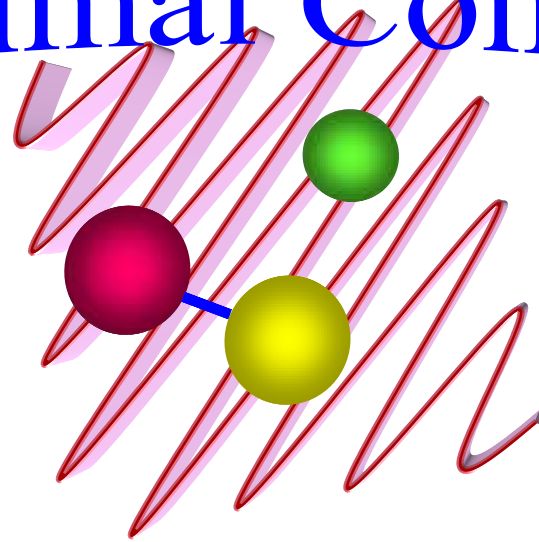
Optimal Control



フェムト秒レーザーパルスを使った分子ダイナミクスの量子最適制御シミュレーション
基礎・展開・挑戦

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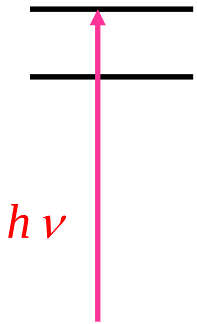
応用例
(この資料ではフェムト秒脱離ダイナミクスへの 応用例だけを示す)

量子制御と最適化

Key principles of quantum control

Static & Dynamical control



$$|2> = \frac{1}{\sqrt{2}}[\,|A> - |B>]$$

$$|1> = \frac{1}{\sqrt{2}}[\,|A> + |B>]$$

50% product A, 50% product B

$$|\Phi_{\pm}> = \frac{1}{\sqrt{2}}[\,|1> \pm |2>] = |A> \; or \; |B>$$

Laser-field manipulation of constructive and destructive interferences of the evolving molecular wave function.

Optimal control experiment (OCE)

lack of the knowledge about molecular Hamiltonian
(existence of experimental noises)

Measurements can destroy a molecular wave function.

Learning Control

need minimal or even no knowledge of the Hamiltonian

statistical solution search

development of laser shaping techniques

Optimal control experiment (OCE)

Optimal Control
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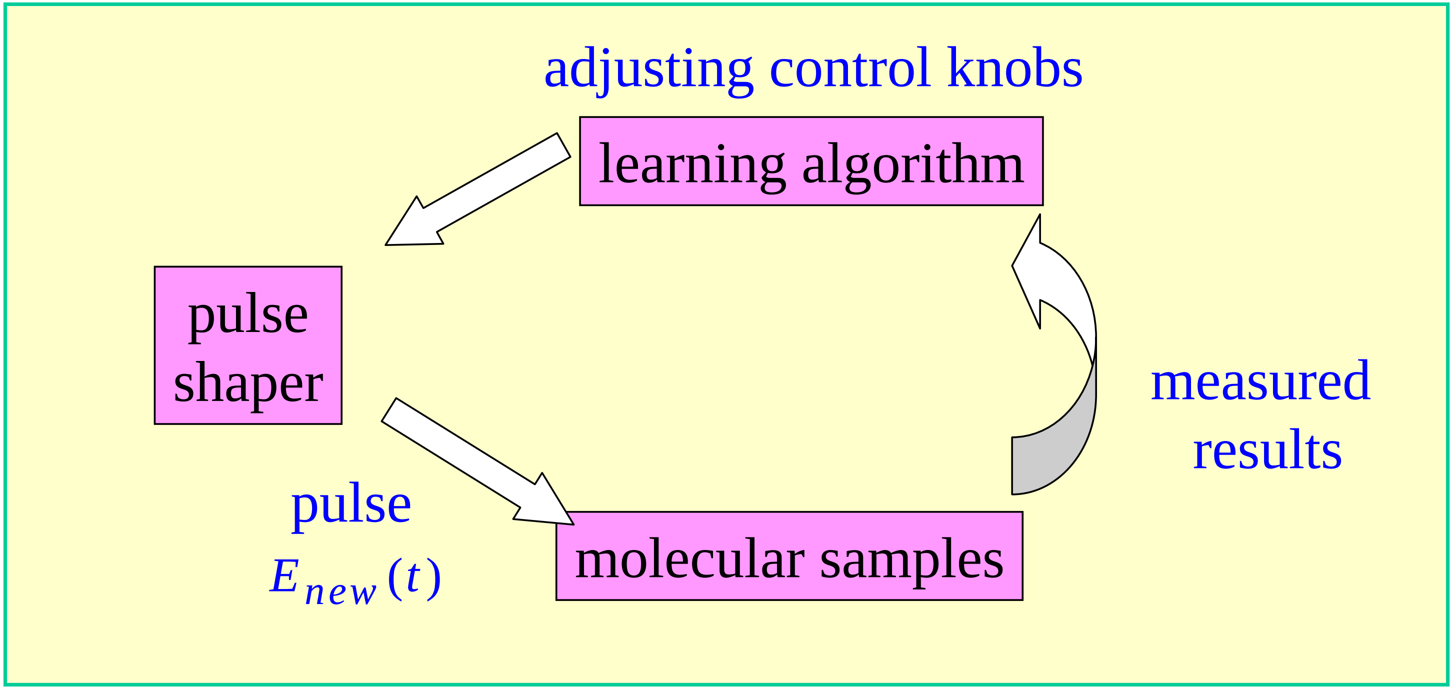
Closed-loop experiment



Examples of OCE's

Isolated systems

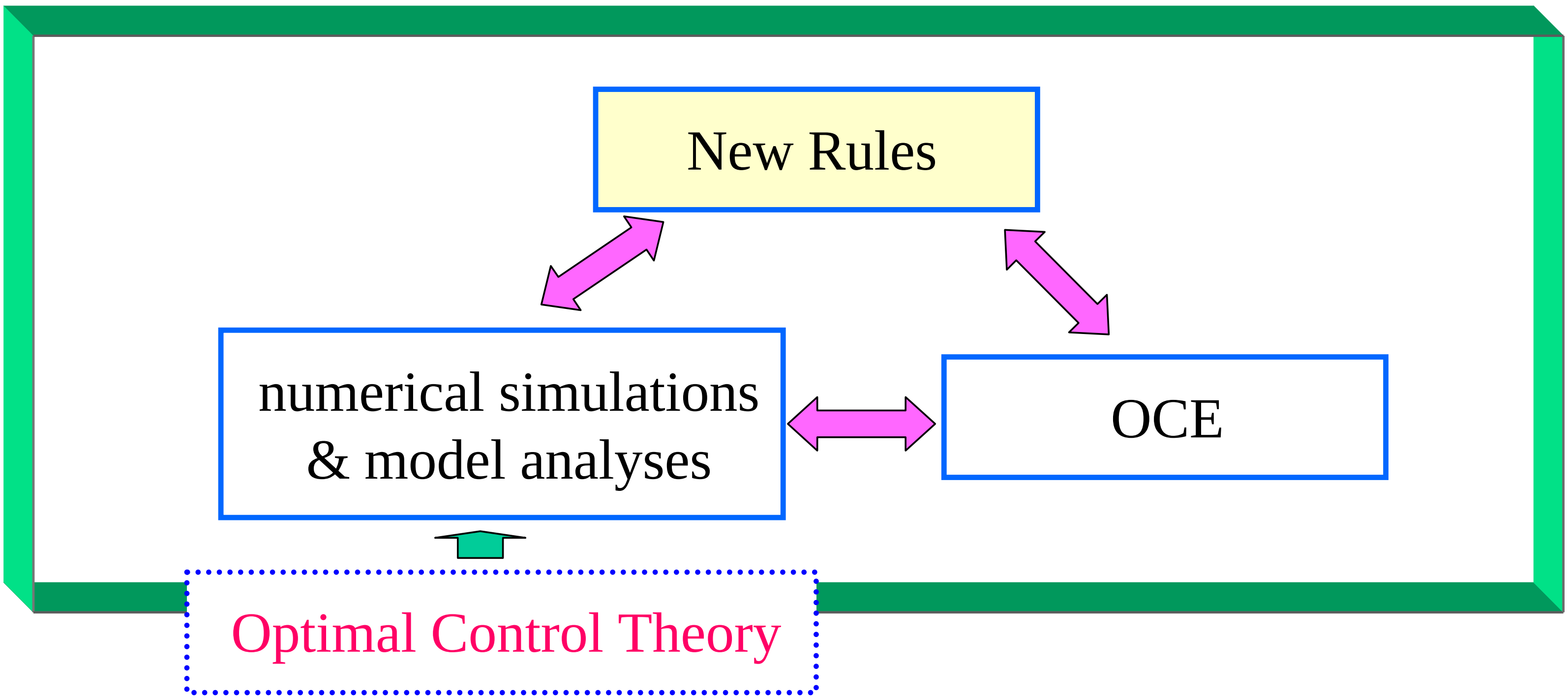
- complex systems
  - charge-transfer coordination complex, ...
- strong-field dynamics
  - dissociation & rearrangement of chemical bonds
  - selective generation of high harmonics

Condensed systems

- pulse propagation
  - self-phase modulation
- application to biological systems
  - branching ratio between intramolecular and intermolecular energy transfer processes

Why optimal control theory ?

It is natural to employ optimal control procedures for clarifying the mechanisms of OCE results.



Research subjects

Fundamentals

Development of solution algorithms

Decoherence effects on quantum control

Applications

Laser-induced surface dynamics

Isotope separation

Biological systems

Challenges

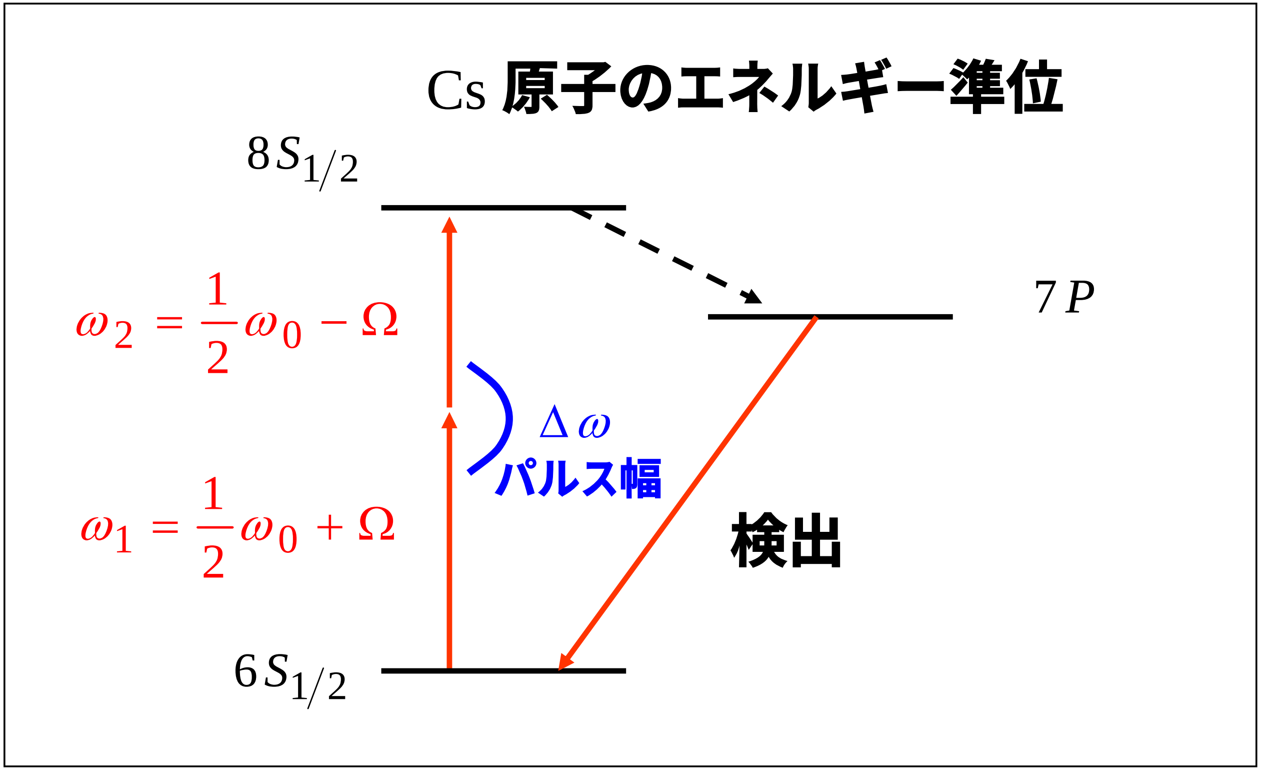
Molecular quantum computer

最適制御実験

2光子遷移の量子制御を例に

フェムト秒パルス励起による2光子遷移量子制御

Meshulach & Silberberg, Nature (1998)



フェムト秒パルス励起による2光子遷移量子制御

Meshulach & Silberberg, Nature (1998)

2光子遷移確率

$$S_{signal} \propto \left| \int d\Omega \; \tilde{E}(\omega_0/2+\Omega)\; \tilde{E}(\omega_0/2-\Omega) \right|^2$$

電場のフーリエ成分

$$\tilde{E}(\omega_0/2 \pm \Omega) = A_{\pm}(\Omega)\, \exp[\, i\, \theta_{\pm}(\Omega)\,]$$

$$S_{signal} \propto \left| \int d\Omega \; A_{+}(\Omega)\, A_{-}(\Omega)\; \exp\{\, i\, [\, \theta_{+}(\Omega) + \theta_{-}(\Omega)\,]\} \right|^2$$

フェムト秒パルス励起による2光子遷移量子制御

【1】 Bright Pulse

$$\theta_{+}(\Omega) = -\theta_{-}(\Omega) = \alpha \sin(\beta\,\Omega)$$ **の場合**

$$S_{signal} \propto \left| \int d\Omega\ A_{+}(\Omega)\, A_{-}(\Omega) \right|^2$$ **位相に依らず一定**

【2】 Dark Pulse

$$\theta_{+}(\Omega) = \theta_{-}(\Omega) = \alpha \cos(\beta\,\Omega)$$ **の場合**

$$S_{signal} \propto \left| \int d\Omega\ A_{+}(\Omega)\, A_{-}(\Omega) \exp[\,2i\alpha \cos(\beta\,\Omega)\,] \right|^2$$

$$; \ \left| \int d\Omega\ A_{+}(\Omega)\, A_{-}(\Omega)\, J_0(2\alpha) \right|^2$$

ゼロ次ベッセル関数のゼロ点でシグナルが弱まる

$(\alpha = 1.2,\ 2.8,\ 4.4, \mathrm{L}\ )$

2光子遷移の量子最適制御実験 (OCE)

Hornung et al., Appl. Phys. B 71 (2000)

Na原子 $3S \rightarrow 5S$ 2光子遷移

n番目のピクセルを通過する振動数成分の位相を制御

拘束条件： $\Theta(n) = \alpha \cos(\beta\,\Omega + \gamma)$ の下で $S_{signal}(\alpha, \beta\, \gamma)$ を最適化

各パラメータを2^7個に離散化し，最適化

⇒ Meshulach & Silberbergの解析から予想された最適解が求められた

遺伝的アルゴリズムを使った統計サーチ

遺伝アルゴリズム (GA)

収率 $Y = Y(x_1, x_2, \mathrm{L}\ , x_n)$

$\{x_1, x_2, \mathrm{L}\ , x_n\}$ パルス形を決めるパラメータ

【例題】 関数 $f(x)$ を最大にする $x \in [0, 1]$ を求める

例えば, 区間を $2^8 = 256$ 点に分割したとする

$$x_0 = 00000000$$

$$x_1 = 00000001$$

⋮

$$x_{255} = 11111111$$

$$x_k = (k-1)\Delta x;\ \Delta x = 1/256$$

各点を8ビット列に
対応させる

遺伝的アルゴリズムを使った統計サーチ

【step 1】 **個体数**を決める

$N\ (\leq 256)$ 個の点を（ランダムに）抽出する

【step 2】 **適合度**を求める

k 番目の個体の適合度は関数値 $f(x_k)$ で与えられる

【step 3】 **繁殖回数**の割り当て（適合度比例選択の場合）

（個体の繁殖回数の期待値）
＝（個体の適合度）÷（集団全体の適合度の平均値）

【step 4】 GA**操作**による新しい世代（子孫）集団の生成

遺伝的アルゴリズムを使った統計サーチ

GA操作の例

$x_k = 111|01110$　　$x_l = 001|10100$　　親

3・4番目のビット間で**交叉**

$x_m = 111|10100$　　$x_n = 001|01110$　　子

$x_{m'} = 10110100$　　$x_n = 00101110$　　子

2番目のビットで**突然変異**

最適制御理論

数値シミュレーション法の開発

文献

K. Nakagami, Y. Ohtsuki, and Y. Fujimura, *J. Chem. Phys*. **117**, 6429 (2002).

Y. Ohtsuki et al., *Chem. Phys*. **287**, 197 (2003).

Y. Ohtsuki, and H. Rabitz, *CRM Proceedings and Lectures*, **33**, 151 (2003).

Y. Ohtsuki, *J. Chem. Phys*. **119**, 661 (2003).

Y. Ohtsuki, G. Turinici, and H. Rabitz, *J. Chem. Phys.* submitted.

Optimal control method in wave function formalism

Schrödinger’s equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)> = [\, H_0 - \mu E(t) \,] |\psi(t)>$$

μ : electric dipole moment operator

$E(t)$: electric field (semiclassical approximation)

optimal control method

(1) Introducing a target operator W to specify a physical objective.

(2) Adding a penalty term due to pulse fluence in order to reduce pulse energy.

(3) Introducing a Lagrange multiplier density $\xi(t)$ that constrains the system to obey the equation of motion.

objective functional

unconstrained objective functional

$$\bar{J} = \langle \psi(t_f) | W | \psi(t_f) \rangle$$ ← (1) expectation value

$$- \int_0^{t_f} dt \frac{1}{\hbar A} [E(t)]^2$$ ← (2) penalty term

$$+ Re\left\{ \frac{i}{\hbar} \int_0^{t_f} dt \langle \xi(t) | \left(i\hbar \frac{\partial}{\partial t} - H^t \right) | \psi(t) \rangle \right\}$$

↑ (3) constraint due to the Schrödinger equation

$| \xi(t) \rangle$ Lagrange multiplier

coupled pulse design equations

optimal control pulse

$$E(t) = -2A\, Im < \xi(t)\, |\mu|\, \psi(t) >$$

A parameter that weighs the significance of penalty

the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\, \psi(t) > = [\, H_0 - \mu E(t)\,]\, |\, \psi(t) >$$

initial condition $|\, \psi(0) > = |\, \psi_0 >$

the equation for Lagrange multiplier

$$i\hbar \frac{\partial}{\partial t} |\, \xi(t) > = [\, H_0 - \mu E(t)\,]\, |\, \xi(t) >$$

final condition $|\, \xi(t_f) > = W\, |\, \psi(t_f) >$

density matrix formalism

Quantum Liouville equation

$$i\hbar \frac{\partial}{\partial t}\rho(t) = [\, H^{t}, \rho(t)\,] - i\hbar\,\Gamma\,\rho(t)$$

$$H^{t} = H_0 - \mu E(t)$$

$\rho(t)$ density matrix

$\Gamma\,\rho(t)$ relaxation term

unconstrained objective functional

$$\bar{J} = tr\{W\rho(t_f)\} - \frac{1}{\hbar A}\int_0^{t_f} dt\,[E(t)]^2$$

$$+ \int_0^{t_f} dt\; tr\{\Xi(t)\left(i\hbar\frac{\partial}{\partial t} - L_T^{t} \right)\rho(t)\}$$

⇒ pulse design equations

density matrix formalism

Double (Liouville)-space notation

Definition of inner product between operators A and B

$$\langle\langle A \,|\, B \rangle\rangle = tr(A^{\dagger} B)$$

$$i\hbar \frac{\partial}{\partial t} |\, \rho(t) \rangle\rangle = L^{t} \,|\, \rho(t) \rangle\rangle - i\hbar \Gamma \,|\, \rho(t) \rangle\rangle$$

unconstrained objective functional

$$\bar{J} = \langle\langle W \,|\, \rho(t_f) \rangle\rangle - \frac{1}{\hbar A} \int_0^{t_f} dt\, [E(t)]^2$$

$$+ \int_0^{t_f} dt \,\langle\langle \Xi(t) \,|\left(i\hbar \frac{\partial}{\partial t} - L_T^{t} \right)|\, \rho(t) \rangle\rangle$$

$|\, \Xi(t) \rangle\rangle$ Lagrange multiplier density

density matrix formalism

optimal control pulse

$$E(t) = \frac{i}{2} A << \Xi(t) \, | M | \, \rho(t) >> \qquad \text{with} \quad M \leftrightarrow [\mu, \quad]$$

A parameter weighing the significance of penalty

the Liouville equation

$$i\hbar \frac{\partial}{\partial t} | \rho(t) >> = L^t | \rho(t) >> - i\hbar \Gamma | \rho(t) >>$$

initial condition $| \rho(t=0) >> = | \rho_0 >>$

the equation of motion for the Lagrange multiplier

$$i\hbar \frac{\partial}{\partial t} | \Xi(t) >> = L^t | \Xi(t) >> + i\hbar \Gamma^\dagger | \Xi(t) >>$$

final condition $| \Xi(t_f) >> = | W >>$

generalized formalism

一般的な最適化問題

$$J = \sum_k \left| \langle X_k(t_f) \rangle - x_k \right|^2 \qquad : J_1$$

$$+ \sum_l \int_0^{t_f} dt \, \nu_l(t) \left| \langle R_l(t) \rangle - r_l(t) \right|^2 \qquad : J_2$$

$$+ \frac{1}{\hbar A} \int_0^{t_f} dt \, [E(t)]^2 \qquad : J_3$$

J_1 目的状態はターゲット演算子の組と目的の期待値とで表される

J_2 制御時間内における系の振る舞いを指定

J_3 電場エネルギーを低く抑えるためのペナルティ

generalized formalism

Double-Space Representation

inner product between operators A and B

$$<< A \mid B >> = tr(A^{\dagger} B)$$

$$J_1 = \sum_k \left| < X_k(t_f) > - x_k \right|^2$$

$$= \sum_k \left| << X_k^{\dagger} \mid \rho(t_f) >> - x_k << 1 \mid \rho(t_f) >> \right|^2$$

$$W_{\otimes} \leftrightarrow \sum_k \mid W_k >><< W_k \mid \quad (\mid W_k >> = \mid X_k^{\dagger} >> - \mid 1 >> x_k)$$

Quadruple-Space Representation

inner product between double-space operators $X_{\otimes}$ and $Y_{\otimes}$

$$<< X_{\otimes} \mid Y_{\otimes} >> = tr_{\otimes}(X_{\otimes}^{\dagger} Y_{\otimes})$$

$$J_1 = << W_{\otimes} \mid \rho_{\otimes}(t_f) >>$$

generalized formalism

$$Y_{\otimes}(t) \leftrightarrow \sum_{l} |Y_{l}(t)>> v_{l}(t) << Y_{l}(t)| \quad (\, |Y_{l}(t)>> = |R_{l}>> - |1>> r_{l}(t) \,)$$

$$J_2 = \int_0^{t_f} dt << Y_{\otimes}(t) | \rho_{\otimes}(t) >>$$

Objective functional in quadruple-space representation

$$J = << W_{\otimes} | \rho_{\otimes}(t_f) >> + \int_0^{t_f} dt << Y_{\otimes}(t) | \rho_{\otimes}(t) >>$$

$$+ \frac{1}{h A} \int_0^{t_f} dt [E(t)]^2$$

with a constraint of satisfying $i h \frac{\partial}{\partial t} | \rho_{\otimes}(t) >> = L_{\otimes}^{t} | \rho_{\otimes}(t) >>$

generalized formalism

運動方程式 (電場と1次の相互作用)

$$i\hbar \frac{\partial}{\partial t} | u(t) \rangle = [\, \alpha - \beta E(t) \,] | u(t) \rangle$$

タイプ I の標準形 (状態ベクトルで制御目的を指定)

$$J_I = 2\,\mathrm{Re} \langle X | u(t_f) \rangle + 2\,\mathrm{Re} \int_0^{t_f} dt \langle Y(t) | u(t) \rangle - \frac{1}{\hbar A} \int_0^{t_f} dt \,[E(t)]^2$$

タイプ II の標準形 (Hermite演算子で制御目的を指定)

$$J_{II} = \langle u(t_f) | X | u(t_f) \rangle + \int_0^{t_f} dt \langle u(t) | Y(t) | u(t) \rangle - \frac{1}{\hbar A} \int_0^{t_f} dt \,[E(t)]^2$$

generalized formalism

最適電場

$$E(t) = -A\,Im < \lambda(t)\,|\,\beta\,|\,u(t) >$$

運動方程式

$$i\hbar \frac{\partial}{\partial t}\,|\,u(t)> = [\,\alpha - \beta\,E(t)\,]\,|\,u(t)>$$

$$|\,u(t=0)> = |\,u_0>$$

ラグランジュ未定乗数の運動方程式

$$i\hbar \frac{\partial}{\partial t}\,|\,\lambda(t)> = [\,\alpha^{\dagger} - \beta^{\dagger}\,E(t)\,]\,|\,\lambda(t)> - i\hbar\,|\,Y(t)>$$

$$|\,\lambda(t_f)> = |\,X>$$

solution algorithm

ラグランジュ未定乗数の運動方程式

$$i\hbar \frac{\partial}{\partial t} |\lambda^{(k)}(t)\rangle = [\alpha^{\dagger} - \beta^{\dagger} \bar{E}^{(k)}(t)] |\lambda^{(k)}(t)\rangle - i\hbar |Y(t)\rangle \qquad |\lambda^{(k)}(t_f)\rangle = |X\rangle$$

$$\bar{E}^{(k)}(t) = -A\,Im \langle \lambda^{(k)}(t) | \beta | u^{(k-1)}(t) \rangle$$

運動方程式

$$i\hbar \frac{\partial}{\partial t} |u^{(k)}(t)\rangle = [\alpha - \beta E^{(k)}(t)] |u^{(k)}(t)\rangle \qquad |u^{(k)}(t=0)\rangle = |u_0\rangle$$

$$E^{(k)}(t) = -A\,Im \langle \lambda^{(k)}(t) | \beta | u^{(k)}(t) \rangle$$

solution algorithm

単調収束の証明

$$|\delta u^{(k,k-1)}(t)> = |u^{(k)}(t)> - |u^{(k-1)}(t)>$$

$$\delta J_I^{(k,k-1)} = J_I^{(k)} - J_I^{(k-1)}$$

$$= 2Re < X \,|\, \delta u^{(k,k-1)}(t_f) > + 2Re \int_0^{t_f} dt < Y(t) \,|\, \delta u^{(k,k-1)}(t) >$$

$$- \frac{1}{\hbar A} \int_0^{t_f} dt \{ [E^{(k)}(t)]^2 - [E^{(k-1)}(t)]^2 \}$$

補助関数の導入

$$P^{(k,k-1)}(t) = 2Re < \lambda^{(k)}(t) \,|\, \delta u^{(k,k-1)}(t) >$$

$$P^{(k,k-1)}(t_f) = 2Re < X \,|\, \delta u^{(k,k-1)}(t_f) >$$

$$P^{(k,k-1)}(0) = 0$$

solution algorithm

$$\frac{d}{dt} P^{(k,k-1)}(t) + 2Re < Y(t) | \delta u^{(k,k-1)}(t) >$$

$$= -\frac{2}{\hbar} Im < \lambda^{(k)}(t) | \beta | u^{(k)}(t) > [E^{(k)}(t) - \bar{E}^{(k)}(t)]$$

$$+ \frac{2}{\hbar} Im < \lambda^{(k)}(t) | \beta | u^{(k-1)}(t) > [E^{(k-1)}(t) - \bar{E}^{(k)}(t)]$$

評価関数は単調増加する

$$\delta J_I^{(k,k-1)} = \frac{1}{\hbar A} \int_0^{t_f} dt \{ [E^{(k)}(t) - \bar{E}^{(k)}(t)]^2 + [\bar{E}^{(k)}(t) - E^{(k-1)}(t)]^2 \} \geq 0$$

summary of this section

標準評価関数から導かれる量子最適制御方程式に対し，単調収束アルゴリズムの存在を証明

トラジェクトリ表示を使って，各アルゴリズムの大域的な収束の様子を解析し，効率を比較

- **高い精度の解探索はしばしばトラッピングされ，収束に要するステップ数が増加**
- **粗い解探索は計算は速いが精度に問題がある**

提案

収束速度 $\delta J_I^{(k,k-1)}$ をモニタ・外挿しながら計算を進める

トラッピングが検出されたら異なる収束パラメータで計算

散乱問題への適用を目指して

$$|\xi(t_f)\rangle = W|\psi(t_f)\rangle$$

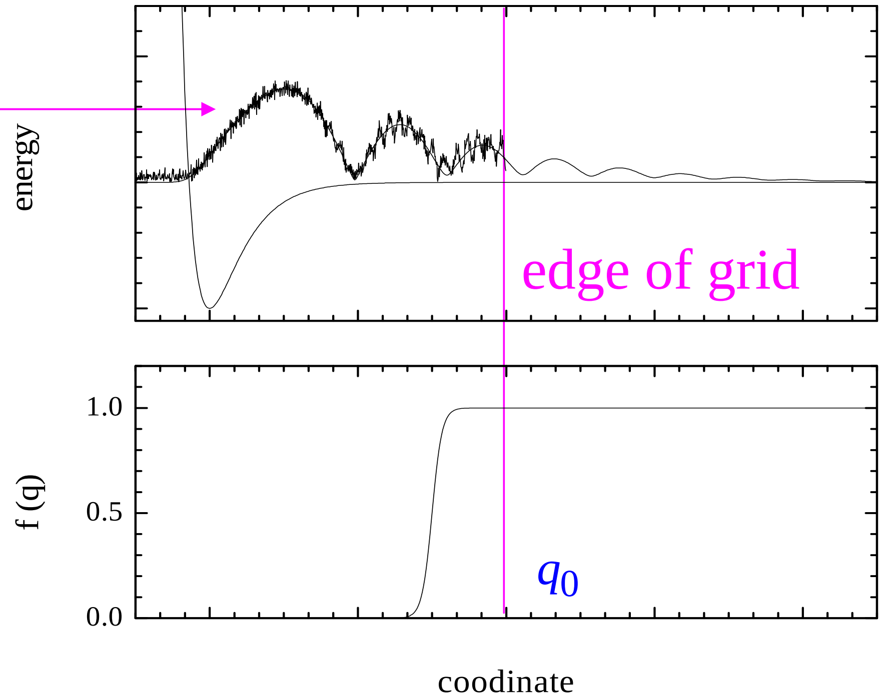
delocalized wave packet → store on memory

delocalized target operator → “truncated projector”

reflected packet

truncated projector

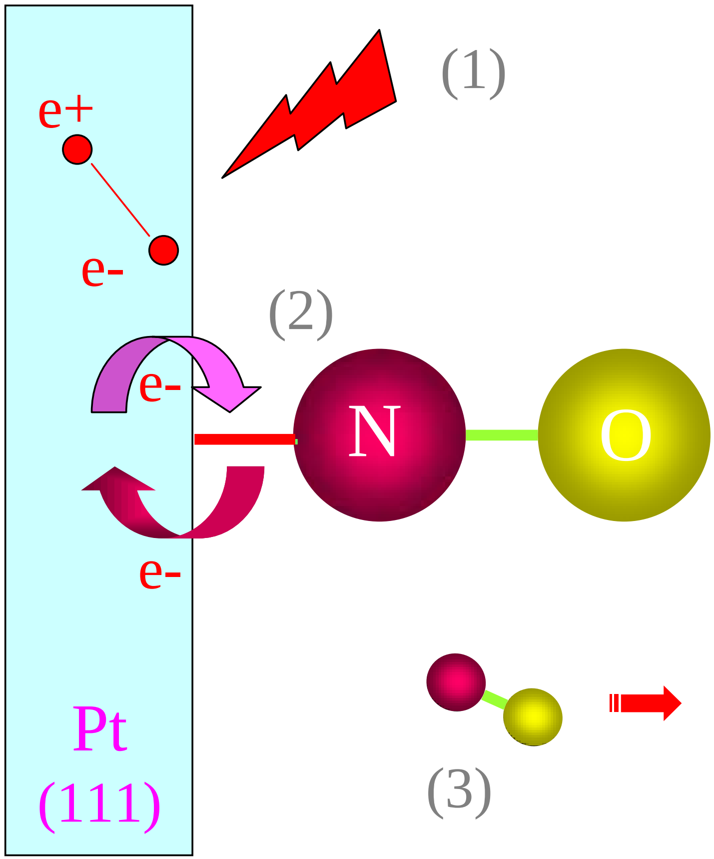
$$W = \int |q\rangle f(q)\, dq \langle q|$$



Hybrid Quantum Optimal Control: Application to Femtosecond Desorption Dynamics

K. Nakagami, Y. Ohtsuki, and Y. Fujimura, Chem. Phys. Lett. **360**, 91-98 (2002).

Laser-induced surface processes of concern here



DIMET of NO/Pt(111)

Desorption Induced by
Multiple Electronic
Transitions

(1)
An intense fs UV pulse generates hot-electrons.

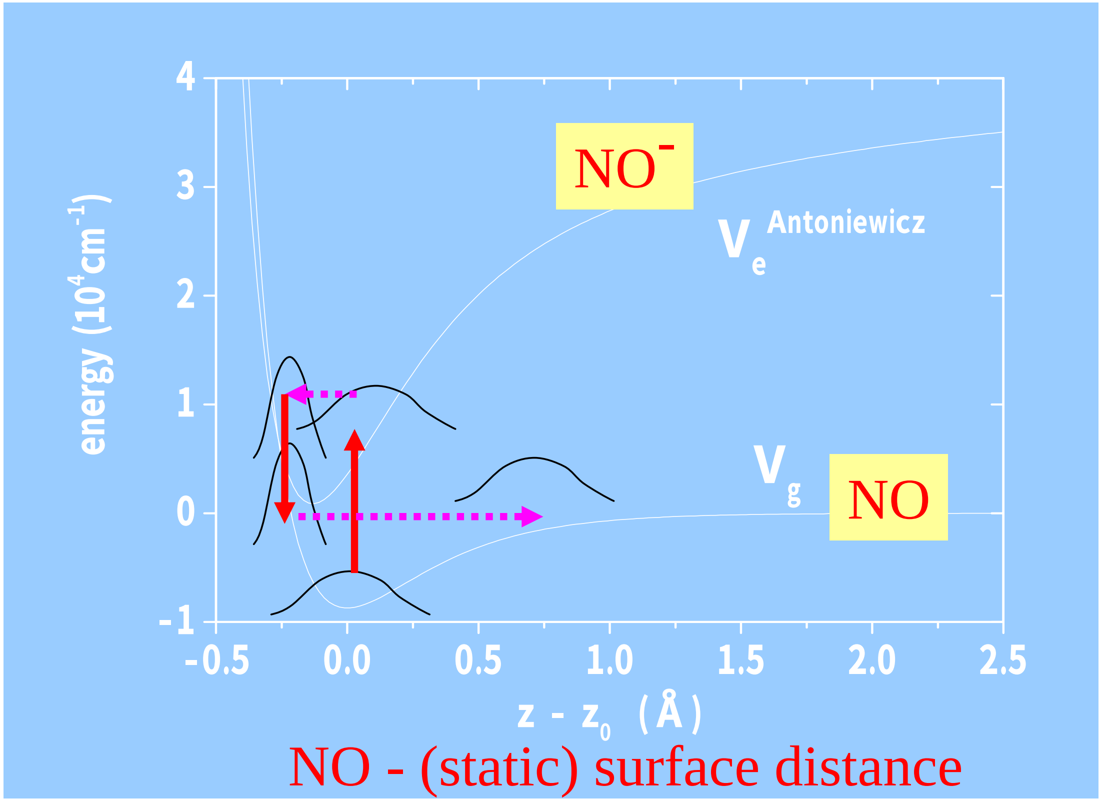
(2)
Multiple events of electron scattering+relaxation heat up the adsorption bond.

(3)
Some NO desorb (<1%).

NO/Pt(111) 1D model potential

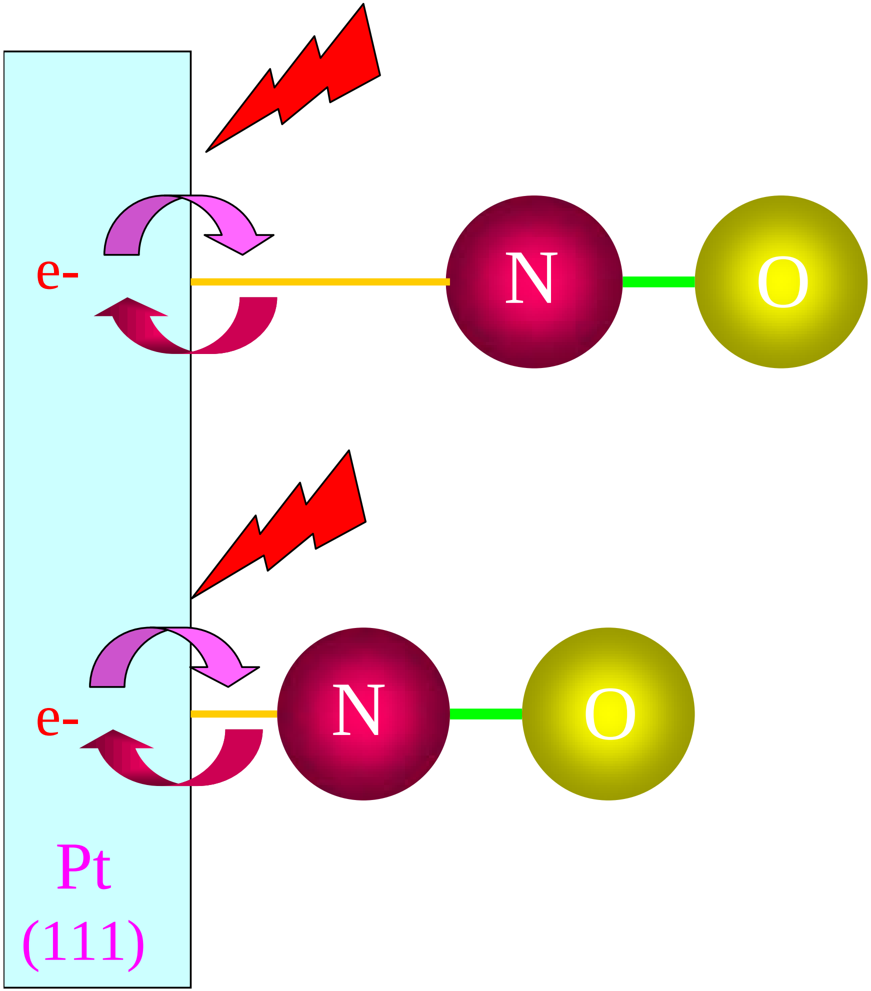
Antoniewicz model

(The ionic state sees an attractive image potential.)



Ref: Gadzuk, et al., Surf. Sci. (1990)

Our idea to control the desorption



Excitation by Hot Electrons
(incoherent process)

on the same time scale

Vibrational Wave Packet
(coherent process)

The incoherent excitation can CLOCK the packet motion
(initial geometry and/or
initial kinetic energy
of the adsorbed complex).

The question is
how to design the IR pulse
that creates the best packet.

Hybrid quantum control

Coherent Excitation

(to be designed)

+

Incoherent Excitation

(given external fields)

⇒ **Hybrid Control**

enhance or suppress the desorption
by optimally designed IR pulses

created by an optimal IR pulse

vibrational wave packet (coherent excitation)

hot electrons (incoherent excitation)

Can vibrational packet survive on a metal surface ?

K. Watanabe, N. Takagi, Y. Matsumoto,
Chem. Phys. Lett. 366, 606 (2002).

experimental observation of
coherent vibrational motion of
Cs/Pt(111)

dephasing time ~ 1.4 ps

Equations of motion for desorption dynamics

equation of motion

$$i\hbar \frac{\partial}{\partial t}\begin{bmatrix}\rho_e(t)\\ \rho_g(t)\end{bmatrix} = \begin{bmatrix} L_e & 0 \\ 0 & L_g \end{bmatrix}\begin{bmatrix}\rho_e(t)\\ \rho_g(t)\end{bmatrix} - \begin{bmatrix}\Gamma_{ee} & -\Gamma_{eg} \\ -\Gamma_{ge} & \Gamma_{gg}\end{bmatrix}\begin{bmatrix}\rho_e(t)\\ \rho_g(t)\end{bmatrix}$$

$\rho_e(t) = \langle e | \rho(t) | e \rangle$ density matrix in the state $|e\rangle$

$L_e \leftrightarrow [H_e, \quad]$ Liouvillian

Lindblad relaxation operator

$$\Gamma_{ee}\,\rho_e(t) = \frac{\gamma_e}{2}\rho_e(t) + \rho_e(t)\frac{\gamma_e}{2}$$

$$\Gamma_{gg}\,\rho_g(t) = \frac{\gamma_g(t)}{2}\rho_g(t) + \rho_g(t)\frac{\gamma_g(t)}{2}$$

$$\Gamma_{ge}\,\rho_e(t) = \sqrt{\gamma_e}\,\rho_e(t)\sqrt{\gamma_e}$$

$$\Gamma_{eg}\,\rho_g(t) = \sqrt{\gamma_g(t)}\,\rho_g(t)\sqrt{\gamma_g(t)}$$

Saalfrank & Kosloff, J. Chem. Phys. (1996)

Parameters

Control time

$$t \in [-1000\ fs, 300\ fs]$$

Relaxation parameters

lifetime $\frac{1}{\gamma_e} = 5\ fs$

detailed balance for transient electronic temperature

$$\gamma_g(t) = \gamma_g(z;t) = \frac{\gamma_e}{1 + \exp\left[-\frac{V_e(z) - V_g(z)}{k_B T_{el}(t)}\right]}$$

Parameters

Optimal Control
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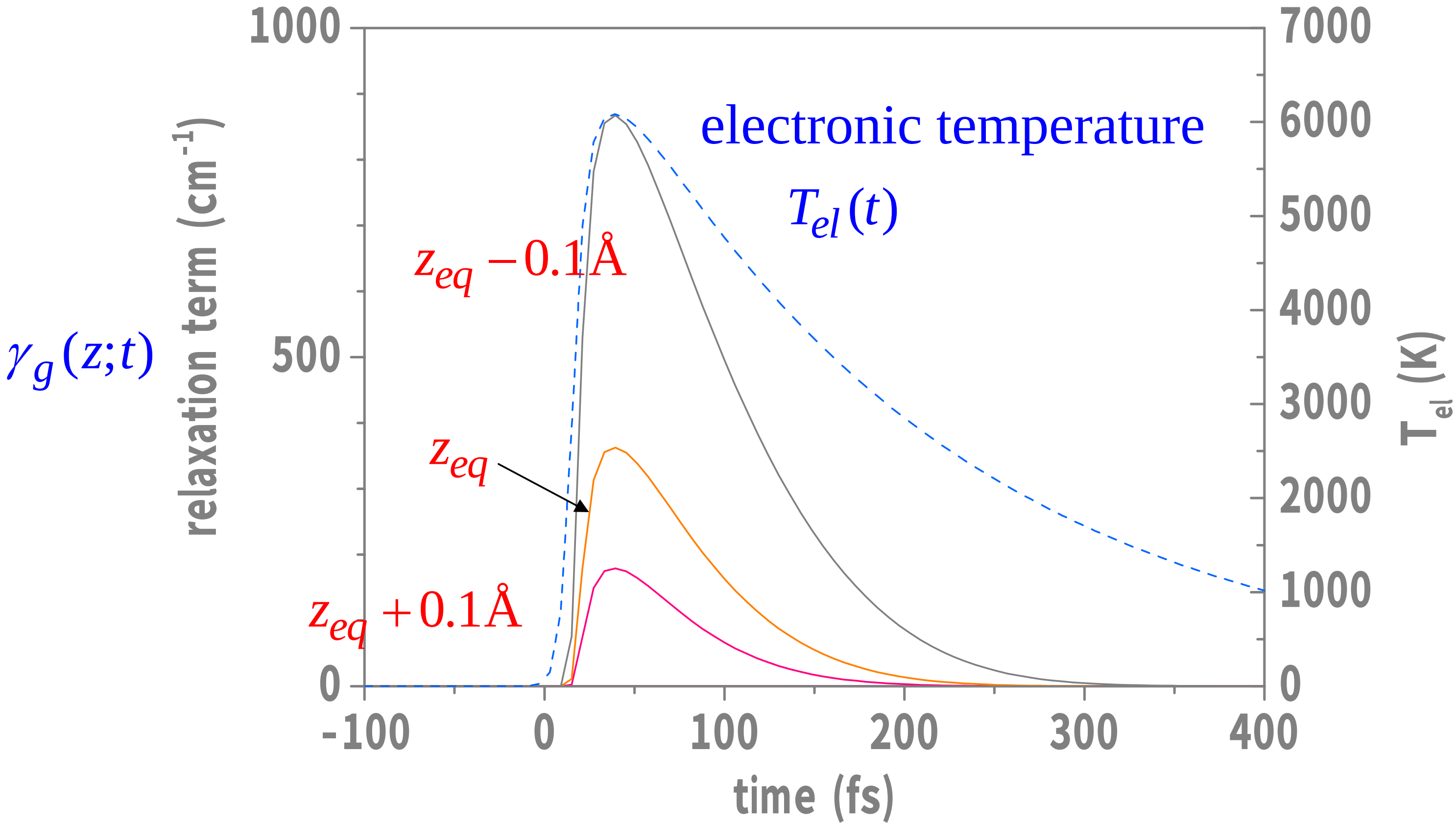
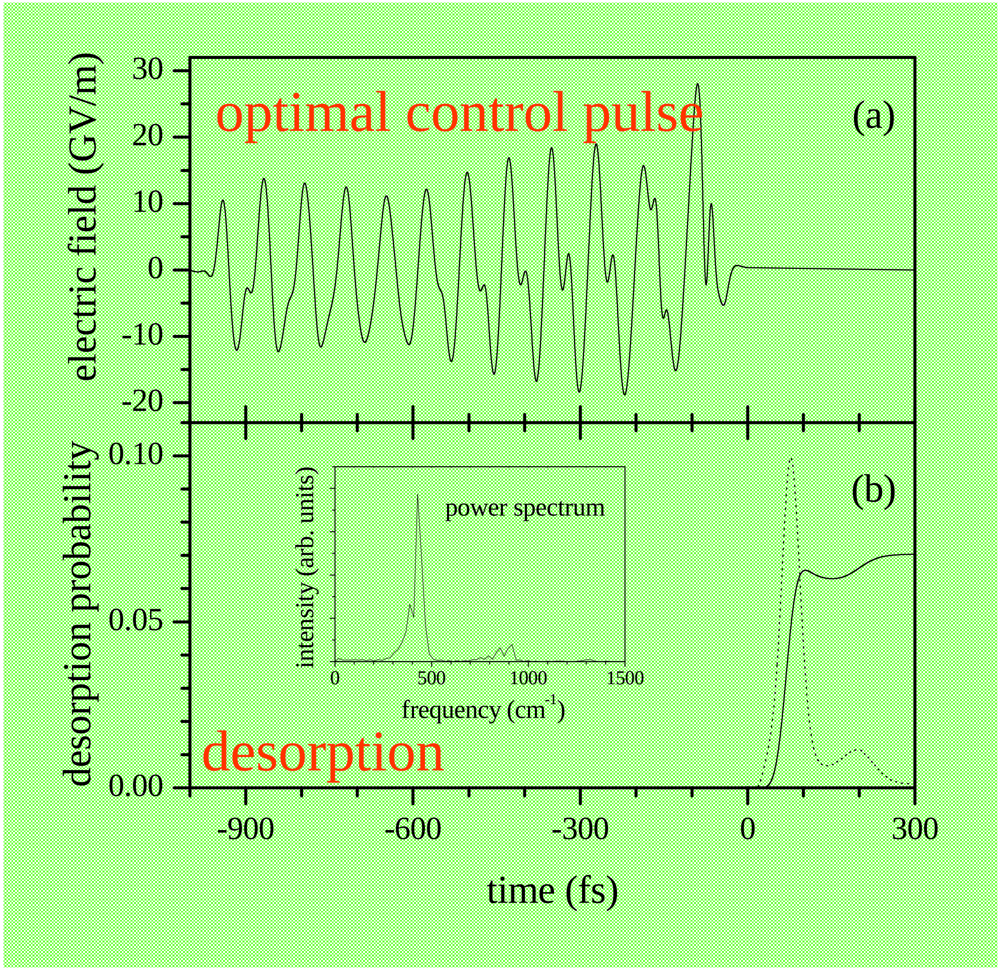
$$\gamma_g(t) = \gamma_g(z;t) = \frac{\gamma_e}{1 + \exp\left[-\dfrac{V_e(z) - V_g(z)}{k_B T_{el}(t)} \right]}$$



Results: optimal pulse enhancing the desorption



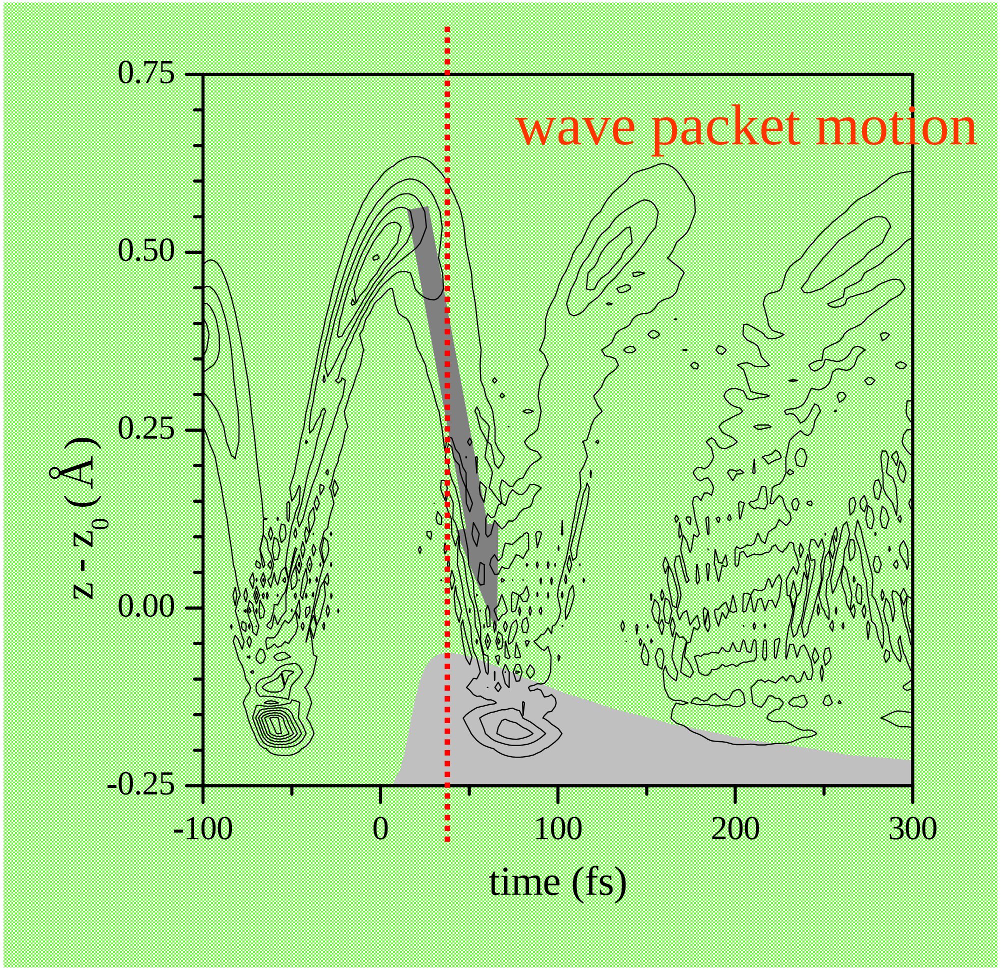
(a)
Optimal control pulse

(b)
Desorption probability
Population in
the excited-state

⇓

increase the desorption probability by
a factor of 8

Results: time evolution of the wave packet



The forces acting on the wave packet have the same direction on both potentials.

Wave packet has the largest inward momentum when transferred to the excited state.

Results: control mechanism

Optimal Control
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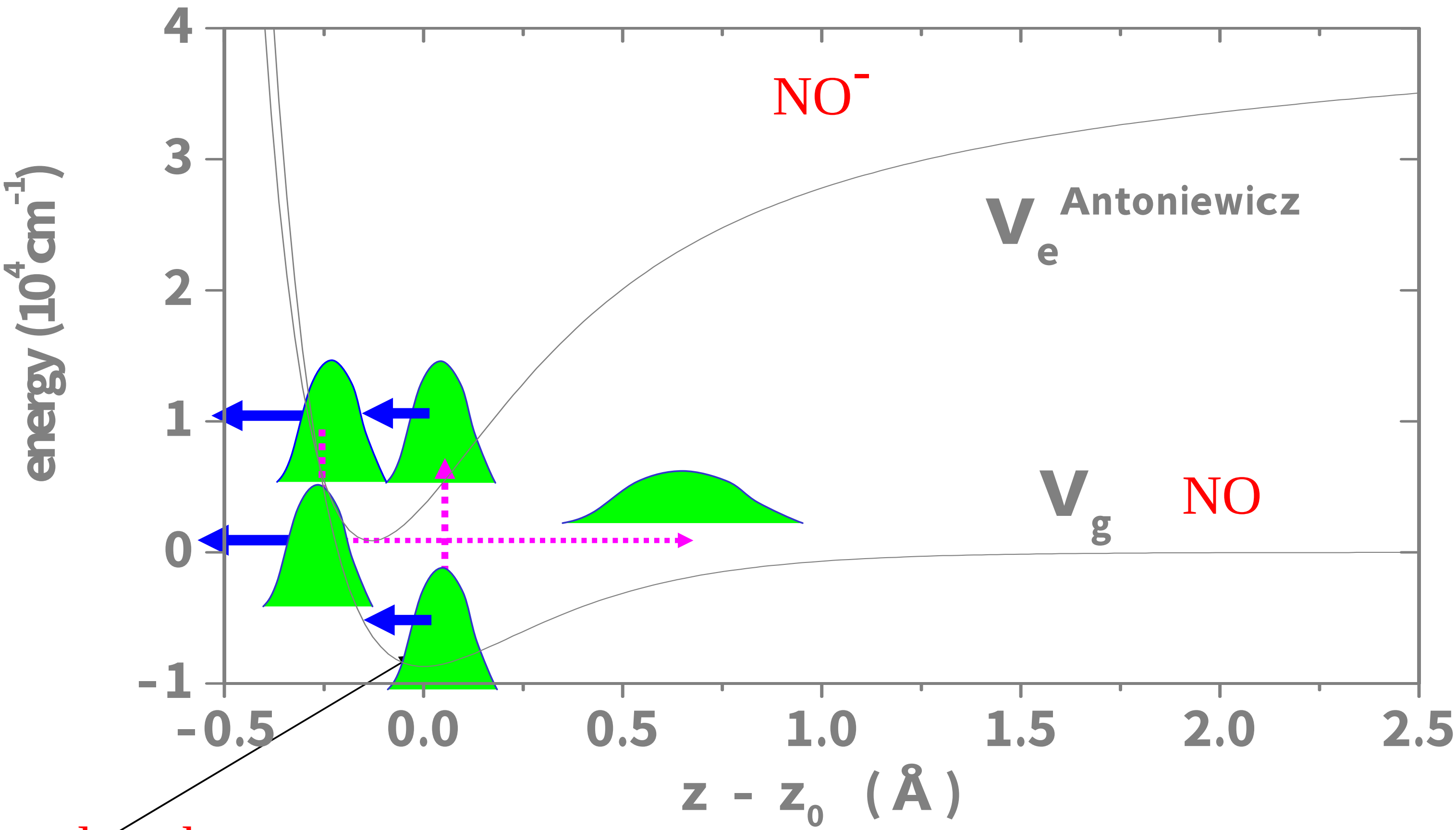
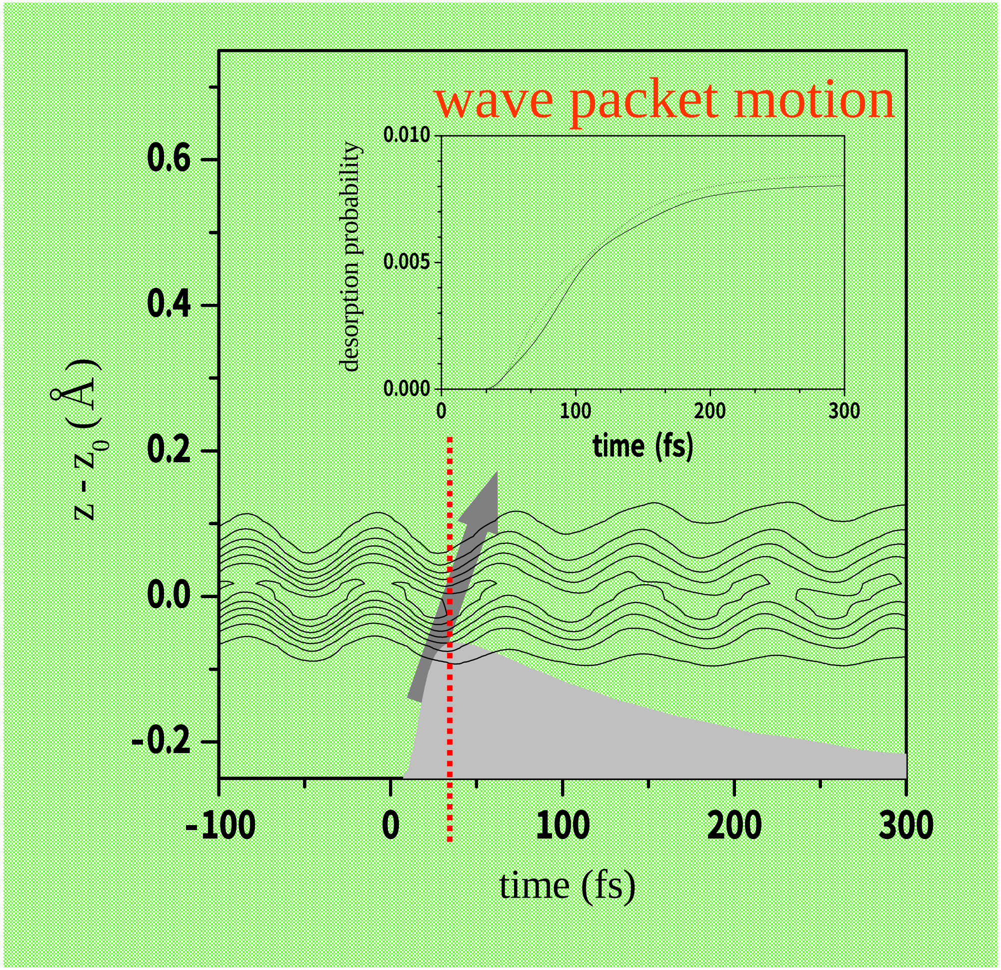


shaped packet

NO - (static) surface distance

Results: packet motion in the case of suppression



Wave packet has the outward momentum when transferred to the excited state.

⇓

The momentum acquired on the excited potential is cancelled by the initially prepared momentum.

Summary

A hybridized control scheme that combines coherent excitation processes with incoherent processes was proposed.

The desorption of NO from Pt(111) is enhanced or suppressed by controlling vibrational wave packet motion.
(“Suppression” means “avoiding surface damages”.)

最適制御理論の現状と展望

量子制御実験：最適制御実験の原理検証はほぼ完了

広範囲にわたって最適制御解が存在
制御効率も高い

量子制御理論：一つの方法は確立

量子制御機構に対する汎用性のある解析法は不明
→　新しいアプローチが必要？

デコヒーレンス抑制の問題は殆ど分かっていない

新しいターゲットへの適用？