsymbol{R})+E_m^{\mathrm{e}}(\boldsymbol{R})\right]\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)+\sum_n c_{mn}\Phi_n^{\mathrm{n}}(\boldsymbol{X},t)$

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    $\bar{E}_l^{e}(\boldsymbol{R})$: approximate
    potential function

- Born-Oppenheimer approximation $\quad \underline{c_{mn}=0}$

  - *Time-dependent* nuclear SE $\quad i\dfrac{\partial}{\partial t}\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)=\left[\hat{T}^{\mathrm{n}}(\boldsymbol{R})+E_m^{\mathrm{e}}(\boldsymbol{R})\right]\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$

  - Total wavefunction $\quad \Psi(\boldsymbol{x},\boldsymbol{X},t)=\Phi_m^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$

    Wave packet, etc.

Molecular Dynamics Simulation

- *Time-dependent* Schrödinger eq. (SE) $i\dfrac{\partial}{\partial t}\Psi(\boldsymbol{x},\boldsymbol{X},t)=\hat{H}\Psi(\boldsymbol{x},\boldsymbol{X},t)$

  - Total Hamiltonian $\hat{H}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{T}^{\mathrm{e}}(\boldsymbol{r})+\hat{V}^{\mathrm{nn}}(\boldsymbol{R})+\hat{V}^{\mathrm{ee}}(\boldsymbol{r})+\hat{V}^{\mathrm{ne}}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{H}^{\mathrm{e}}(\boldsymbol{r},\boldsymbol{R})$

    WFT/DFT

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    $\bar{E}_l^{e}(\boldsymbol{R})$: approximate potential function

- Born-Oppenheimer approximation $c_{mn}=0$

  - Newton's equation-of-motion (EOM) $-\dfrac{\partial E_m^{\mathrm{n}}(\boldsymbol{R})}{\partial \boldsymbol{R}_P}=M_P\dfrac{\partial^2 \boldsymbol{R}_P}{\partial t^2}$

***Classical* MD**

MO & MD

MD Simulation

- Solve nuclear EOM on PES

MO Calculation

- Solve electronic SE to obtain PES

Transition Structure A — Second Order Saddle Point — Transition Structure B — Minimum for Product B — Minimum for Product A — Second Order Saddle Point — Minimum for Reactant — Valley-Ridge Inflection Point

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Molecular Dynamics Simulation

- *Time-dependent* Schrödinger eq. (SE) $i\dfrac{\partial}{\partial t}\Psi(\boldsymbol{x},\boldsymbol{X},t)=\hat{H}\Psi(\boldsymbol{x},\boldsymbol{X},t)$

  - Total Hamiltonian $\hat{H}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{T}^{\mathrm{e}}(\boldsymbol{r})+\hat{V}^{\mathrm{nn}}(\boldsymbol{R})+\hat{V}^{\mathrm{ee}}(\boldsymbol{r})+\hat{V}^{\mathrm{ne}}(\boldsymbol{r},\boldsymbol{R})=\hat{T}^{\mathrm{n}}(\boldsymbol{R})+\hat{H}^{\mathrm{e}}(\boldsymbol{r},\boldsymbol{R})$

    WFT/DFT

- *Time-independent* electronic SE $\hat{H}^{\mathrm{e}}(\boldsymbol{r};\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})=E_m^{\mathrm{e}}(\boldsymbol{R})\Phi_m^{\mathrm{e}}(\boldsymbol{x};\boldsymbol{X})$

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    $$\Psi(\boldsymbol{x},\boldsymbol{X},t)=\sum_m \Phi_m^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_m^{\mathrm{n}}(\boldsymbol{X},t)$$
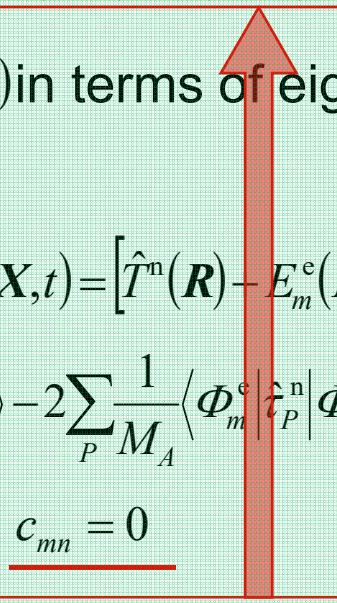
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- Born-Oppenheimer approximation $\quad c_{mn}=0$

  "on the fly"

  - Newton's equation-of-motion (EOM) $\qquad -\dfrac{\partial E_m^{\mathrm{n}}(\boldsymbol{R})}{\partial \boldsymbol{R}_P}=M_P\dfrac{\partial^2 \boldsymbol{R}_P}{\partial t^2}$

Car-Parrinello (CP) MD (1985)   *Ab Initio MD*

Potential Energy Surface (PES)

- Equilibrium structure $\{R_e\}$
- Transition state (TS)
- Intrinsic reaction coordinate (IRC)
- Vibrational normal mode $\{\nu_e\}$
- Reaction heat
- Activation barrier $\{E_a\}$
- Dissociation Energy $\{D_e\}$
- …

PES

BO surface

Adiabatic surface
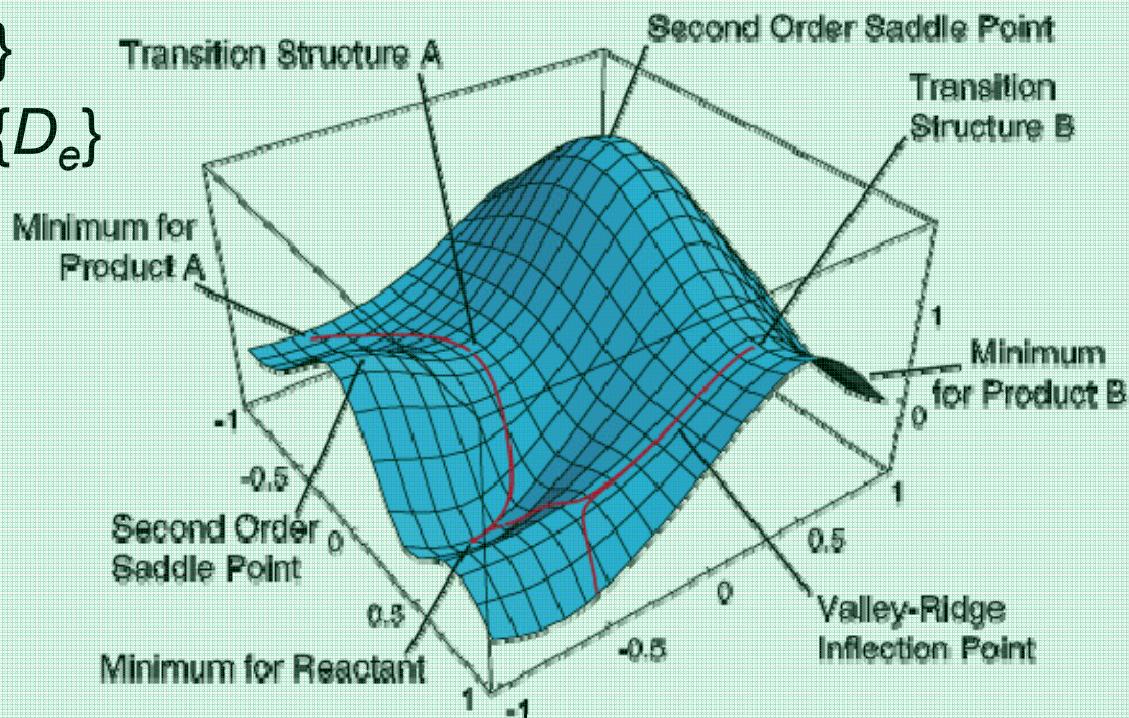
Schrödinger Equation of H Atom

- Hydrogen-like atom

  - Hamiltonian $\hat{H} = -\dfrac{\hbar^2}{2m_e}\nabla^2 + \dfrac{1}{4\pi\varepsilon_0}\dfrac{Ze^2}{r}$
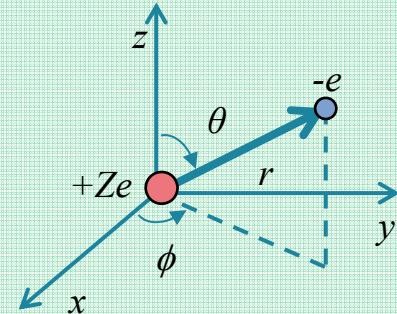
  - Schrödinger equation $\hat{H}(r,\theta,\phi)\,\psi_{n,l,m}(r,\theta,\phi) = E_n\,\psi_{n,l,m}(r,\theta,\phi)$

  - Energy level $E_n = -\dfrac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$

  - Rydberg constant (BO) $R_H = 109737\,\text{cm}^{-1}\quad(\text{theory})$

    $109678\,\text{cm}^{-1}\quad(\text{experiment})$

  - Reduced mass $\mu = \dfrac{m_e M_H}{m_e + M_H}$ $\left(\begin{array}{l}m_e = 9.1093897\times10^{-31}\,\text{kg}\\ M_H = 1.6726231\times10^{-27}\,\text{kg}\\ M_H/m_e = 1836.1527\end{array}\right)$

  - Rydberg constant (non-BO) $R_H = 109678\,\text{cm}^{-1}\quad(\text{theory})$

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- **What is NOMO?**

- How to use NOMO?

- Summary and Perspective

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What is NOMO?
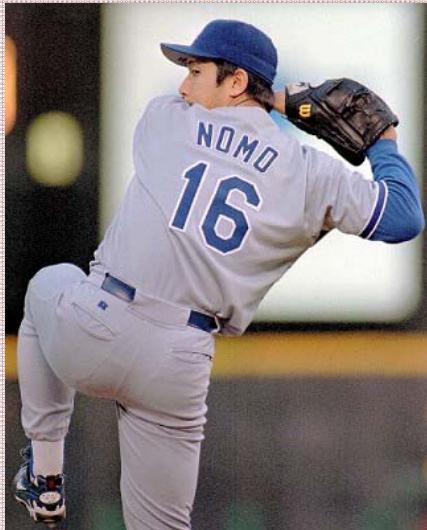
- Nuclear Orbital plus Molecular Orbital Method

  - Solving Schrödinger equation of molecular systems without Born-Oppenheimer approximation

  - Determining nuclear and electronic wave functions simultaneously

  - Describing non-adiabatic effect, nuclear quantum effect, …

NOMO/HF Theory

- Total wave function $\Phi_0(\boldsymbol{x},\boldsymbol{X})=\Phi_0^{\mathrm{e}}(\boldsymbol{x})\Phi_0^{\mathrm{n}}(\boldsymbol{X})$

  - Electronic WF $\Phi_0^{e}(\boldsymbol{x})=\left\|\phi_i^{\mathrm{e}}(\boldsymbol{x}_1)\phi_j^{\mathrm{e}}(\boldsymbol{x}_2)\cdots\phi_k^{\mathrm{e}}(\boldsymbol{x}_{N^{\mathrm{e}}})\right\|$

  - Nuclear WF $\Phi_0^{\mathrm{n}}(\boldsymbol{X})=\left\|\phi_I^{\mathrm{n}}(\boldsymbol{X}_1)\phi_J^{\mathrm{n}}(\boldsymbol{X}_2)\cdots\phi_K^{\mathrm{n}}(\boldsymbol{X}_{N^{\mathrm{n}}})\right\|\approx\phi_I^{\mathrm{n}}(\boldsymbol{X}_1)\phi_J^{\mathrm{n}}(\boldsymbol{X}_2)\cdots\phi_K^{\mathrm{n}}(\boldsymbol{X}_{N^{\mathrm{n}}})$

  $$\left(\boldsymbol{x}=\{\boldsymbol{x}_1,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_{N^{\mathrm{n}}}\}=\{\boldsymbol{r}_1,\omega_1,\boldsymbol{r}_2,\omega_2,\cdots,\boldsymbol{r}_{N^{\mathrm{e}}},\omega_{N^{\mathrm{e}}}\},\quad \boldsymbol{X}=\{\boldsymbol{X}_1,\boldsymbol{X}_2,\cdots,\boldsymbol{X}_{N^{\mathrm{n}}}\}=\{\boldsymbol{R}_1,\Omega_1,\boldsymbol{R}_2,\Omega_2,\cdots,\boldsymbol{R}_{N^{\mathrm{n}}},\Omega_{N^{\mathrm{n}}}\}\right)$$

- HF equation $\hat{f}^{\mathrm{e}}\phi_i^{\mathrm{e}}=\varepsilon_i^{\mathrm{e}}\phi_i^{\mathrm{e}}$

  $$\hat{f}^{\mathrm{n}}\phi_I^{\mathrm{n}}=\varepsilon_I^{\mathrm{n}}\phi_I^{\mathrm{n}}$$

  - Fock operator $\hat{f}^{\mathrm{e}}=\hat{t}^{\mathrm{e}}+\sum_j^{\mathrm{elec}}\left(\hat{J}_j^{\mathrm{e}}-\hat{K}_j^{\mathrm{e}}\right)+\sum_I^{\mathrm{nuc}}\hat{J}_I^{\mathrm{e}}$

    $$\hat{f}^{\mathrm{n}}=\hat{t}^{\mathrm{n}}+\sum_J^{\mathrm{nuc}}\hat{J}_I^{\mathrm{n}}+\sum_j^{\mathrm{elec}}\hat{J}_j^{\mathrm{n}}$$

    Coupling term

- ✓ Extension from MO to NOMO is straightforward.
- ✓ NOMO/HF WF satisfies Koopmans theorem and Brillouin theorem.
- ✓ Various correlated methods developed within BOA are applicable to NOMO.

NOMO/HFR Method

- Basis set expansion

  - Molecular orbital (MO)

    $$\varphi_i^{\mathrm{e}}(\boldsymbol{r}_p) = \sum_P \sum_{\mu \in P} c_{\mu i}^{\mathrm{e}} \chi_\mu^{\mathrm{e}}(\boldsymbol{r}_p; \underline{\boldsymbol{R}_P^0})$$

  - Nuclear orbital (NO)

    $$\varphi_I^{\mathrm{n}}(\boldsymbol{R}_P) = \sum_{\mu \in P} c_{\mu I}^{\mathrm{n}} \chi_\mu^{\mathrm{n}}(\boldsymbol{R}_P; \underline{\boldsymbol{R}_P^0})$$

  Orbital center

- Gaussian basis function

  - EBF $\quad \chi_\mu^{\mathrm{e}}(\boldsymbol{r}_p; \boldsymbol{R}_P^0) = \sum_s d_{s\mu}^{\mathrm{e}} N_{s\mu}^{\mathrm{e}} (x_p - X_P^0)^{l_s^{\mathrm{e}}} (y_p - Y_P^0)^{m_s^{\mathrm{e}}} (z_p - Z_P^0)^{n_s^{\mathrm{e}}} \exp[-\alpha_s^{\mathrm{e}} (\boldsymbol{r}_p - \boldsymbol{R}_P^0)^2]$

  - NBF $\quad \chi_\mu^{\mathrm{n}}(\boldsymbol{R}_P; \boldsymbol{R}_P^0) = \sum_s d_{s\mu}^{\mathrm{n}} N_{s\mu}^{\mathrm{n}} (X_P - X_P^0)^{l_s^{\mathrm{n}}} (Y_P - Y_P^0)^{m_s^{\mathrm{n}}} (Z_P - Z_P^0)^{n_s^{\mathrm{n}}} \exp[-\alpha_s^{\mathrm{n}} (\boldsymbol{R}_P - \boldsymbol{R}_P^0)^2]$

- HFR equation

$$\boldsymbol{F}^{\mathrm{e}} \boldsymbol{C}^{\mathrm{e}} = \boldsymbol{S}^{\mathrm{e}} \boldsymbol{C}^{\mathrm{e}} \boldsymbol{E}^{\mathrm{e}} \qquad F_{\mu\nu}^{\mathrm{e}} = \left\langle \chi_\mu^{\mathrm{e}} \left| \hat{f}^{\mathrm{e}} \right| \chi_\nu^{\mathrm{e}} \right\rangle$$

$$\boldsymbol{F}^{\mathrm{n}} \boldsymbol{C}^{\mathrm{n}} = \boldsymbol{S}^{\mathrm{n}} \boldsymbol{C}^{\mathrm{n}} \boldsymbol{E}^{\mathrm{n}} \qquad F_{\mu\nu}^{\mathrm{n}} = \left\langle \chi_\mu^{\mathrm{n}} \left| \hat{f}^{\mathrm{n}} \right| \chi_\nu^{\mathrm{n}} \right\rangle$$

NOMO/FCI(exact) Theory

- Full-CI wave function

$$\Psi(\boldsymbol{x}, \boldsymbol{X}) = (C_0 + \hat{C}_1 + \hat{C}_2 + \cdots)\Phi_0(\boldsymbol{x}, \boldsymbol{X})$$

- Excitation operator

$$\hat{C}_1 = \sum_{I,A}^{\text{nuc}} C_I^A a_A^\dagger a_I + \sum_{i,a}^{\text{elec}} C_i^a a_a^\dagger a_i$$

$$\hat{C}_2 = \frac{1}{4} \sum_{I,J,A,B}^{\text{nuc}} C_{IJ}^{AB} a_B^\dagger a_J a_A^\dagger a_I + \sum_{I,A}^{\text{nuc}} \sum_{i,a}^{\text{elec}} C_{Ii}^{Aa} a_a^\dagger a_i a_A^\dagger a_I + \frac{1}{4} \sum_{i,j,a,b}^{\text{elec}} C_{ij}^{ab} a_b^\dagger a_j a_a^\dagger a_i$$

- Creation/Annihilation operator

$$\left\{ a_a^\dagger, a_b^\dagger \right\} \quad \left\{ a_i, a_j \right\} \quad \left\{ a_A^\dagger, a_B^\dagger \right\} \quad \left\{ a_I, a_J \right\}$$

✓ CI, MBPT, and CC have been developed based on NOMO.

Computational Cost of NOMO

- MO/HF vs. NOMO/HF Calculations
  - System : All-trans-retinal
  - Basis function :
    - Electron … cc-pVDZ
    - Nucleus [H, C, O] … (5s5p) primitive
  - Work station : Pentium4/2.8GHz

	MO/HF	NOMO/HF
AO Dimension	455	1,435 (980+455)
2P Integral	942,393,134 (14.72GB)	1,339,511,851 (20.93GB)
SCF [iter]	13.0	51.0
CPU [sec]	1311.4	10352.8
[sec/iter]	100.9	203.0
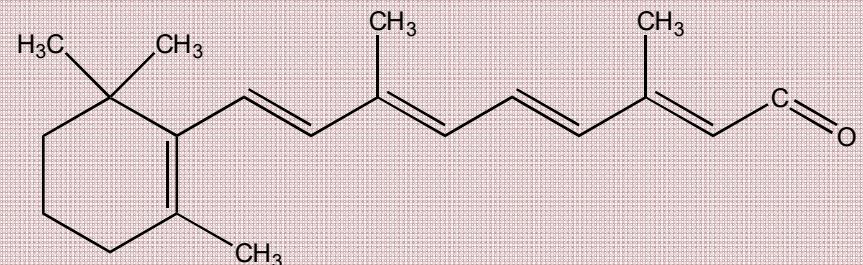
✓ NOMO is inexpensive in computational cost.
✓ NOMO does not need to prepare costly multi-dimensional PES in order to get the nuclear (vibrational) wave function.

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What is NOMO?

- Nuclear Orbital plus Molecular Orbital Method

  - Solving Schrödinger equation of molecular systems without Born-Oppenheimer approximation

  - Determining nuclear and electronic wave functions simultaneously

  - Describing non-adiabatic effect, nuclear quantum effect, …

- But, …

  - Introducing new problems:

    - Electron-nucleus (e-n) and nucleus-nucleus (n-n) correlations

    - Contaminations of translational and rotational motions

Translation & Rotation

- Treatment of translational and rotational motions

Nuclear motion	Exact wave function	Gaussian basis function
Vibration	Gaussian	*good*
Translation	Plane wave	*poor*
Rotation	Spherical harmonics	*poor*
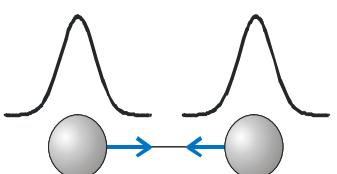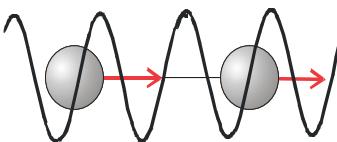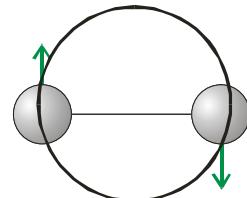
TF- & TRF-NOMO Theory

- Translational Hamiltonian

$$\hat{T}_{\mathrm{T}}^{\mathrm{n}} = -\frac{1}{2M}\sum_P \nabla(\boldsymbol{R}_P)^2 - \frac{1}{M}\sum_P \nabla(\boldsymbol{R}_P)\cdot\nabla(\boldsymbol{R}_P)$$

  - Translation-free (TF) Hamiltonian

$$\hat{H}_{\mathrm{TF}} = \hat{H} - \hat{T}_{\mathrm{T}}^{\mathrm{n}}$$

- Rotational Hamiltonian

$$\hat{T}_{\mathrm{R}}^{\mathrm{n}} = \sum_{\alpha}^{X,Y,Z}\frac{1}{2\hat{I}_\alpha}\left(\sum_P \hat{L}_{\alpha,P}^2 + 2\sum_{P<Q}\hat{L}_{\alpha,P}\hat{L}_{\alpha,Q}\right) \approx \hat{T}_{\mathrm{R}_0}^{\mathrm{n}} + \hat{T}_{\mathrm{R}_1}^{\mathrm{n}} + O\!\left(\Delta\boldsymbol{R}^2\right)$$

  - Translation-and-rotation-free (TRF) Hamiltonian

$$\hat{H}_{\mathrm{TRF}} = \hat{H}_{\mathrm{TF}} - \hat{T}_{\mathrm{R}}^{\mathrm{n}} \cong \hat{H}_{\mathrm{TF}} - \hat{T}_{\mathrm{R}_0}^{\mathrm{n}}$$

Total Energy by NOMO

- Total energies of H_2, D_2, & T_2 by TRC-, TF-, & TRF-NOMO
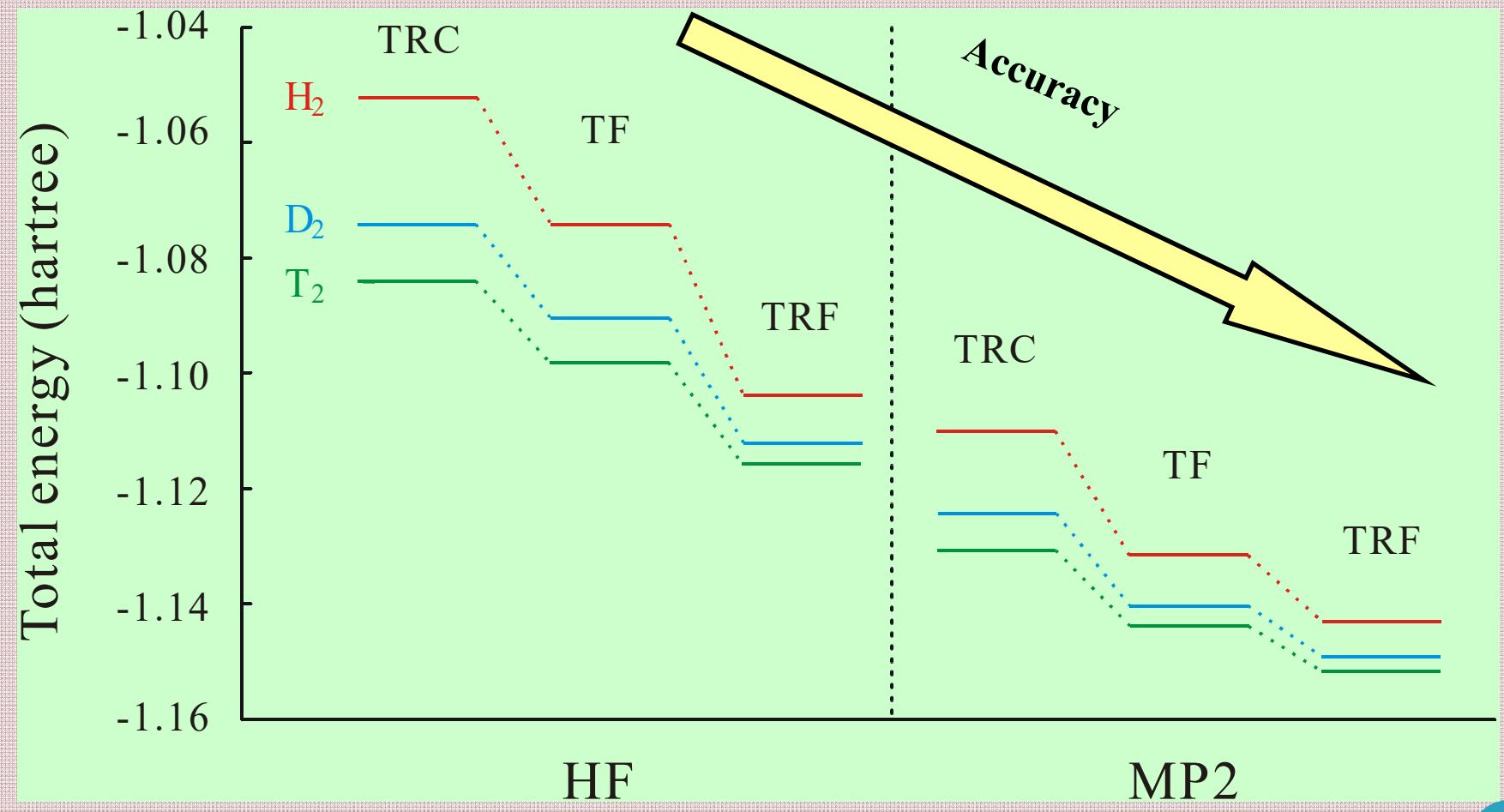
Accuracy of NOMO

- Total Energy of H_2: $\qquad$ $E(H_2)$
  - TRC-NOMO/HF(MO,1s-opt) (CPL, 1998) -0.685947 au
  - TRC-NOMO/HF(VB,1s-opt) (IJQC, 2002) -1.042012 au
  - TRC-NOMO/HF (IJQC, 2002) -1.052371 au
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  - TRF-NOMO/HF (JCP, 2005) -1.104088 au
  - TRF-NOMO/MP2 (JCP, 2006) -1.143040 au
  - TR_1F-NOMO/MP2 (JCTC, 2006) -1.143494 au

  - …
  - ECG (Adamowicz, 2003) -1.164025 au

ECG Theory

- ECG Wave Function
  - CI expansion

$$\Psi(\mathbf{x}, \mathbf{X}) = \sum_{\kappa=1}^{K} C_\kappa \hat{P} \Phi_\kappa(\mathbf{x}, \mathbf{X}),$$

- ECG Basis Function
  - Exponent

$$\Phi_\kappa(\mathbf{x}, \mathbf{X}) = \exp\left(-[\,\mathbf{r}^\dagger \ \mathbf{R}^\dagger\,]\bar{\mathbf{A}}_\kappa \begin{bmatrix} \mathbf{r} \\ \mathbf{R} \end{bmatrix}\right)\theta(\boldsymbol{\omega})\Theta(\boldsymbol{\Omega}),$$

$$[\,\mathbf{r}^\dagger \ \mathbf{R}^\dagger\,]\bar{\mathbf{A}}\begin{bmatrix} \mathbf{r} \\ \mathbf{R} \end{bmatrix} = \sum_{p,q} \mathbf{r}_p A_{pq} \mathbf{r}_q + \sum_{P,Q} \mathbf{R}_P A_{PQ} \mathbf{R}_Q$$

$$+ \sum_{p}\sum_{P} 2\mathbf{r}_p A_{pP} \mathbf{R}_P = \boxed{\sum_{p} \alpha_p \mathbf{r}_p^2} \quad \text{1-Particle Gaussian}$$

$$+ \boxed{\sum_{P} \alpha_P \mathbf{R}_P^2} + \boxed{\sum_{p,q} \alpha_{pq}(\mathbf{r}_p - \mathbf{r}_q)^2} \quad \text{2-Particle Gaussian}$$

$$+ \boxed{\sum_{P,Q} \alpha_{PQ}(\mathbf{R}_P - \mathbf{R}_Q)^2} + \boxed{\sum_{p,P} \alpha_{pP}(\mathbf{r}_p - \mathbf{R}_P)^2},$$

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ECG-NOMO Theory

- NOMO wave function $\Phi_0(\boldsymbol{x},\boldsymbol{X}) = \Phi_0^{\mathrm{e}}(\boldsymbol{x})\Phi_0^{\mathrm{n}}(\boldsymbol{X})$

  - Molecular orbital (MO) $\varphi_i^{\mathrm{e}}(\boldsymbol{r}_p) = \sum_P \sum_{\mu \in P} c_{\mu i}^{\mathrm{e}} \chi_\mu^{\mathrm{e}}(\boldsymbol{r}_p; \underline{\boldsymbol{R}_P^0})$

    Orbital center

  - Nuclear orbital (NO) $\varphi_I^{\mathrm{n}}(\boldsymbol{R}_P) = \sum_{\mu \in P} c_{\mu I}^{\mathrm{n}} \chi_\mu^{\mathrm{n}}(\boldsymbol{R}_P; \underline{\boldsymbol{R}_P^0})$

- ECG-NOMO wave function $\Phi_0(\boldsymbol{x},\boldsymbol{X}) = \Phi_0^{\mathrm{e}}(\boldsymbol{x},\boldsymbol{X})\Phi_0^{\mathrm{n}}(\boldsymbol{X})$

  - Molecular orbital (MO) $\varphi_i^{\mathrm{e}}(\boldsymbol{r}_p, \underline{\boldsymbol{R}_P}) = \sum_P \sum_{\mu \in P} c_{\mu i}^{\mathrm{e}} \chi_\mu^{\mathrm{e}}(\boldsymbol{r}_p, \underline{\boldsymbol{R}_P})$

    Nuclear coordinate

  - Nuclear orbital (NO) $\varphi_I^{\mathrm{n}}(\boldsymbol{R}_P) = \sum_{\mu \in P} c_{\mu I}^{\mathrm{n}} \chi_\mu^{\mathrm{n}}(\boldsymbol{R}_P; \underline{\boldsymbol{R}_P^0})$

    Orbital center

ECG-NOMO/HF Theory

- NOMO/HF equation $\hat{f}^{\mathrm{e}} \phi_i^{\mathrm{e}} = \varepsilon_i^{\mathrm{e}} \phi_i^{\mathrm{e}}$

$$\hat{f}^{\mathrm{n}} \phi_I^{\mathrm{n}} = \varepsilon_I^{\mathrm{n}} \phi_I^{\mathrm{n}}$$

  - Fock operator $\hat{f}^{\mathrm{e}} = \hat{t}^{\mathrm{e}} + \sum_j^{\mathrm{elec}} \left(\hat{J}_j^{\mathrm{e}} - \hat{K}_j^{\mathrm{e}} \right) + \sum_J^{\mathrm{nuc}} \hat{J}_I^{\mathrm{e}}$

$$\hat{f}^{\mathrm{n}} = \hat{t}^{\mathrm{n}} + \sum_J^{\mathrm{nuc}} \hat{J}_I^{\mathrm{n}} + \sum_j^{\mathrm{elec}} \hat{J}_j^{\mathrm{n}}$$

- ECG-NOMO/HF equation

$$\left\langle \Phi_0^{\mathrm{n}}(\boldsymbol{X}) \left| \hat{f}^{\mathrm{e}}(\boldsymbol{x}_p, \boldsymbol{X}) \phi_i^{\mathrm{e}}(\boldsymbol{x}_p, \boldsymbol{X}) - \varepsilon_i^{\mathrm{e}} \phi_i^{\mathrm{e}}(\boldsymbol{x}_p, \boldsymbol{X}) \right| \Phi_0^{\mathrm{n}}(\boldsymbol{X}) \right\rangle_{\mathrm{n}} = 0$$

$$\hat{f}_I^{\mathrm{n}}(\boldsymbol{X}_P) \phi_I^{\mathrm{n}}(\boldsymbol{X}_P) - \varepsilon_I^{\mathrm{n}} \phi_I^{\mathrm{n}}(\boldsymbol{X}_P) = 0$$

  - Fock operator

$$\hat{f}^{\mathrm{e}} = \hat{t}^{\mathrm{e}} + \sum_P \hat{t}_P^{\mathrm{n}} - \sum_P \hat{\tau}_P^{\mathrm{n}} \cdot \hat{\tau}_{P'}^{\mathrm{n}} - \sum_j^{\mathrm{elec}} (\hat{\Gamma}_j^{\mathrm{e}} - \hat{\Lambda}_j^{\mathrm{e}}) + \sum_j^{\mathrm{elec}} (\hat{J}_j^{\mathrm{e}} - \hat{K}_j^{e}) + \sum_P \hat{v}_{Pp}^{\mathrm{ne}}$$

$$\hat{f}_I^{\mathrm{n}} = \hat{t}^{\mathrm{n}} + \sum_{J \neq I}^{\mathrm{nuc}} \hat{J}_J^{\mathrm{n}} + \sum_j^{\mathrm{elec}} \hat{J}_j^{\mathrm{n}} + \left\langle \Phi_0^{\mathrm{n}} \left| a_I^{\dagger} \hat{U}_0^{\mathrm{n}} a_I \right| \Phi_0^{\mathrm{n}} \right\rangle - \left\langle \Phi_0^{\mathrm{n}} \left| a_I^{\dagger} \sum_i^{\mathrm{elec}} \varepsilon_i^{\mathrm{e}} \left(\left\langle \phi_i^{\mathrm{e}} \middle| \phi_i^{\mathrm{e}} \right\rangle_{\mathrm{e}} - 1 \right) a_I \right| \Phi_0^{\mathrm{n}} \right\rangle$$

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ECG-NOMO/HFR Method

- NOMO/HFR equation

$$F^{\mathrm{e}} C^{\mathrm{e}} = S^{\mathrm{e}} C^{\mathrm{e}} E^{\mathrm{e}}$$

$$F^{\mathrm{n}} C^{\mathrm{n}} = S^{\mathrm{n}} C^{\mathrm{n}} E^{\mathrm{n}}$$

$$F_{\mu\nu}^{\mathrm{e}} = \left\langle \chi_\mu^{\mathrm{e}} \middle| \hat{f}^{\mathrm{e}} \middle| \chi_\nu^{\mathrm{e}} \right\rangle$$

$$F_{\mu\nu}^{\mathrm{n}} = \left\langle \chi_\mu^{\mathrm{n}} \middle| \hat{f}^{\mathrm{n}} \middle| \chi_\nu^{\mathrm{n}} \right\rangle$$

- ECG-NOMO/HFR equation

$$F^{\mathrm{e}} C^{\mathrm{e}} = S^{\mathrm{e}} C^{\mathrm{e}} E^{\mathrm{e}}$$

$$F_{\mu\nu}^{\mathrm{e}} = \left\langle \Phi_0^{\mathrm{n}}(\boldsymbol{X}) \middle| \left\langle \chi_\mu^{\mathrm{e}}(\boldsymbol{r}_p, \boldsymbol{R}) \middle| \hat{f}^{\mathrm{e}}(\boldsymbol{r}_p, \boldsymbol{R}) \middle| \chi_\nu^{\mathrm{e}}(\boldsymbol{r}_p, \boldsymbol{R}) \right\rangle_{\mathrm{e}} \middle| \Phi_0^{\mathrm{n}}(\boldsymbol{X}) \right\rangle$$

$$F^{\mathrm{n}} C^{\mathrm{n}} = S^{\mathrm{n}} C^{\mathrm{n}} E^{\mathrm{n}}$$

$$F_{\mu\nu}^{\mathrm{n}} = \left\langle \chi_\mu^{\mathrm{n}}(\boldsymbol{R}_P) \middle| \hat{f}_I^{\mathrm{n}}(\boldsymbol{R}_P) \middle| \chi_\nu^{\mathrm{n}}(\boldsymbol{R}_P) \right\rangle$$

ECG-NOMO/MP2 & CCSD Methods

- ECG-NOMO/MP2 energy

$$E^{(2)}_{\text{ECG-NOMO/MP2}} = \frac{1}{4} \sum_{i,j,a,b} \frac{\left| \left\langle \Phi_0^{\text{n}} \left| \left\langle \varphi_i^{\text{e}} \varphi_j^{\text{e}} \left\| \varphi_a^{\text{e}} \varphi_b^{\text{e}} \right\rangle_{\text{e}} \right| \Phi_0^{\text{n}} \right\rangle_{\text{n}} \right|^2}{\varepsilon_i^{\text{e}} + \varepsilon_j^{\text{e}} - \varepsilon_a^{\text{e}} - \varepsilon_b^{\text{e}}}$$

- ECG-NOMO/CCSD energy

$$E_{\text{ECG-NOMO/CCSD}} - E_0 = \left\langle \Phi_0^{\text{n}} \left| \left\langle \Phi_0^{\text{e}} \left| \overline{H}^{\text{e}} \right| \Phi_0^{\text{e}} \right\rangle_{\text{e}} \right| \Phi_0^{\text{n}} \right\rangle_{\text{n}}$$

$$= \frac{1}{4} \sum_{i,j,a,b} \left\langle \Phi_0^{\text{n}} \left| \left\langle \varphi_i^{\text{e}} \varphi_j^{\text{e}} \left\| \varphi_a^{\text{e}} \varphi_b^{\text{e}} \right\rangle_{\text{e}} \right| \Phi_0^{\text{n}} \right\rangle_{\text{n}} t_{ij}^{ab}$$

$$+ \frac{1}{2} \sum_{i,j,a,b} \left\langle \Phi_0^{\text{n}} \left| \left\langle \varphi_i^{\text{e}} \varphi_j^{\text{e}} \left\| \varphi_a^{\text{e}} \varphi_b^{\text{e}} \right\rangle_{\text{e}} \right| \Phi_0^{\text{n}} \right\rangle_{\text{n}} t_i^a$$

Accuracy of NOMO

- Total Energy of H_2: $E(H_2)$
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  - TRC-NOMO/HF(VB,1s-opt) (IJQC, 2002) -1.042012 au
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  - ECG-NOMO/CCSD (CPL, 2012) -1.160017 au
  - …
  - ECG (Adamowicz, 2003) -1.164025 au

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Approach of ECG-NOMO

Deviation of calculated zero-point energy of H_2 from experimental value
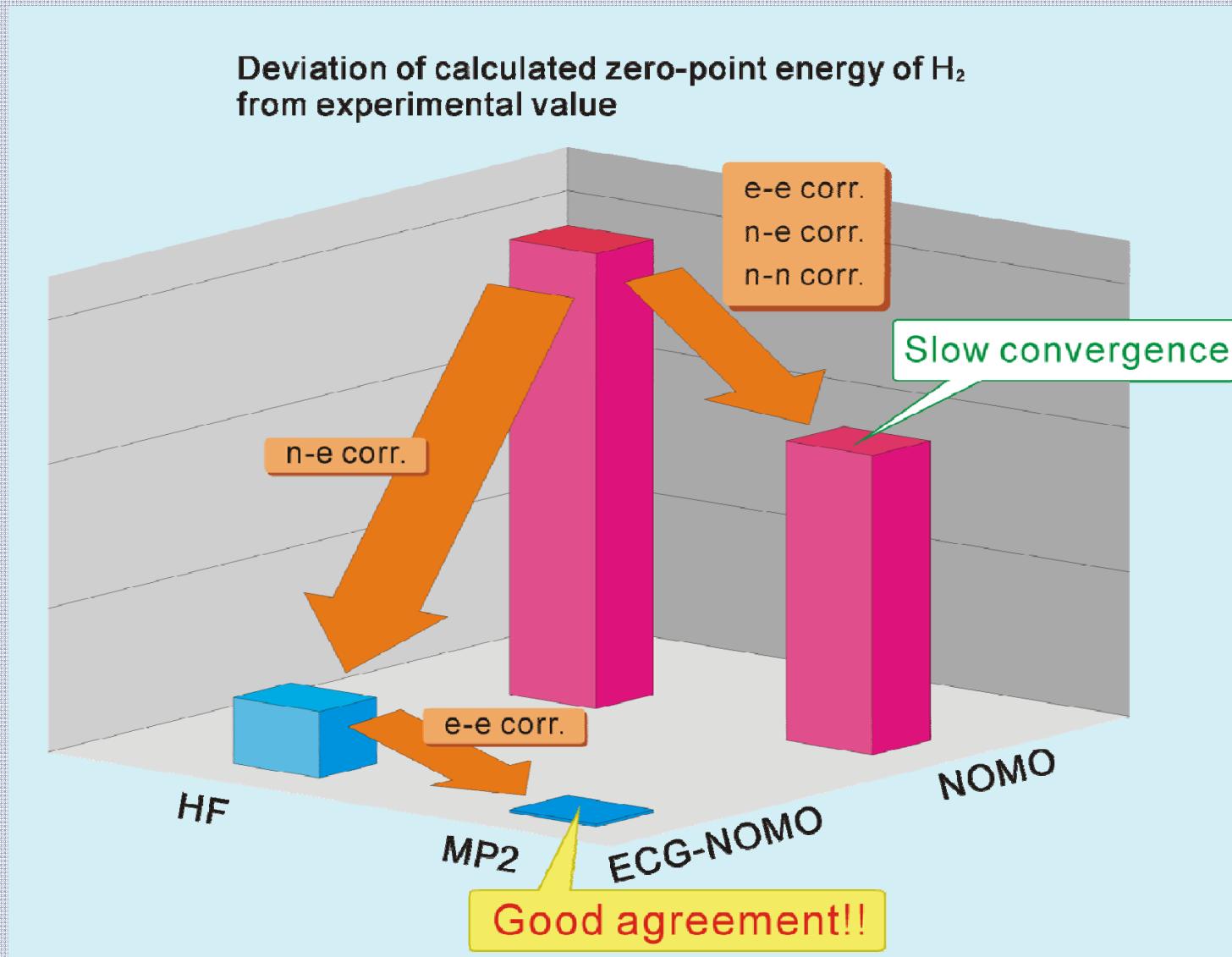
Non-BO Theory
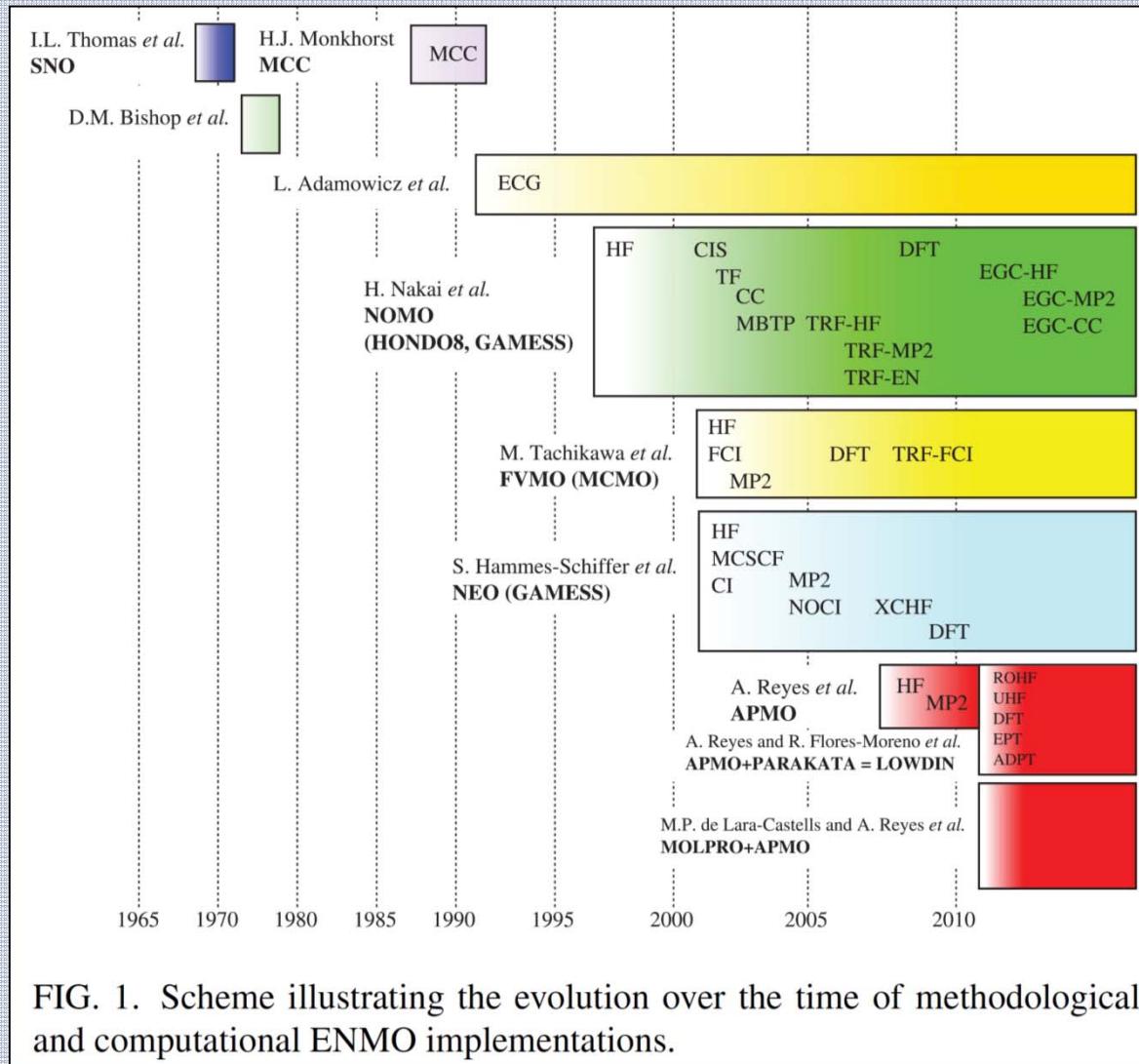
FIG. 1. Scheme illustrating the evolution over the time of methodological and computational ENMO implementations.

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- **Shigeta**, Nagao, Nishikawa, Yamaguchi, *Int. J. Quantum Chem.* **75**, 875 (1999).
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Exact Theory for Non-BO Problem

- **Free Complement (FC) Method** by **Nakatsuji** *et al.*
  - "Solving the electron-nuclear Schrodinger equations of helium atom and its isoelectronic ions with the free iterative-complement-interaction method", Nakashima, Nakatsuji, *J. Chem. Phys.* **128**, 154107 (2008).
  - "Solving the electron and electron-nuclear Schrodinger equations for the excited states of helium atom with the free iterative-complement-interaction method", Nakashima, Hijikata, Nakatsuji, *J. Chem. Phys.* **128**, 154108 (2008).
  - "Solving non-Born-Oppenheimer Schrodinger equation for hydrogen molecular ion and its isotopomers using the free complement method", Hijikata, Nakashima, Nakatsuji, *J. Chem. Phys.* **130**, 024102 (2009).
  - "Accurate solutions of the Schrödinger and Dirac equations of H_2^+, HD^+, and HT^+: With and without Born–Oppenheimer approximation and under magnetic field", Ishikawa, Nakashima, Nakatsuji, *Chem. Phys.* **401**, 62 (2012).
  - "Solving the non-Born-Oppenheimer Schrödinger equation for hydrogen molecular ion with the free complement method II: Highly-accurate electronic, vibrational, and rotational excited states", Nakashima, Hijikata, Nakatsuji, *Astrophys. J.* **770**, 144 (2013).
  - "Non-Born-Oppenheimer potential energy curve: Hydrogen molecular ion with highly accurate free complement method", Nakashima, Nakatsuji, *J. Chem. Phys.* **139**, 074105 (2013).

Free Complement (FC) Method

- H_2^+ (^1S): Hijikata, Nakashima, Nakatsuji, *J. Chem. Phys.* **130**, 024102 (2009).

n [a]	M_n [b]	α	β	Energy (a.u.)
0	1	0.6695	5.9054	**−0.5**73 217
1	7	0.6136	4.2868	**−0.59**6 661
2	30	0.7362	4.0989	**−0.597 13**3 402
3	83	0.7343	4.1261	**−0.597 139 0**17 109
4	179	0.7519	4.2305	**−0.597 139 06**2 391
5	330	0.7848	4.4119	**−0.597 139 063 1**03 997
6	544	0.8248	4.3588	**−0.597 139 063 12**2 799
7	834	0.8596	4.3279	**−0.597 139 063 123** 383
8	1 211	0.8984	4.3119	**−0.597 139 063 123 40**4 198
9	1 687	0.9365	4.3183	**−0.597 139 063 123 405** 038 451
10	2 273	0.9685	4.3826	**−0.597 139 063 123 405 07**3 177
11	2 981	1.0035	4.3200	**−0.597 139 063 123 405 074** 767
12	3 822	1.0386	4.3200	**−0.597 139 063 123 405 074 831** 055
13	4 808	1.0736	4.3200	**−0.597 139 063 123 405 074 833** 976
14	5 950	1.1086	4.3200	**−0.597 139 063 123 405 074 834** 125 011
15	7 260	1.1437	4.3200	**−0.597 139 063 123 405 074 834 133** 503
16	8 749	1.1787	4.3200	**−0.597 139 063 123 405 074 834 134** 052 479
17	10 429	1.2137	4.3200	**−0.597 139 063 123 405 074 834 134 09**2 554
18	12 311	1.2487	4.3200	**−0.597 139 063 123 405 074 834 134 095** 736
19	14 407	1.2838	4.3200	**−0.597 139 063 123 405 074 834 134 096 00**1 111
20	16 728	1.3188	4.3200	**−0.597 139 063 123 405 074 834 134 096 02**3 914
21	19 286	1.3538	4.3200	**−0.597 139 063 123 405 074 834 134 096 025** 974 142

Ref. 33   −0.597 139 063 123 405 074 834 134 096 021

[a]Number of iteration or order.

Free Complement (FC) Method

- Hijikata, Nakashima, Nakatsuji, *J. Chem. Phys.* **130**, 024102 (2009).

TABLE V. Energies and the expectation values $\langle r_1 \rangle$, $\langle r_2 \rangle$, and $\langle R \rangle$ for the ground and a few excited states of the same symmetry for H_2^+ and its isotopomers. For H_2^+ (^1S), D_2^+, and T_2^+, the g and ψ_0 in Eqs. (11) and (12) were used at $n=14$ and $M_n=5950$ and, for H_2^+ (^3P), Eqs. (11) and (13) were used at $n=11$ and $M_n=6094$, and Eqs. (11) and (14) were used at $n=11$ and $M_n=5914$ for HD^+, HT^+, and DT^+. The nuclear mass data used were $m_H=1836.152\,672\,47$, $m_D=3670.482\,965\,4$, and $m_T=5496.921\,526\,9$. Values of $\alpha=1.1086$ and $\beta=4.32$ were employed for the nonlinear parameters.

	v [a]	Energy (a.u.)	Frequency (cm^{-1})	$\langle r_1 \rangle$	$\langle r_2 \rangle$	$\langle R \rangle$
H_2^+ (^1S)	0	−0.597 139 063 079 175 256 939 373 016		1.692 966 208	1.692 966 208	2.063 913 867
	1	−0.587 155 679 095 614 799 279	2191.099 519	1.764 752 230	1.764 752 230	2.199 125 136
	2	−0.577 751 904 414 194 283	2063.889 981	1.839 368 775	1.839 368 775	2.339 751 003
H_2^+ (^3P)	0	−0.596 873 738 784 476 119 983		1.694 397 351	1.694 397 351	2.066 619 898
	1	−0.586 904 320 918 598 361	2188.034 311	1.766 243 642	1.766 243 642	2.201 944 950
	2	−0.577 514 034 056 498	2060.929 747	1.840 928 825	1.840 928 825	2.342 700 915
D_2^+	0	−0.598 788 784 304 562 857 674 903 269		1.682 346 538	1.682 346 538	2.044 070 029
	1	−0.591 603 121 831 520 710 239	1577.070 622	1.732 573 538	1.732 573 538	2.138 662 460
	2	−0.584 712 206 896 550 366	1512.381 015	1.784 134 235	1.784 134 235	2.235 803 372
T_2^+	0	−0.599 506 910 096 112 180 587 249 172		1.677 707 679	1.677 707 679	2.035 386 031
	1	−0.593 589 927 768 924 154 523	1298.627 515	1.718 559 684	1.718 559 684	2.112 318 407
	2	−0.587 871 233 588 277 177	1255.108 297	1.760 279 582	1.760 279 582	2.190 908 363
HD^+	0	−0.597 897 968 608 954 700 621		1.688 442 006	1.687 732 429	2.054 803 238
	1	−0.589 181 829 556 745 679 654	1912.971 405	1.750 355 477	1.749 545 901	2.171 318 411
	2	−0.580 903 700 218 035 070	1816.839 385	1.814 343 968	1.813 414 961	2.291 782 413
HT^+	0	−0.598 176 134 637 481 345 390		1.686 767 475	1.685 825 362	2.051 456 621
	1	−0.589 932 814 045 479 912 796	1809.199 748	1.745 058 766	1.743 992 245	2.161 124 416
	2	−0.582 080 048 852 003 373	1723.482 746	1.805 179 364	1.803 965 860	2.274 267 594
DT^+	0	−0.599 130 662 833 885 811 307		1.680 255 515	1.680 023 340	2.039 939 515
	1	−0.592 545 017 179 965 882 666	1445.382 152	1.726 030 854	1.725 774 951	2.126 123 588
	2	−0.586 206 019 855 001 345	1391.249 101	1.772 906 374	1.772 623 450	2.214 406 291

[a]Excitation level.

Full-CI by Quantum Computing

- NOMO/qFCI

International Journal of
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## Quantum Chemistry beyond Born–Oppenheimer Approximation on a Quantum Computer: A Simulated Phase Estimation Study

Libor Veis,[a]† Jakub Višňák,[a]† Hiroaki Nishizawa,[b] Hiromi Nakai,[c] and Jiří Pittner*[a]

We present an *efficient* quantum algorithm for beyond-Born–Oppenheimer molecular energy computations. Our approach combines the quantum full configuration interaction method with the nuclear orbital plus molecular orbital method. We give the details of the algorithm and demonstrate its performance by classical simulations. Two isotopomers of the hydrogen molecule (H_2, HT) were chosen as representative examples and calculations of the lowest rotationless vibrational transition energies were simulated. © 2016 Wiley Periodicals, Inc.

- IPEA (iterative phase estimation algorithm)

Accuracy of NOMO

- Total Energy of H_2: $E(H_2)$
  - TRC-NOMO/HF(MO,1s-opt) (CPL, 1998)   -0.685947 au
  - TRC-NOMO/HF(VB,1s-opt) (IJQC, 2002)   -1.042012 au
  - TRC-NOMO/HF (IJQC, 2002)   -1.052371 au
  - TF-NOMO/HF (IJQC, 2002)   -1.074315 au
  - TF-NOMO/MP2 (JCP, 2003)   -1.131626 au
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  - ECG-NOMO/HF (JCP, 2011)   -1.112548 au
  - ECG-NOMO/MP2 (CPL, 2012)   -1.155409 au
  - ECG-NOMO/CCSD (CPL, 2012)   -1.160017 au
  - TRF-NOMO/qFCI (2016)   -1.130346 au (?)
  - ECG (Adamowicz, 2003)   -1.164025 au

Contents

- Introduction: Born-Oppenheimer Approximation

- What is NOMO?

- How to use NOMO?

- Summary and Perspective

How to use NOMO?

- Non-adiabatic effect
  - Diagonal Born-Oppenheimer correction (DBOC)
  - Non-adiabatic transition
  - …
- Nuclear quantum effect
  - Zero point vibration
  - Geometric isotope effect
  - Kinetic isotope effect
  - Proton tunneling
  - …

Geometric Isotope Effect

- Bond distances of H_2 by TRC-, TF-, & TRF-NOMO

		Calc		Exptl
R_e	MO	0.7344	(-0.0070)	0.7414
R_0	TRC-NOMO	0.7764	(0.0254)	0.7510
	TF-NOMO	0.7641	(0.0131)	
	TRF-NOMO	0.7528	(0.0018)	

[Hartree]
-1.00
-1.05
-1.051   TRC-NOMO
-1.074   TF-NOMO
-1.10
-1.104   TRF-NOMO
-1.123   MO+ZPE
-1.133
-1.15
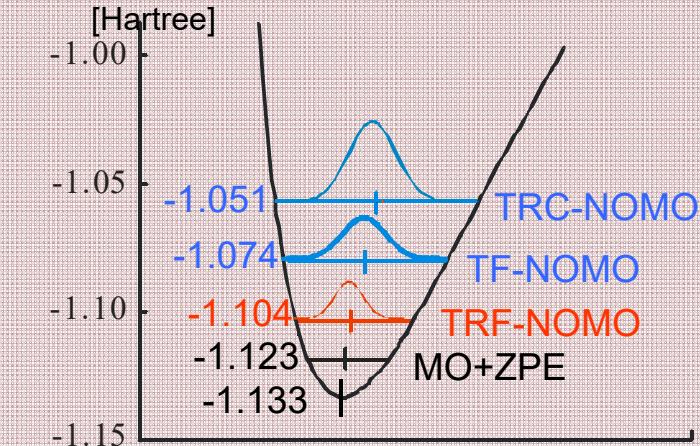
- Bond distances of H_2, D_2, & T_2 by TRF-NOMO

		Calc		Exptl
H_2	TRF-NOMO	0.7528	(0.0018)	0.7510
D_2	TRF-NOMO	0.7475	(-0.0008)	0.7483
T_2	TRF-NOMO	0.7453	(-0.0016)	0.7469

H_2
D_2
T_2
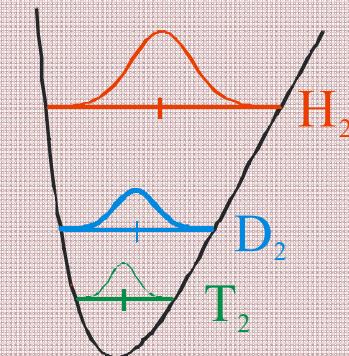
✓ TRF-NOMO can well describe averaged bond distance (< 0.01 Å).
✓ Geometric isotope effect (GIE) can be discussed.

Geometric Isotope Effect

- GIE for hydrogen bond
  - Intra-molecular X—H bond: $R_0(X—H) > R_0(X—D)$
  - Inter-molecular X…H bond: $R_0(X…H) < R_0(X…D)$ ← Ubbelohde effect
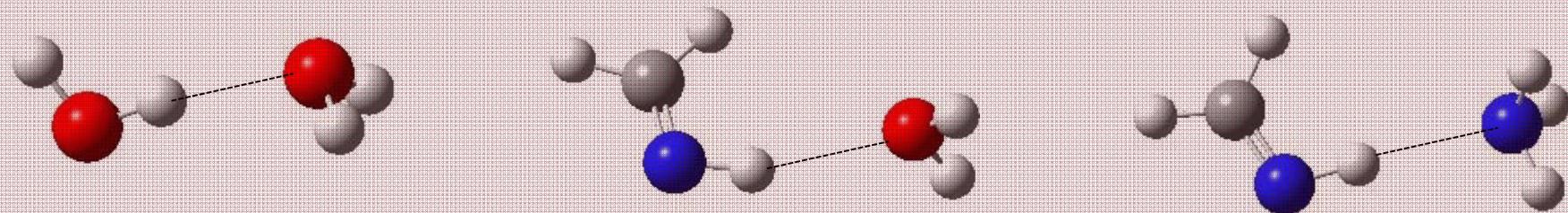
- GIE for dihydrogen bond
  - $X^{\delta+}H^{\delta-}…H^{\delta+}Y^{\delta-}$

Li H_a H_b C   C   H

$LiH···C_2H_{2.}$

H
H
H   N H_a H_b Be   H

$NH_4^+···BeH_{2.}$

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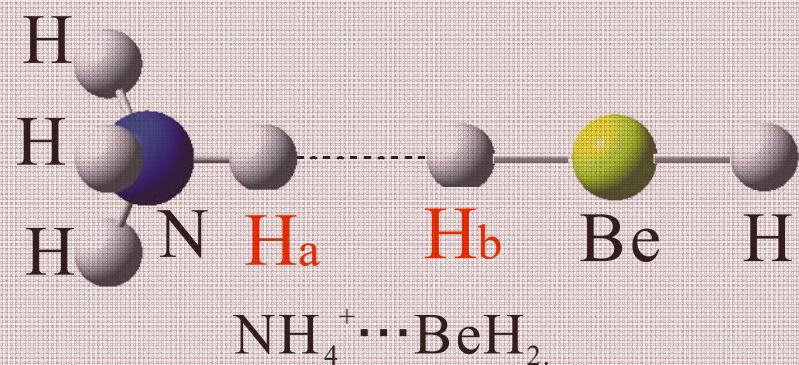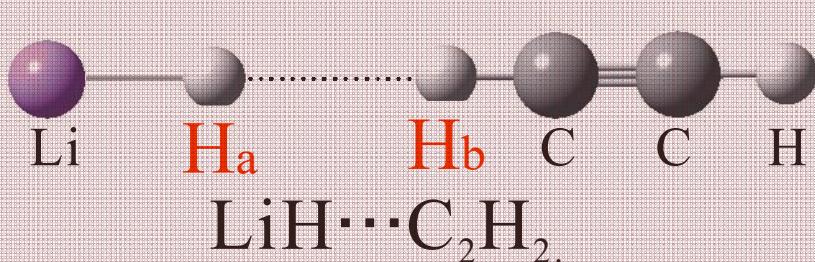
Geometric Isotope Effect

- GIE for hydrogen bond

	System	Bond	H	D	Δ
Intramolecular distance	$HOX\cdots OH_2$	$R(O_a-X)$	0.9657	0.9612	(-0.0045)
	$HOX\cdots NH_3$	$R(O-X)$	0.9713	0.9666	(-0.0047)
	$H_2CNX\cdots OH_2$	$R(N-X)$	1.0227	1.0179	(-0.0047)
	$H_2CNX\cdots NH_3$	$R(N_a-X)$	1.0257	1.0206	(-0.0051)
	$HSX\cdots OH_2$	$R(S-X)$	1.3463	1.3349	(-0.0114)
	$HSX\cdots NH_3$	$R(S-X)$	1.3523	1.3409	(-0.0115)
	$H_3CX\cdots OH_2$	$R(C-X)$	1.0978	1.0905	(-0.0073)
	$H_3CX\cdots NH_3$	$R(C-X)$	1.0981	1.0908	(-0.0073)
Intermolecular distance	$HOX\cdots OH_2$	$R(X\cdots O_b)$	1.9517	1.9604	(0.0086)
	$HOX\cdots NH_3$	$R(X\cdots N)$	1.9731	1.9818	(0.0087)
	$H_2CNX\cdots OH_2$	$R(X\cdots O)$	2.2254	2.2300	(0.0046)
	$H_2CNX\cdots NH_3$	$R(X\cdots N_b)$	2.1983	2.2138	(0.0155)
	$HSX\cdots OH_2$	$R(X\cdots O_b)$	2.1983	2.2060	(0.0076)
	$HSX\cdots NH_3$	$R(X\cdots N)$	2.1909	2.1972	(0.0063)
	$H_3CX\cdots OH_2$	$R(X\cdots O)$	2.6003	2.6073	(0.0070)
	$H_3CX\cdots NH_3$	$R(X\cdots N)$	2.7464	2.7538	(0.0074)

Intramolecular Shrinkage

Intermolecular Elongation

Bond Distance (Å)

✓ TRF-NOMO/MP2 can reproduce the GIE!

Ubbelohde Effect

- Elongation of hydrogen bond by D-substitution affects phase transition temperature in ferroelectric materials (e.g. KDP (KH_2PO_4)).

	Tc (K)		ΔTc (K)
	H-compound	D-compound	
KH_2PO_4 (KDP)	122	218	96
RbH_2PO_4 (RDP)	147	238	91
CsH_2PO_4 (CDP)	153	267	114
KH_2AsO_4 (KDA)	96	161	65
RbH_2AsO_4 (RDA)	100	173	73
CsH_2AsO_4 (CDA)	143	212	69
$(NH_4)H_2PO_4$ (ADP)	147	242	95
$(NH_4)H_2AsO_4$ (ADA)	216	304	88
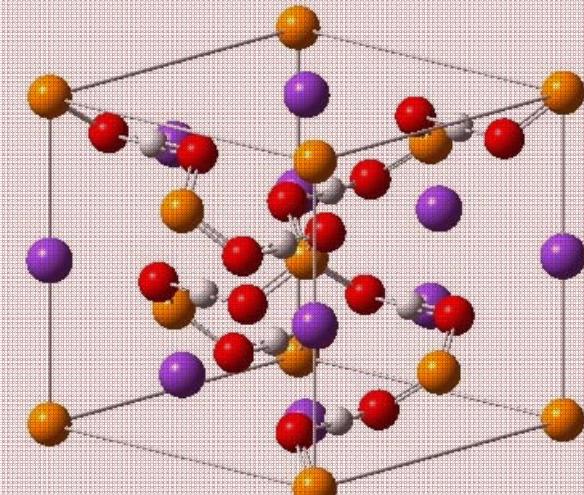
Crystal structure of KDP

Kinetic Isotope Effect

- hydrogen abstract reaction
  - HO + HOR → HOH + OR

  - Rate constant $\dfrac{k_a^H}{k_a^D} = \exp\left[-\dfrac{E_a^D - E_a^H}{RT}\right]$

R	Reaction Barrier		Rate Constant	Exponent			
	E_a^H	E_a^D	k_a^H/k_a^D	α_{IS}^H	α_{TS}^H	α_{IS}^D	α_{TS}^D
CH$_3$	27.43	28.90	12.0	23.80	21.27	34.66	30.93
H	29.61	30.49	4.4 (6.0 ± 2.0)	23.71	20.79	34.55	30.20
CN	39.54	40.01	2.6	21.93	19.78	32.27	28.24

*Ishimoto, **Tachikawa**, Nagashima, *IJQC*, **109**, 2677 (2009).

[Hartree]
-1.00
-1.05
-1.051 TRC-NOMO
-1.074 TF-NOMO
-1.10
-1.104 TRF-NOMO
-1.123
-1.133 MO+ZPE
-1.15
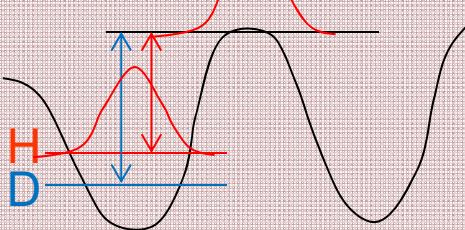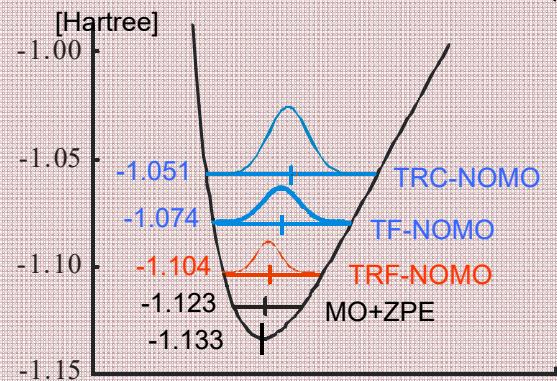
✓ Kinetic isotope effect (KIE) should be carefully discussed.

How to use NOMO?

- Non-adiabatic effect
  - Diagonal Born-Oppenheimer correction (DBOC)
  - Non-adiabatic transition
  - …
- Nuclear quantum effect
  - Zero point vibration
  - Geometric isotope effect
  - Kinetic isotope effect
  - Vibrational wave function
  - …
- Annihilation of nuclei (positively charge particles)
  - Proton annihilation
  - Positron annihilation
  - …

Nuclear Orbital Energy

- Correlation Energy Calculation

$$E_{\text{NOMO/MP2}} = E_{\text{NOMO/HF}} + \frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{\left| \left\langle \varphi_i \varphi_j \mid \varphi_a \varphi_b \right\rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$+ \sum_{i,a} \sum_{I,A} \frac{\left| \left\langle \varphi_i \varphi_I \mid \varphi_a \varphi_A \right\rangle \right|^2}{\varepsilon_i + \varepsilon_I - \varepsilon_a - \varepsilon_A} + \frac{1}{4} \sum_{I,J} \sum_{A,B} \frac{\left| \left\langle \varphi_I \varphi_J \mid \varphi_a \varphi_b \right\rangle \right|^2}{\varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B}$$

- Vibrational (Nuclear) Excited State Calculation

$$\Psi_{\text{NOMO/CIS}} = \sum_{i,a} c_i^a \Phi_i^a + \sum_{I,A} c_I^A \Phi_I^A$$

(a) E' (b) E' (c) A$_1$'

(d) E' (e) E' (f) A$_1$'
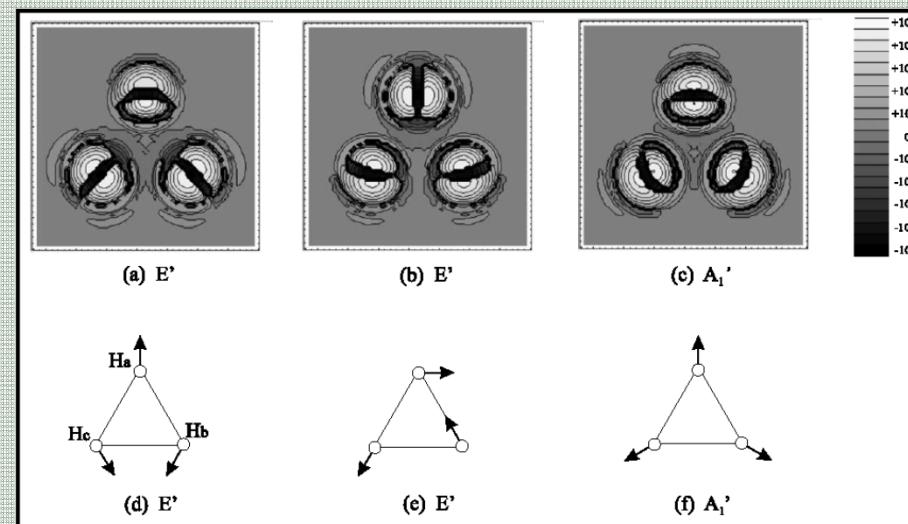
Koopmans' Theorem

- Electronic Orbital Energy
  - Energy difference based in the frozen orbital approximation

$$\text{IP} = {}^{N-1}E_r - {}^N E_0$$

$$= \left(\sum_{i \neq r}^{N_{occ}} \langle i|h|i \rangle + \frac{1}{2} \sum_{i \neq r}^{N_{occ}} \sum_{j \neq r}^{N_{occ}} \langle ij\|ij \rangle \right) - \left(\sum_{i}^{N_{occ}} \langle i|h|i \rangle - \frac{1}{2} \sum_{i}^{N_{occ}} \sum_{j}^{N_{occ}} \langle ij\|ij \rangle \right)$$

$$= -\left(\langle r|h|r \rangle + \sum_{j}^{N_{occ}} \langle rj\|rj \rangle \right)$$

$$= -\varepsilon_r$$

- Nuclear Orbital Energy
  - Energy difference based in the frozen orbital approximation
    $\Rightarrow$??

Proton Annihilation?

- Proton annihilation
  - gaseous basicity
  - proton affinity
  - acidity
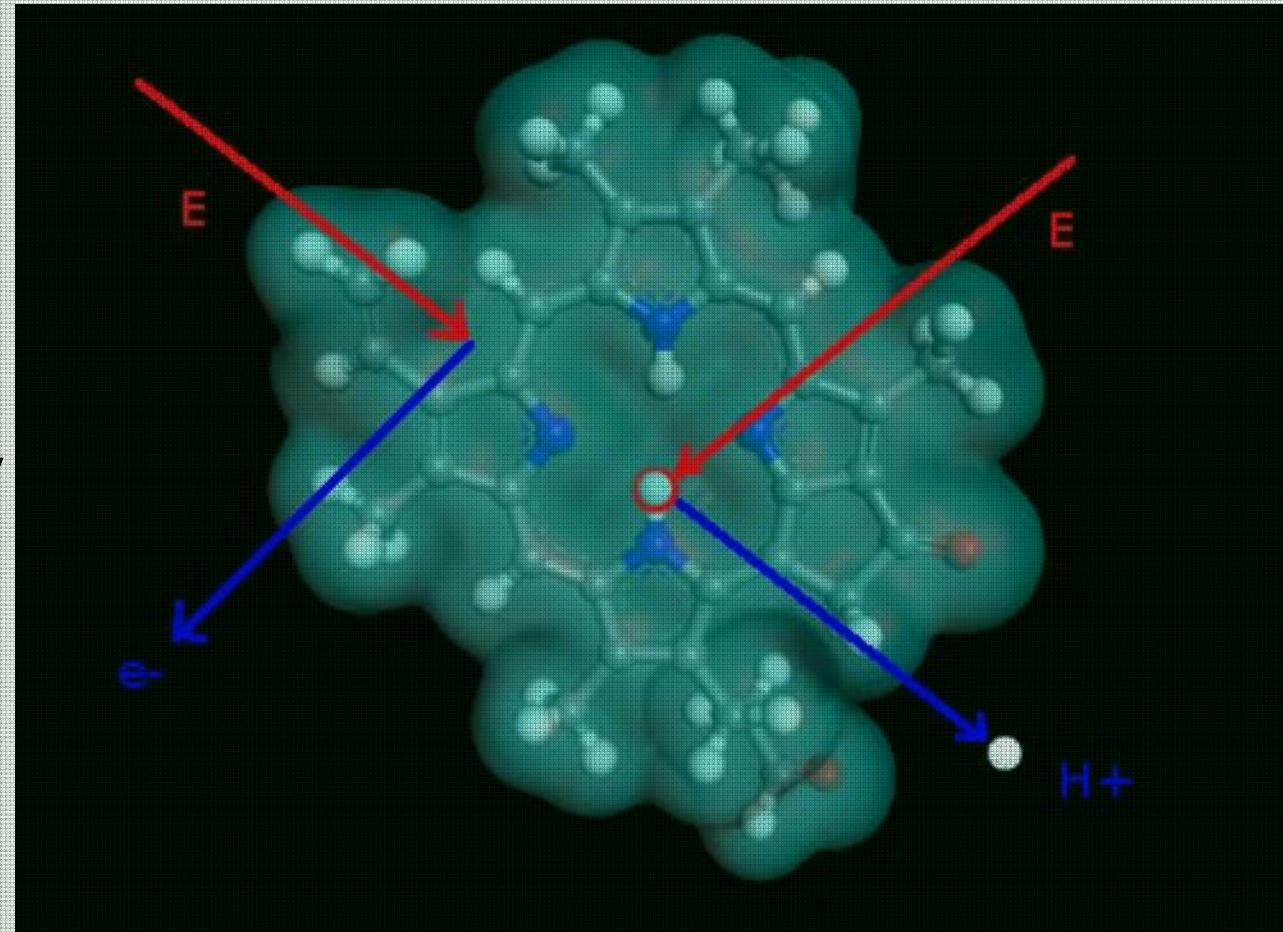
"A generalized any-particle propagator theory: Prediction of proton affinities and acidity properties with the proton propagator"
Díaz-Tinoco, Romero, Ortiz, **Reyes**, Flores-Moreno,
J. Chem. Phys. **138**, 194108 (2013).

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Proton Propagator

- Green function

$$G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\varphi_i(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_2)}{\omega - \varepsilon_I} + \sum_a \frac{\varphi_a(\mathbf{r}_1)\varphi_a^*(\mathbf{r}_2)}{\omega - \varepsilon_a}$$

$$+ \sum_I \frac{\varphi_I(\mathbf{r}_1)\varphi_I^*(\mathbf{r}_2)}{\omega - \varepsilon_I} + \sum_A \frac{\varphi_A(\mathbf{r}_1)\varphi_A^*(\mathbf{r}_2)}{\omega - \varepsilon_A}$$

$$\left(G_0(\omega)\right)_{ij} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_j^*(\mathbf{r}_1) G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) \varphi_j(\mathbf{r}_2) = \frac{\delta_{ij}}{\omega - \varepsilon_i}$$

$$\left(G_0(\omega)\right)_{IJ} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_J^*(\mathbf{r}_1) G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) \varphi_J(\mathbf{r}_2) = \frac{\delta_{IJ}}{\omega - \varepsilon_I}$$

- Dyson equation

$$\mathbf{G}(\omega) = \mathbf{G_0}(\omega) + \mathbf{G_0}(\omega)\Sigma(\omega)\mathbf{G}(\omega)$$

Proton Propagator

- Dyson equation for nucleus (proton)

$$G^{n^{-1}}(E) = G_0^{n^{-1}}(E) - \Sigma^{n-n}(E) - \Sigma^{n-e}(E)$$

- NOMO/PP2 method
  - Second-order approximation for self-energy
  - Diagonal approximation

$$\Sigma_{II}^{\text{en}(2)}(\omega_P) = \sum_i \sum_a \frac{\left|\langle \varphi_I \varphi_a \mid \varphi_I \varphi_i \rangle\right|^2}{\omega_P + \varepsilon_a - \varepsilon_I - \varepsilon_i} + \sum_{A \in P} \sum_i \sum_a \frac{\left|\langle \varphi_I \varphi_i \mid \varphi_A \varphi_a \rangle\right|^2}{\omega_P + \varepsilon_i - \varepsilon_A - \varepsilon_a}$$

2ph + 2hp
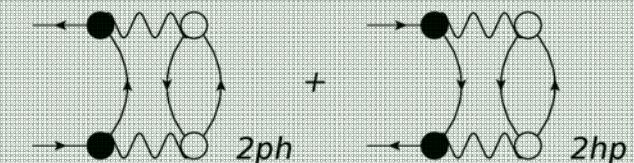
$$\Sigma_{II}^{\text{nn}(2)}(\omega_P) = \sum_{J \notin P} \sum_{A \notin P} \frac{\left|\langle \varphi_I \varphi_A \mid \varphi_I \varphi_J \rangle\right|^2}{\omega_P + \varepsilon_A - \varepsilon_I - \varepsilon_J} + \sum_{J \notin P} \sum_{A \in P} \sum_{B \notin P} \frac{\left|\langle \varphi_I \varphi_J \mid \varphi_A \varphi_B \rangle\right|^2}{\omega_P + \varepsilon_J - \varepsilon_A - \varepsilon_B}$$

2ph + 2hp
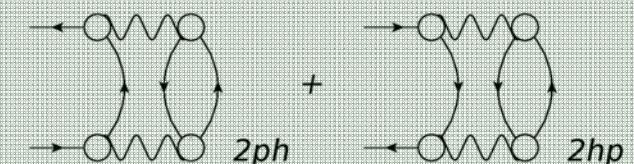
$$E_p^n = \varepsilon_p^n + \Sigma_p^{n-n}(E_p^n) + \Sigma_p^{n-n}(E_p^n)$$

Proton Propagator

- Accuracy of PP2 with NOMO method
  - Basis sets: cc-pVTZ/7s7p7d
  - $AX \rightarrow A^- + H^+$

Mol.	TRC-NOMO/HF Koopmas		TF-NOMO/HF Koopmas		TRF-NOMO/HF Koopmas		Exptl.
HF	22.95	(6.89)	23.02	(6.96)	24.16	(8.09)	16.06
DF	23.56	(7.42)	23.64	(7.51)	24.44	(8.30)	16.13
HCl	23.26	(8.84)	23.30	(8.89)	24.55	(10.13)	14.42
DCl	23.91	(9.43)	23.96	(9.49)	24.84	(10.37)	14.47
HCN	23.81	(8.65)	23.86	(8.70)	24.04	(8.88)	15.16
H_2S	25.26	(10.08)	25.30	(10.12)	26.12	(10.94)	15.18
MAD		8.57		8.61		9.45	

Proton Propagator

- Accuracy of PP2 with NOMO method
  - Basis sets: cc-pVTZ/7s7p7d
  - $AX \rightarrow A^- + H^+$

Mol.	TRC-NOMO/PP2		TF-NOMO/PP2		TRF-NOMO/PP2		Exptl.
HF	16.05	(−0.01)	16.07	(−0.01)	16.29	(0.23)	16.06
DF	16.21	(0.07)	16.23	(0.09)	16.39	(0.26)	16.13
HCl	14.01	(−0.41)	14.02	(−0.40)	14.28	(−0.14)	14.42
DCl	14.17	(−0.31)	14.18	(−0.29)	14.37	(−0.11)	14.47
HCN	15.08	(−0.08)	15.09	(−0.07)	15.13	(−0.02)	15.16
H_2S	15.54	(0.35)	15.55	(0.36)	15.74	(0.56)	15.18
MAD		0.21		0.22		0.22	

Proton Propagator

- Accuracy of PP2 with NOMO method
  - Basis sets: cc-pVTZ/7s7p7d
  - $AX \rightarrow A^- + H^+$

Mol.	MO/HF ΔSCF		NOMO/HF ΔSCF		NOMO/HF Koopmas		NOMO/PP2		Exptl.
HF	16.98	(0.92)	13.67	(−2.39)	22.97	(8.55)	16.06	(0.00)	16.06
DF	17.06	(0.93)	13.95	(−2.18)	23.58	(9.11)	16.21	(0.08)	16.13
HCl	14.59	(0.17)	16.09	(1.67)	23.28	(7.22)	14.02	(−0.40)	14.42
DCl	14.65	(0.18)	16.39	(1.92)	23.92	(7.79)	14.17	(−0.30)	14.47
HCN	15.28	(0.12)	16.09	(0.93)	23.81	(8.65)	15.07	(−0.09)	15.16
H_2S	15.51	(0.33)	14.48	(−0.70)	25.27	(10.09)	15.54	(0.36)	15.18
MAD		0.44		1.63		8.57		0.21	

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Divde-and-Conquer Correlation

■ Total Correlation Energy

$$E_{\text{corr}} \approx \sum_{\alpha}^{\text{subsystem}} E_{\text{corr}}^{\alpha}$$

■ Subsystem Correlation Energy estimated by Energy Density Analysis (EDA)[1]

$$E_{\text{corr}}^{\alpha} = \sum_{i,j}^{\text{occ}(\alpha)} \sum_{a,b}^{\text{vir}(\alpha)} w_{\text{occ}} \sum_{\mu \in S(\alpha)} C_{\mu i}^{\alpha} \left\langle \mu j^{\alpha} \middle| a^{\alpha} b^{\alpha} \right\rangle [2\tilde{t}_{ij,ab}^{\alpha} - \tilde{t}_{ij,ba}^{\alpha}]$$

$S(\alpha)$: subsystem α

MP2 [2] : $\tilde{t}_{ij,ab}^{\alpha} = -\dfrac{\left\langle a^{\alpha} b^{\alpha} \middle| i^{\alpha} j^{\alpha} \right\rangle}{\varepsilon_a^{\alpha} + \varepsilon_b^{\alpha} - \varepsilon_i^{\alpha} - \varepsilon_j^{\alpha}}$

CCSD [3]: $\tilde{t}_{ij,ab}^{\alpha} = t_{i,a}^{\alpha} t_{j,b}^{\alpha} + t_{ij,ab}^{\alpha}$

Subsystem

Central region

Buffer region

Localization region
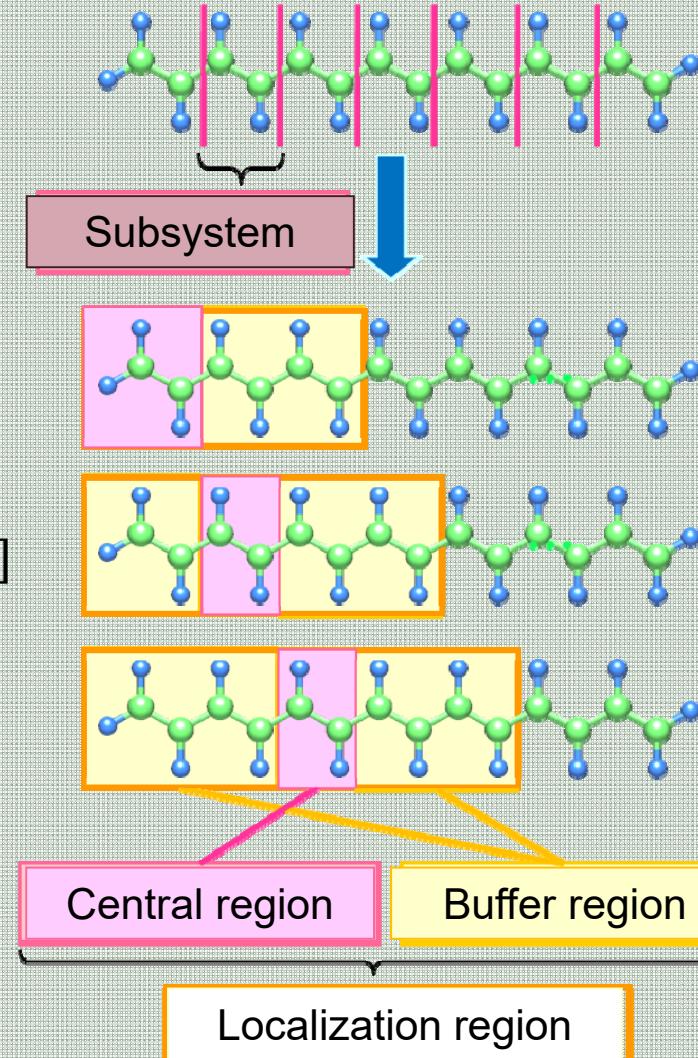
[1] H. Nakai, *CPL* **363**, 73 (2002).
[2] M. Kobayashi, Y. Imamura, H. Nakai, *JCP*, **127**, 074103 (2007).
[3] M. Kobayashi , H. Nakai, *JCP*, **129**, 044103 (2008).

Combination of DC and PP2

■ NOMO/DC-PP2 Method

$$\omega_P = \varepsilon_I + \sum_i \sum_a \frac{\left|\left\langle \varphi_I \varphi_a^\alpha \mid \varphi_I \varphi_i^\alpha \right\rangle\right|^2}{\omega_P + \varepsilon_a^\alpha - \varepsilon_I - \varepsilon_i^\alpha} + \sum_{A \in P} \sum_i \sum_a \frac{\left|\left\langle \varphi_I \varphi_i^\alpha \mid \varphi_A \varphi_a^\alpha \right\rangle\right|^2}{\omega_P + \varepsilon_i^\alpha - \varepsilon_A - \varepsilon_a^\alpha}$$
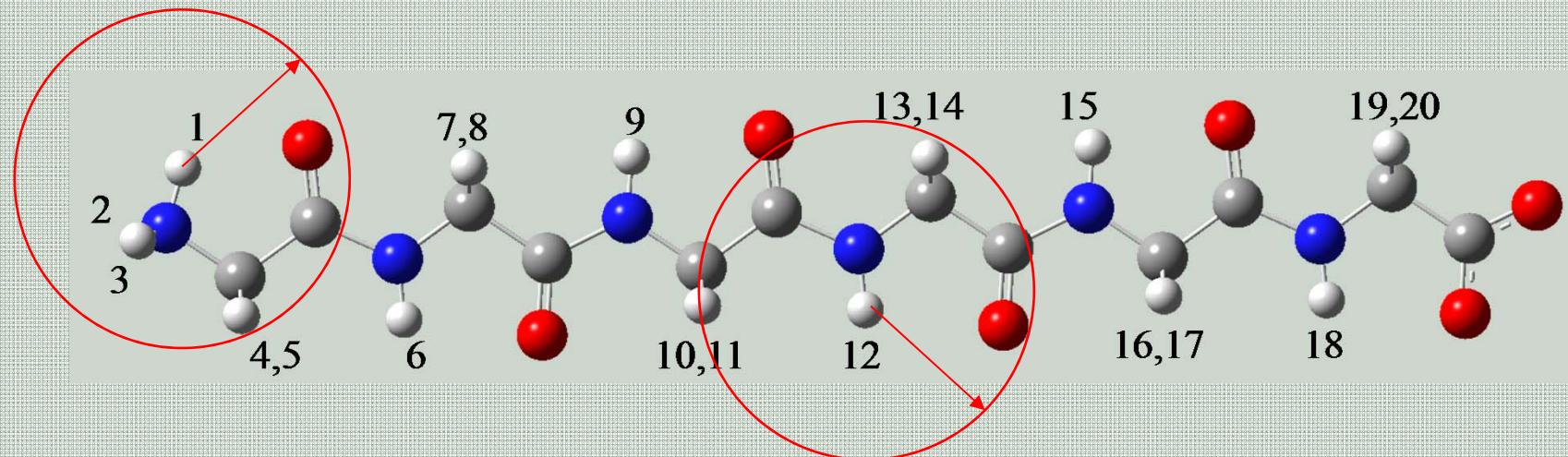
NOMO/DC-PP2 Calculation

- $(Gly)_n$ peptide
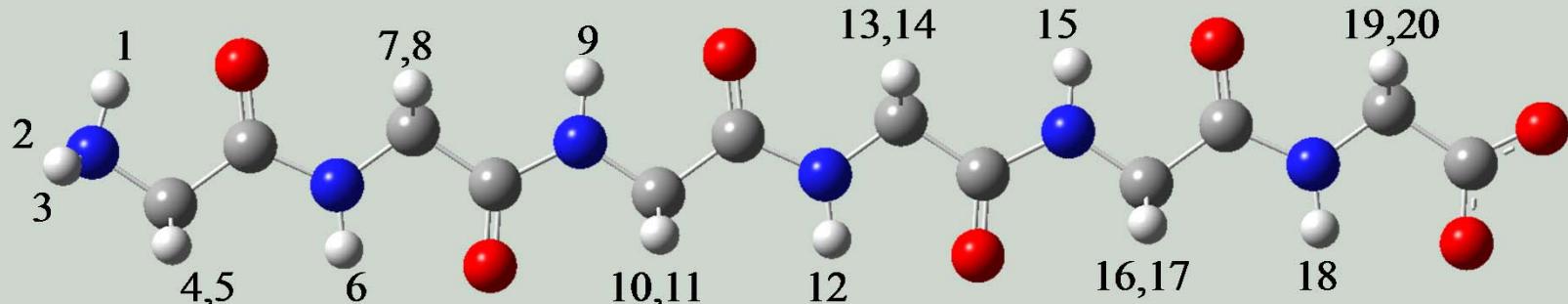
- Accuracy
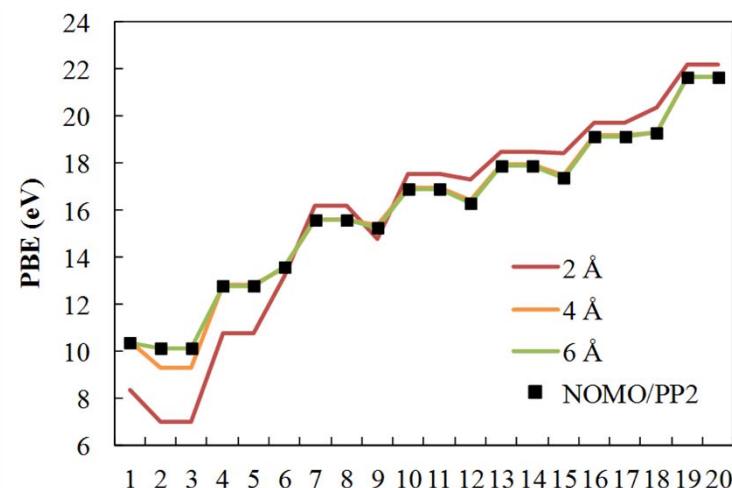
- Efficiency

n	PP2	DC-PP2
4	15.9	6.1
6	47.1	9.9
8	110.6	20.3
10	219.0	28.8
12	408.9	34.4

NOMO/DC-PP2 Calculation

- Chignolin
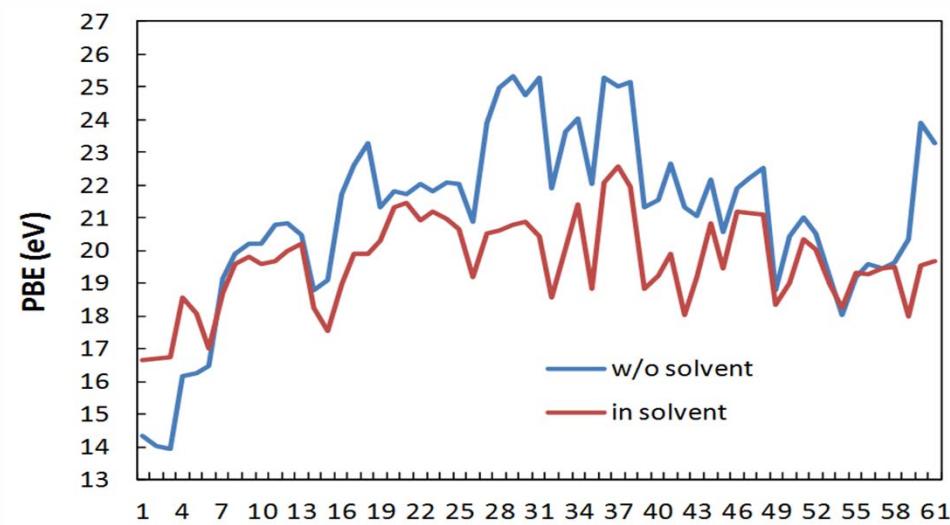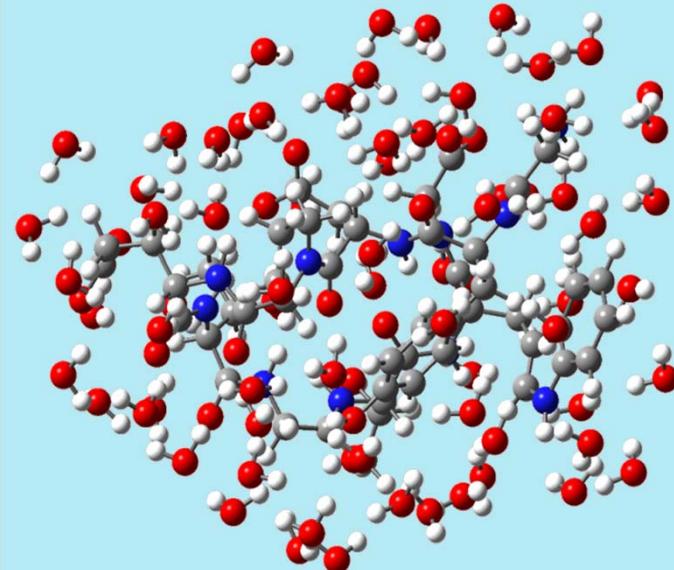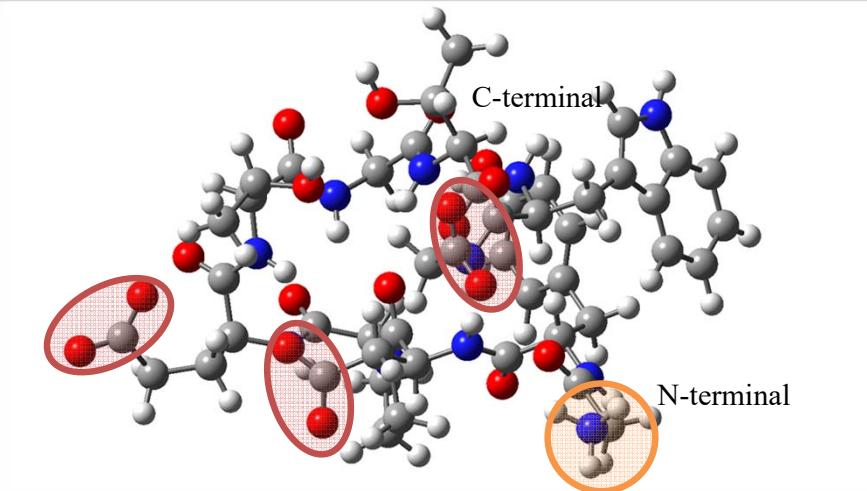
Summary & Perspective

- Accuracy & Cost

	Energy	Wave function	Computational cost
TRC-NOMO	bad	not good, physically correct	inexpensive
TF-NOMO	not good	unphysical	inexpensive
TRF-NOMO	good	unphysical	inexpensive
ECG-NOMO	accurate	good	expensive
ECG (Adamowicz)	~exact	~exact	extremely expensive
FC (Nakatsuji)	~exact	~exact	extremely expensive

Summary & Perspective

- How to *correctly* use NOMO is important!

- To describe non-adiabatic effect such as DBOC and non-adiabatic coupling, we need spectroscopic-accuracy methods.

  - ECG & FC are promising.

  - ECG-NOMO might be applicable.

- To describe nuclear quantum effect such as zero point vibration, geometric & kinetic isotope effects, and vibrational wave function, we need chemical-accuracy methods.

  - TRF-NOMO is promising due to its accuracy and feasibility.

  - For large systems in which contaminations of translation and rotation are not serious, TRC-NOMO is promising to describe the nuclear wave function.

- To describe annihilation of nuclei (positively charge particles) such as proton affinity and positron annihilation , we need chemical-accuracy methods.

  - NOMO/DC-PP2 is promising due to its accuracy and feasibility.

  - NOMO wave function is needed to describe the positron binding state.

Colleague

- Prof. Andres Reyes (Universidad Nacional de Colombia)
- Mr. Jonathan Romero (Universidad Nacional de Colombia)

- Prof. Feng Wang (Swinburne University of Technology)

- Prof. Shiaki Hyodo (Hyogo Prefectural University)

- Prof. Masanori Tachikawa (Yokohama City University)
- Dr. Keitaro Sodeyama (NIMS) Chignolin
- Dr. Minoru Hoshino (Nissan Chemicals)
- Dr. Yutaka Imamura (RIKEN)
- Dr. Hiroaki Nishizawa (Waseda University, IMS)
- Dr. Yasuhiro Ikabata (Waseda University)
- Dr. Masato Kobayashi (Waseda University)
- Mr. Kaito Miyamoto
- Mr. Hiroyoshi Kiryu
- Mr. Yasuhiro Tsukamoto
- Ms. Risa Aiba

Acknowledgment

Dr. Yasuhiro IKABATA