Ultrafast electron dynamics as a route to explore chemical processes

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Les Houches, 2019

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The general solution is, therefore,

$$\Psi(\underline{x},t) = \Phi_E(\underline{x})e^{-\frac{i}{\hbar}Et}$$

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$$|\Psi(\underline{x},t)|^2 = |a|^2|\Phi_1(\underline{x})|^2 + |b|^2|\Phi_2(\underline{x})|^2 + 2Re\{a^*b\Phi_1^*(\underline{x})\Phi_2(\underline{x})e^{-\frac{i}{\hbar}(E_1-E_2)t}\}$$

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If we want to have non-trivial dynamics, we need to create a **wave packet**!

Def:

wave packet $\equiv$ coherent superposition of eigenstates

Time scales

Let us discuss what kind of eigenstates we have to deal with.

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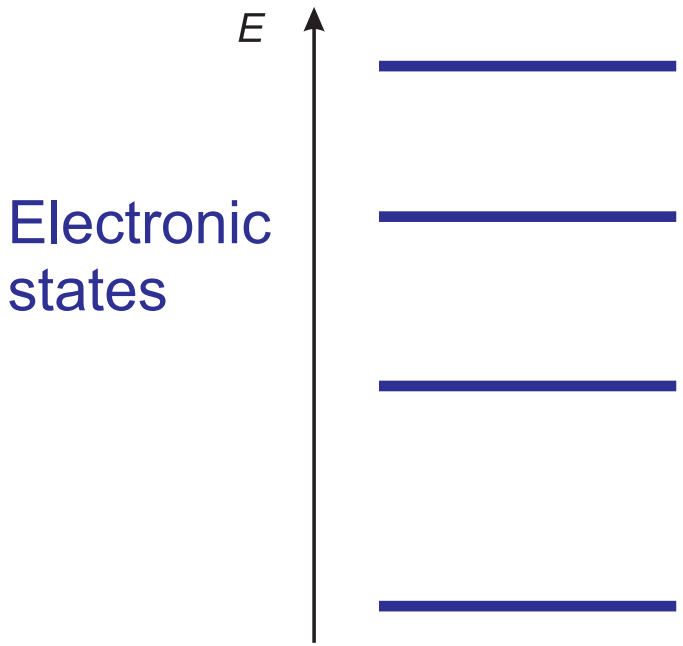

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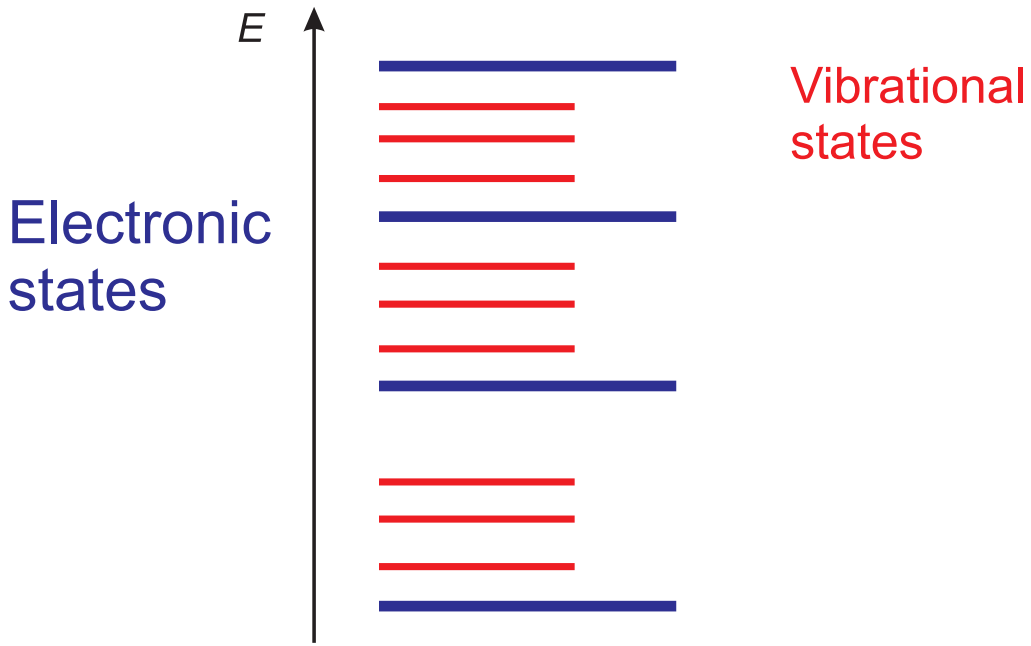

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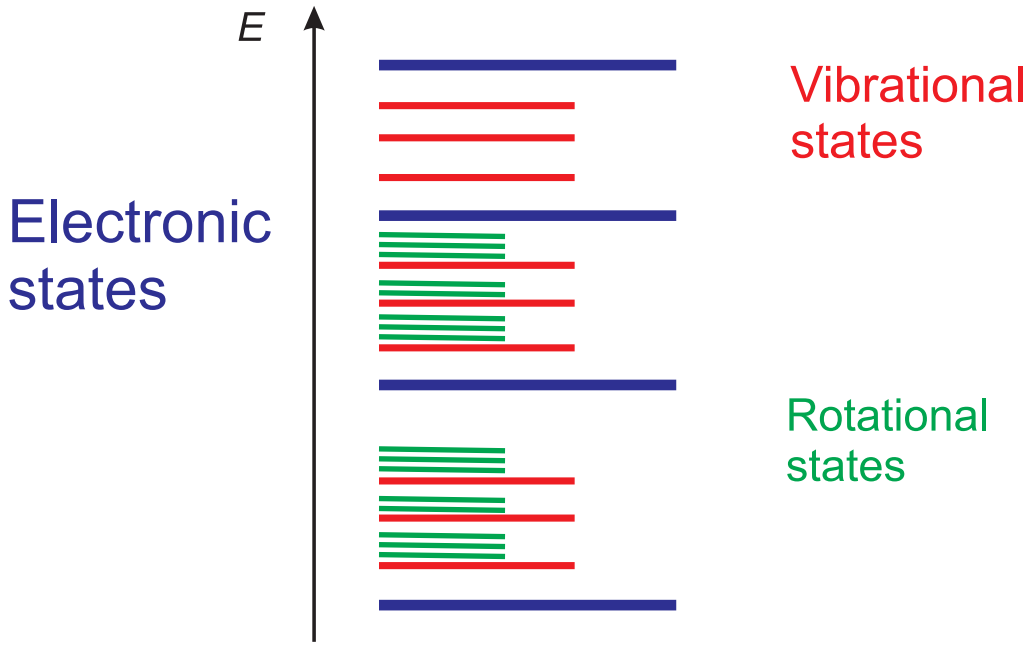

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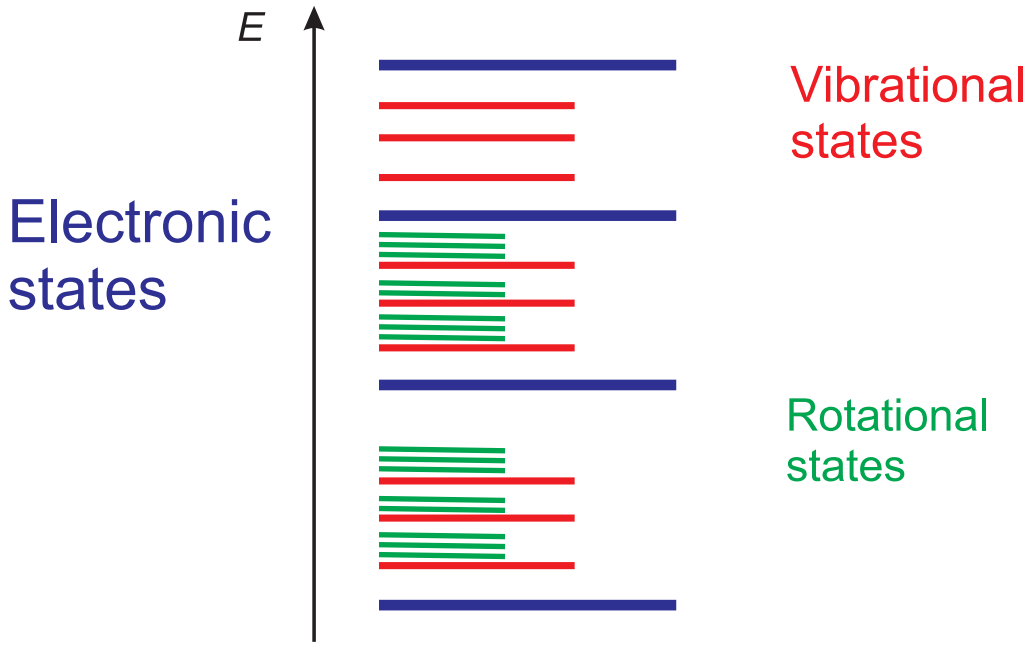

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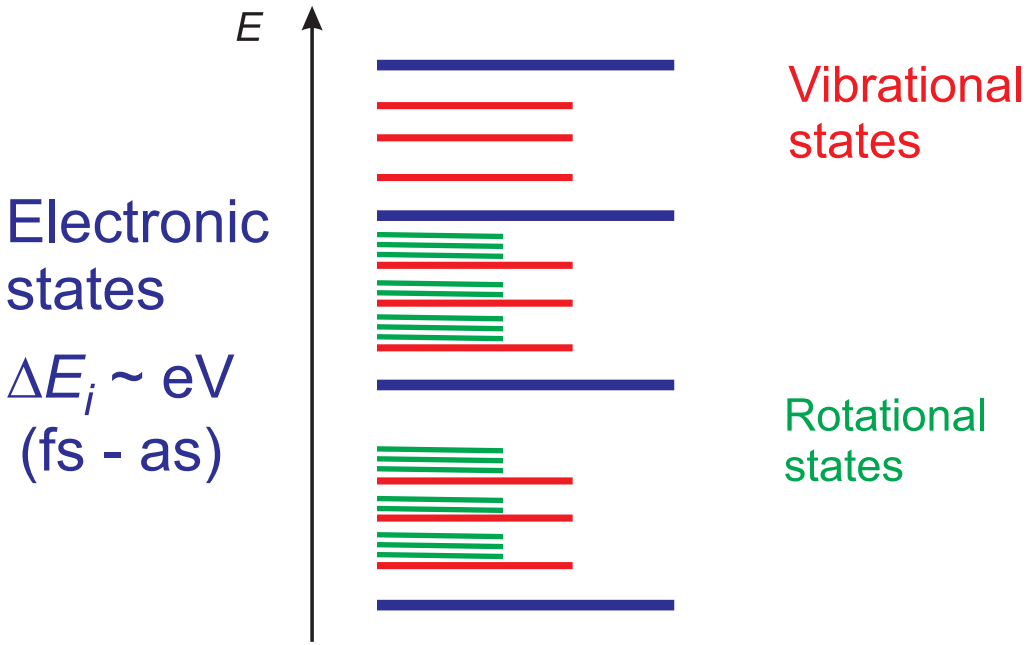

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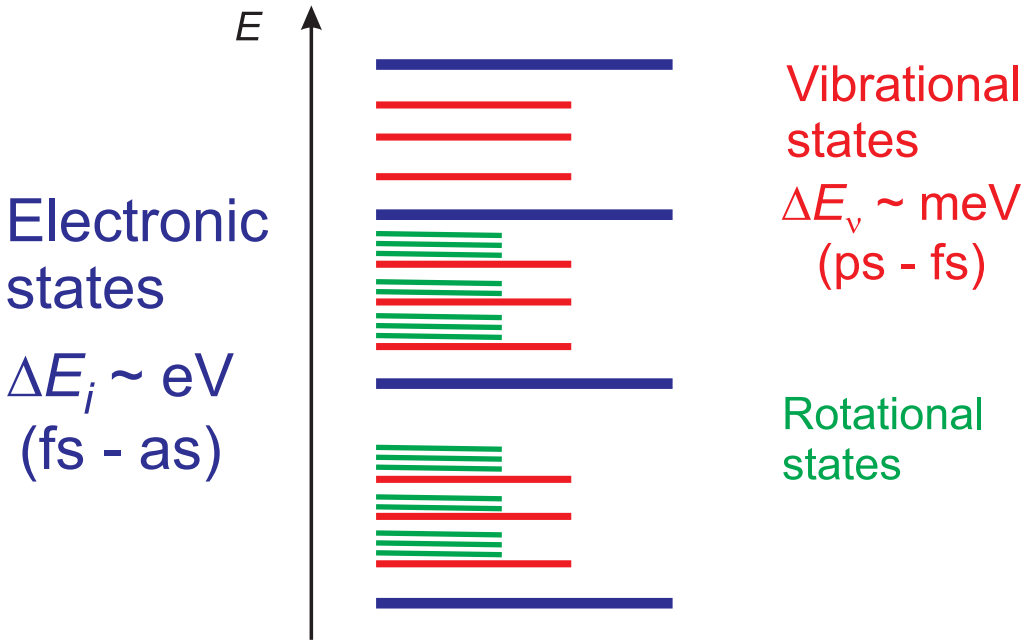

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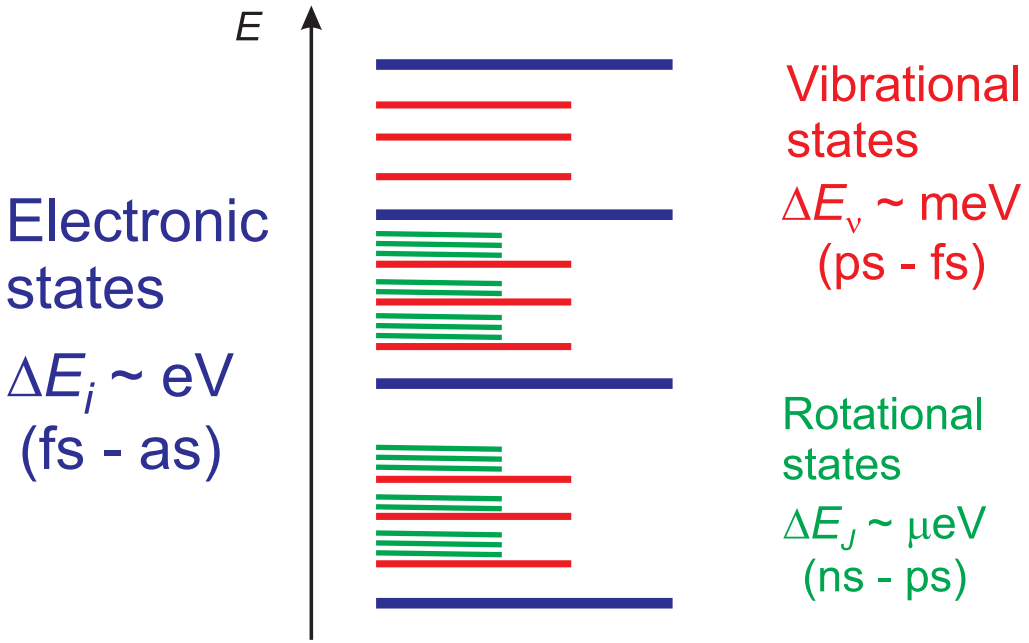

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Separation of electronic and nuclear motion

The eigenstates are solutions of the time-independent SE, describing how the electrons and the nuclei interact with each other.

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Even if we take only the Coulomb interaction between the particles, for N electrons and M nuclei we have (in atomic units)

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \quad + \quad \sum_{\alpha=1}^{M} -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$
$$+ \quad \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} + \sum_{i=1}^{M}\sum_{\alpha=1}^{M} -\frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|}$$

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Exact solution only for 2 particles! $\Rightarrow$ **We need approximations!**

Separation of electronic and nuclear motion

Born-Oppenheimer approximation (1927)

The motion of the nuclei and the electrons in a molecule can be separated:

$$\Psi(\underline{r},\underline{R}) = \Phi(\underline{r};\{\underline{R}\})\chi(\underline{R}),$$

where $\Phi(\underline{r};\{\underline{R}\})$ satisfies

$$\hat{H}_e\Phi(\underline{r};\{\underline{R}\}) = E(\underline{R})\Phi(\underline{r};\{\underline{R}\}) \qquad \text{with} \qquad \hat{H}_e = \hat{T}_e + V_{ee} + V_{en}$$

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- BO is an approximation and can breakdown severely!

The electronic problem

Nuclei are fixed and we consider only the electronic problem

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Hartree-Fock approximation (1927-30)

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Orbital

- The wave function of a single particle (electron) $\varphi_i(\vec{r})$
- Very important conceptually, but still a theoretical construct!

Describing correlated electrons

The simplest wave function to describe the N-electron ground state is the Slater determinant:

$$|\Psi_0\rangle \equiv \Psi_0(\vec{r}_1, ..., \vec{r}_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{r}_1) & \cdots & \varphi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \varphi_1(\vec{r}_N) & \cdots & \varphi_N(\vec{r}_N) \end{vmatrix} \equiv |\Phi_0\rangle$$

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Configuration interaction (CI)

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a|\Phi_i^a\rangle + \sum_{i<j,a<b} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \cdots$$

where $|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i|\Phi_0\rangle$ with $\hat{a}_p^\dagger$, $\hat{a}_q$ being creation and destruction operators, respectively.

Ionization of a molecule

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One can show that due to the electron correlation, if the electron is removed from a molecular orbital, one nearly inevitably triggers pure electron dynamics.
This problem was studied in

L.S. Cederbaum and J. Zobeley, Chem. Phys. Lett. **307**, 205 (1999)

showing that the created hole may migrate throughout the system.
The process was termed **charge migration**

Describing charge migration

Density of the initially created hole (hole density):

$$Q(\vec{r},t) := \langle\Psi_0|\hat{\rho}(\vec{r},t)|\Psi_0\rangle - \langle\Phi_i|\hat{\rho}(\vec{r},t)|\Phi_i\rangle = \rho_0(\vec{r}) - \rho_i(\vec{r},t)$$

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Representation in a one-particle basis:

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Representation in a one-particle basis:

$$Q(\vec{r},t) = \sum_{pq} \varphi_p^*(\vec{r})\varphi_q(\vec{r})N_{pq}(t),$$

Diagonalization of the matrix $\mathbf{N}(t)$ leads to

$$\boxed{Q(\vec{r},t) = \sum_p |\tilde{\varphi}_p(\vec{r},t)|^2 \tilde{n}_p(t)}$$

$\tilde{\varphi}_p(\vec{r},t)$ – *natural charge orbitals* $\tilde{n}_p(t)$ – *hole occupation numbers*

J. Breidbach and L. S. Cederbaum, JCP **118**, 3983 (2003).

A. I. Kuleff, J. Breidbach, and L. S. Cederbaum, JCP **123**, 044111 (2005).

Mechanisms of charge migration

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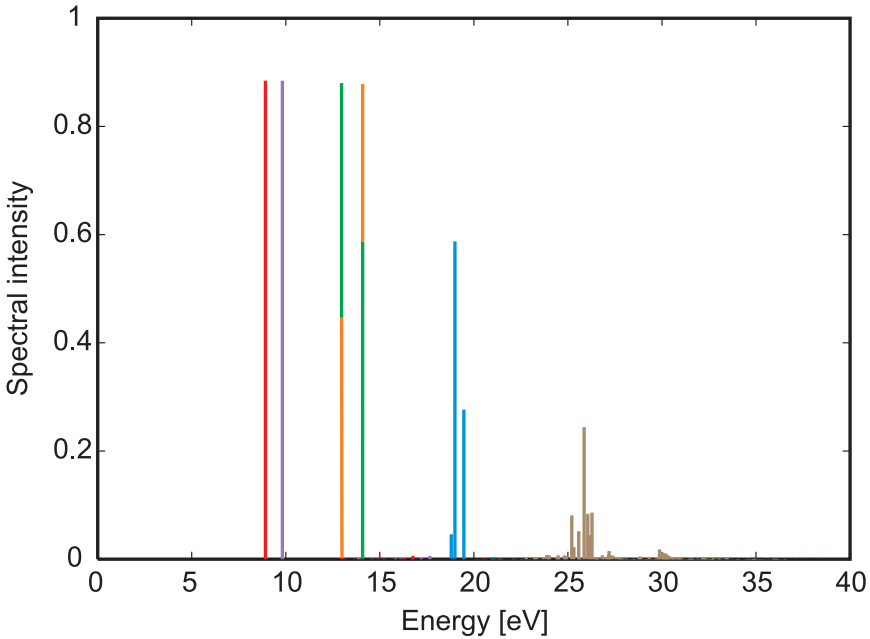

$$|x_I|^2 = |\langle I|\Phi_i\rangle|^2 \quad \leftarrow \text{spectral intensity}$$

where $|\Phi_i\rangle = \hat{a}_i|\Phi_0\rangle$

$$E_I \quad \leftarrow \text{ionization energy (IP)}$$

$$|I\rangle = \sum_j c_j^{(I)} \hat{a}_j|\Phi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} \hat{a}_a^\dagger \hat{a}_k \hat{a}_l|\Phi_0\rangle + \cdots \quad \leftarrow \text{cationic eigenstate}$$

For details: A. I. Kuleff and L. S. Cederbaum, J. Phys. B **47**, 124002 (2014)

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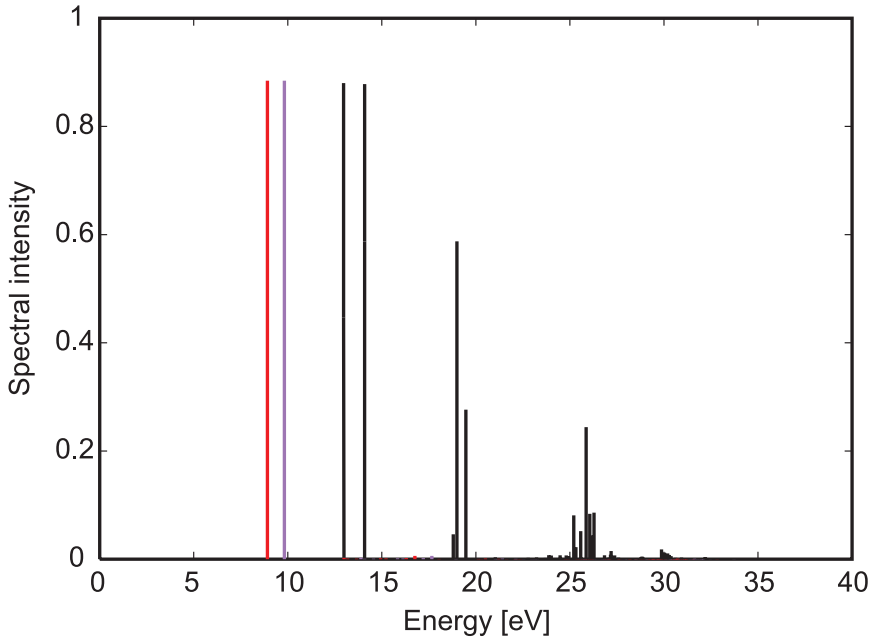

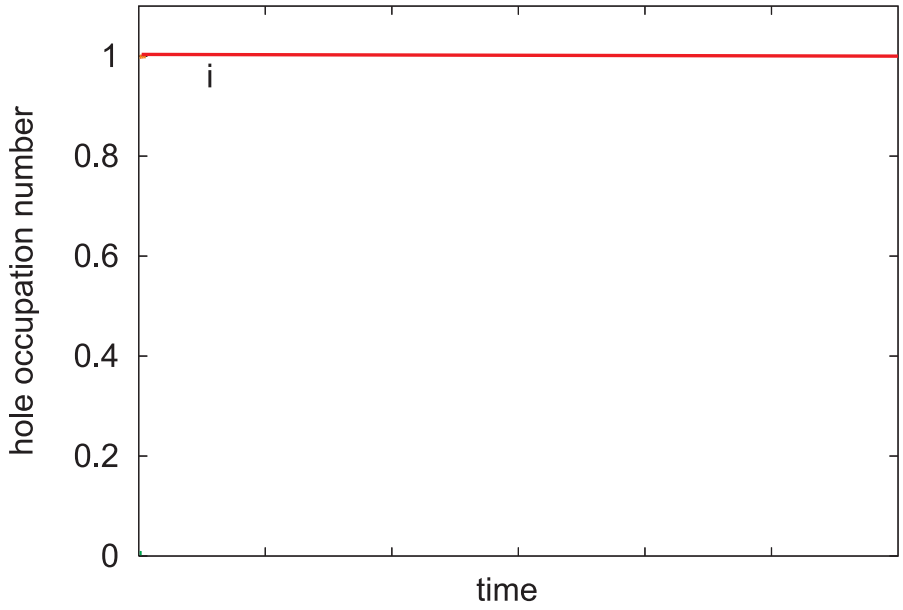

$$|I\rangle \approx \hat{a}_j|\Phi_0\rangle$$

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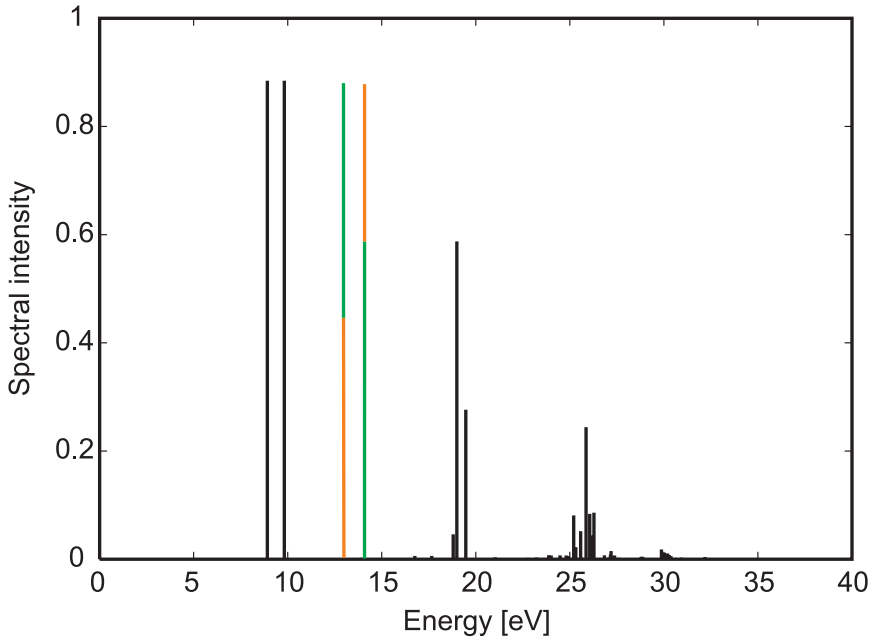

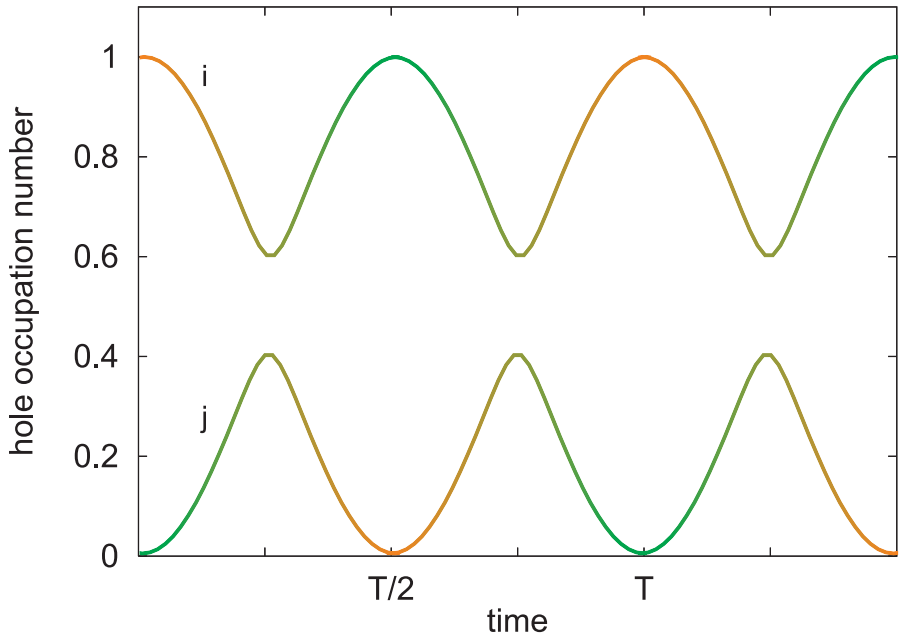

$$|I\rangle \approx c_i^{(I)} \hat{a}_i |\Phi_0\rangle + c_j^{(I)} \hat{a}_j |\Phi_0\rangle$$

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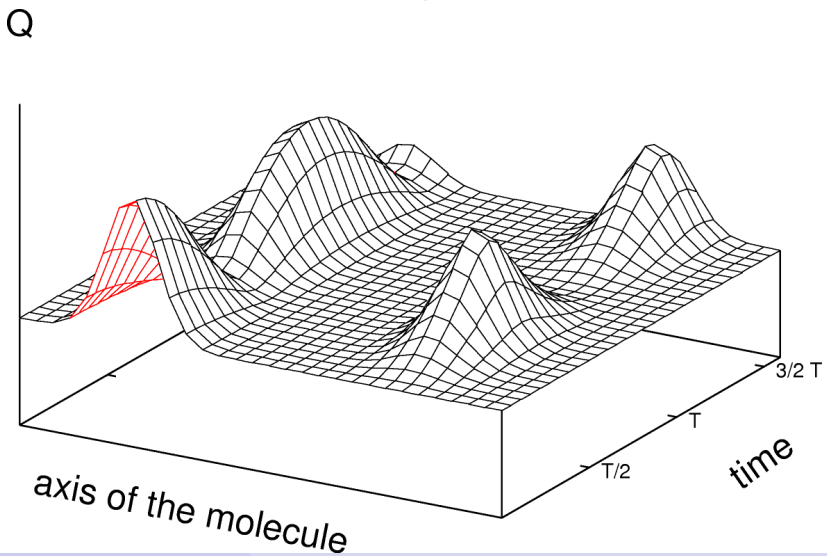

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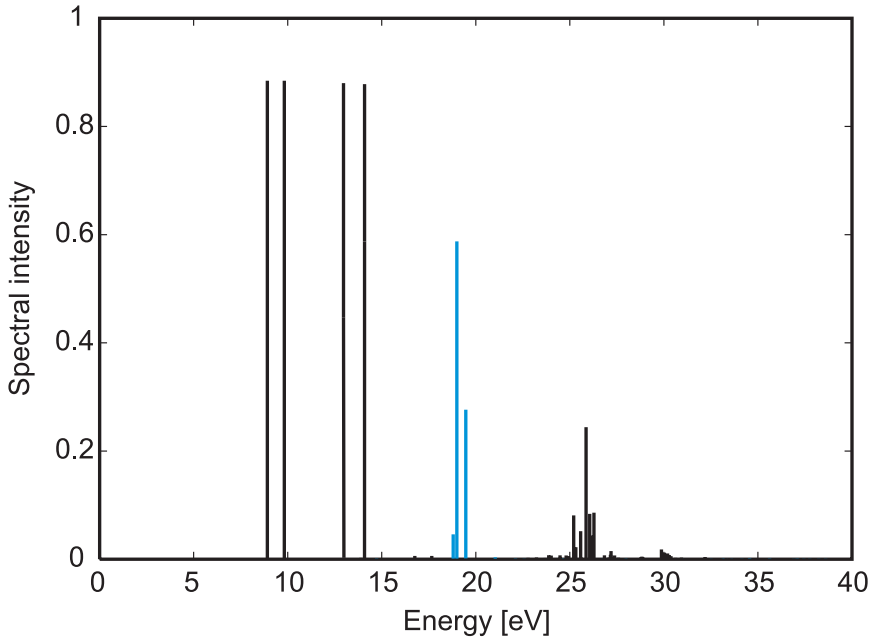

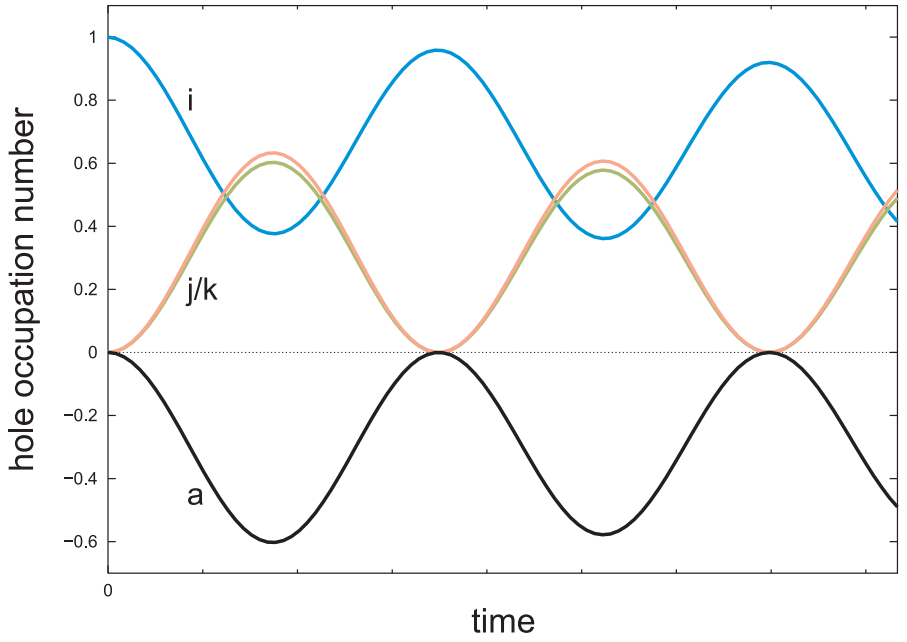

$$|I\rangle \approx c_i^{(I)} \hat{a}_i |\Phi_0\rangle + c_{ajk}^{(I)} \hat{a}_a^\dagger \hat{a}_j \hat{a}_k |\Phi_0\rangle$$

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Correlation satellite

j and $k \neq i$

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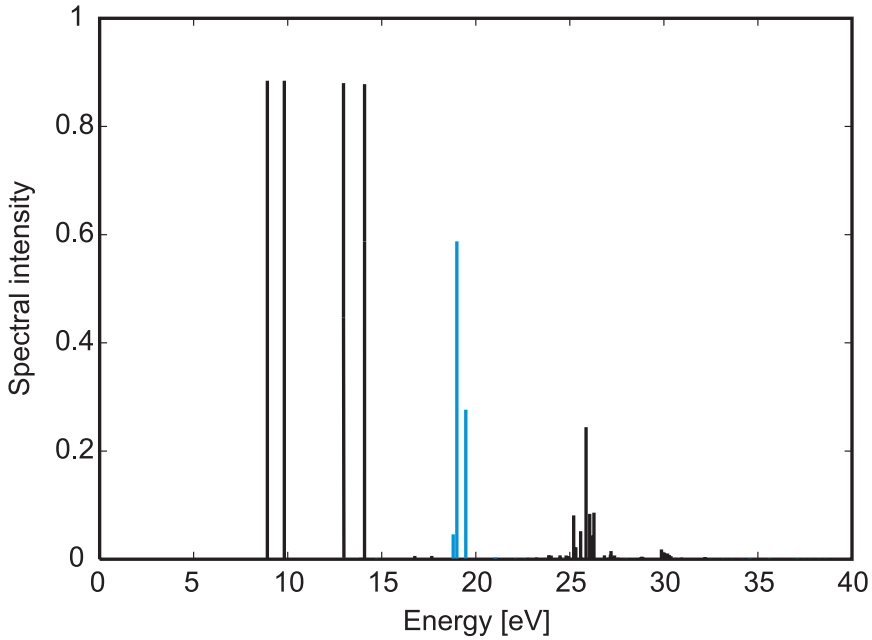
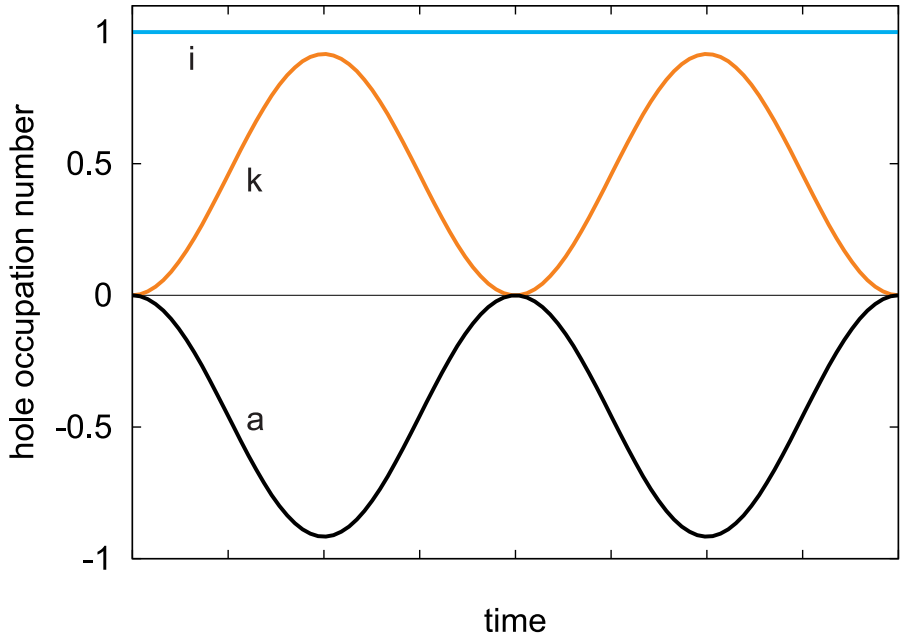




$$|I\rangle \approx c_i^{(I)} \hat{a}_i |\Phi_0\rangle + c_{ajk}^{(I)} \hat{a}_a^\dagger \hat{a}_j \hat{a}_k |\Phi_0\rangle$$

$$|J\rangle \approx c_i^{(J)} \hat{a}_i |\Phi_0\rangle + c_{ajk}^{(J)} \hat{a}_a^\dagger \hat{a}_j \hat{a}_k |\Phi_0\rangle$$

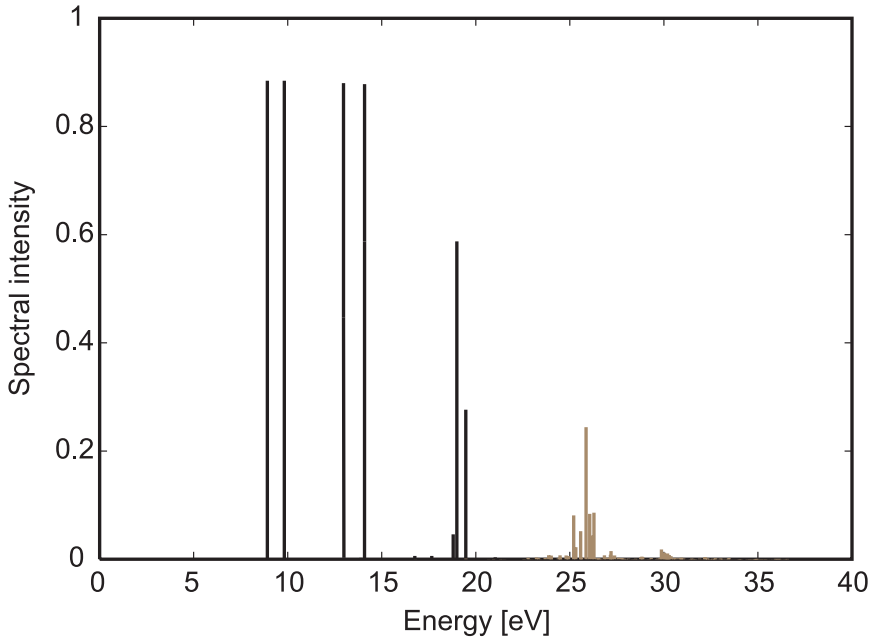
Relaxation satellite

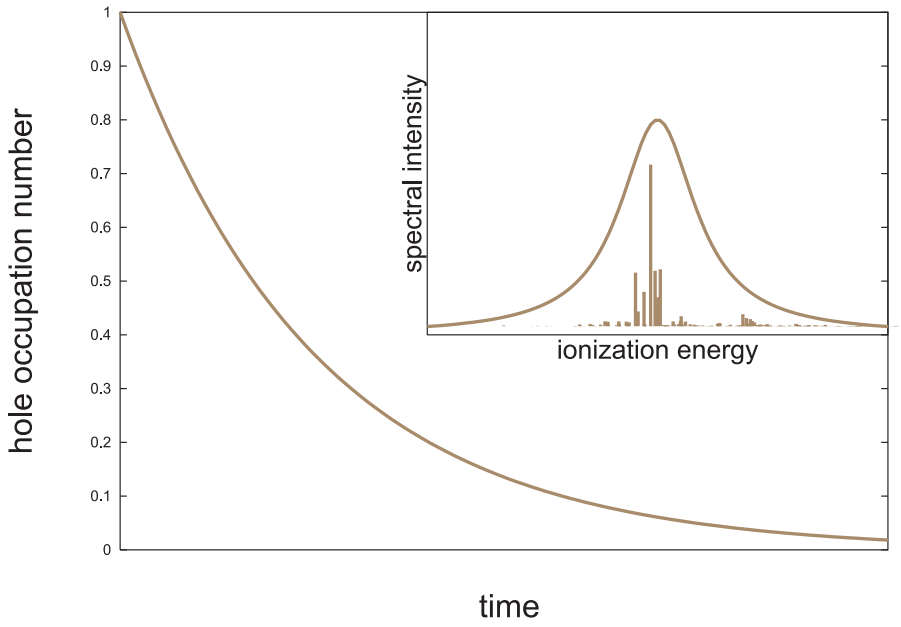
j or $k = i$

For details: A. I. Kuleff and L. S. Cederbaum, J. Phys. B **47**, 124002 (2014)

Mechanisms of charge migration

L.S. Cederbaum and J. Zobeley, Chem. Phys. Lett. **307**, 205 (1999)



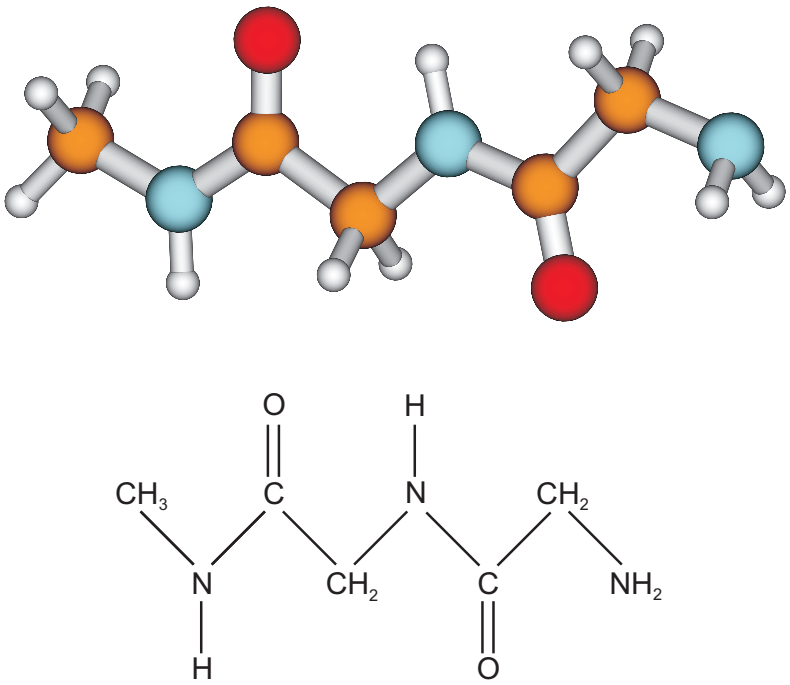


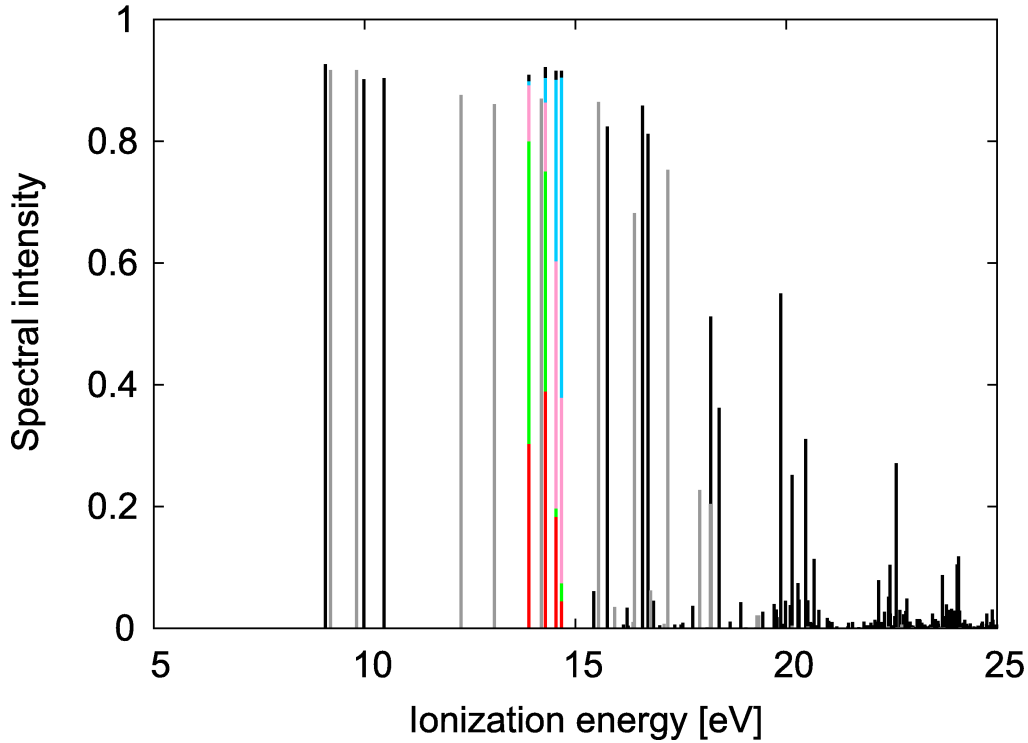
$$|I\rangle = c_j^{(I)} \hat{a}_j |\Phi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} \hat{a}_a^\dagger \hat{a}_k \hat{a}_l |\Phi_0\rangle$$

$$\vdots$$

For details: A. I. Kuleff and L. S. Cederbaum, J. Phys. B **47**, 124002 (2014)

Examples: Inner-valence hole mixing

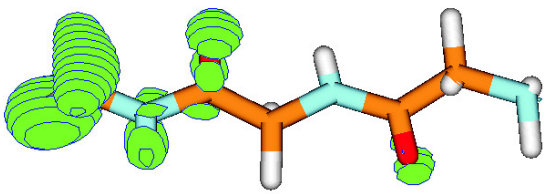




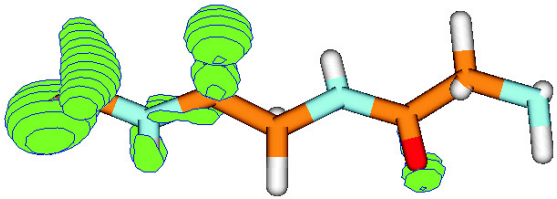
$$|I\rangle = \sum_j c_j^{(I)} \hat{a}_j |\Phi_0\rangle + \sum_{a,k<l} c_{akl}^{(I)} \hat{a}_a^\dagger \hat{a}_k \hat{a}_l |\Phi_0\rangle + \cdots ,$$

Hole mixing: $|I_{jk}\rangle \approx a|\Phi_j\rangle + b|\Phi_k\rangle, \quad |I_{kj}\rangle \approx b|\Phi_j\rangle - a|\Phi_k\rangle; \quad a^2 + b^2 \approx 1$

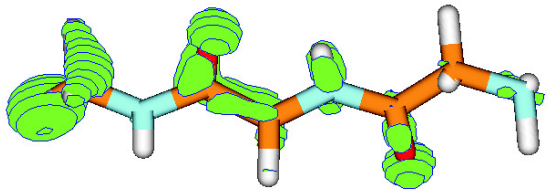
Examples: Inner-valence hole mixing



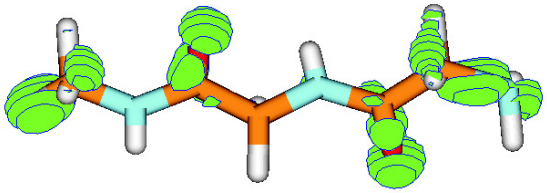
t = 0



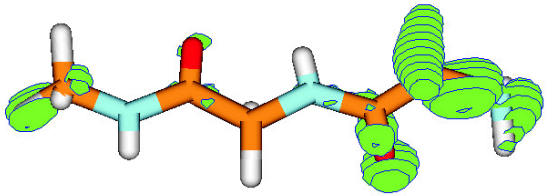
t = 1 fs



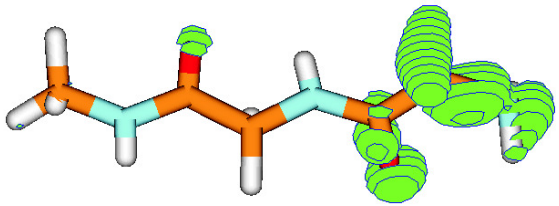
t = 2 fs



t = 4 fs



t = 5 fs

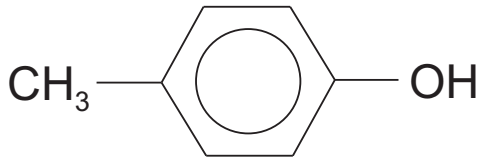


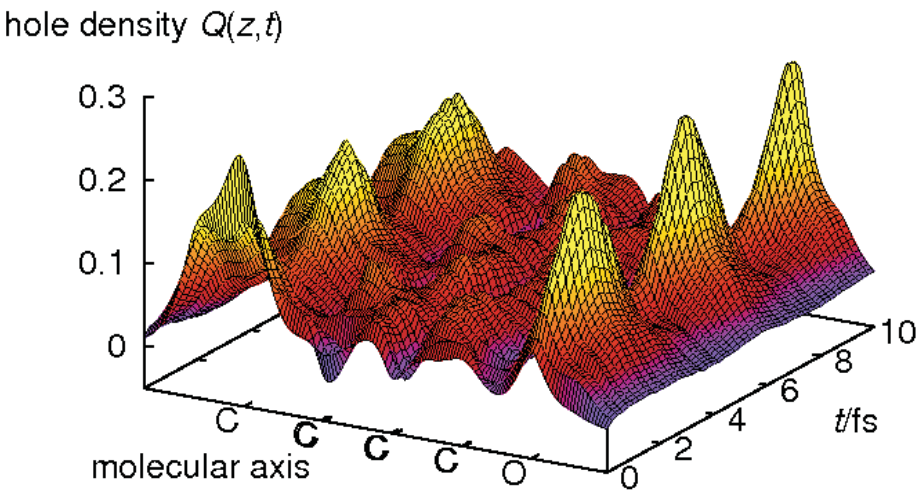
t = 6 fs

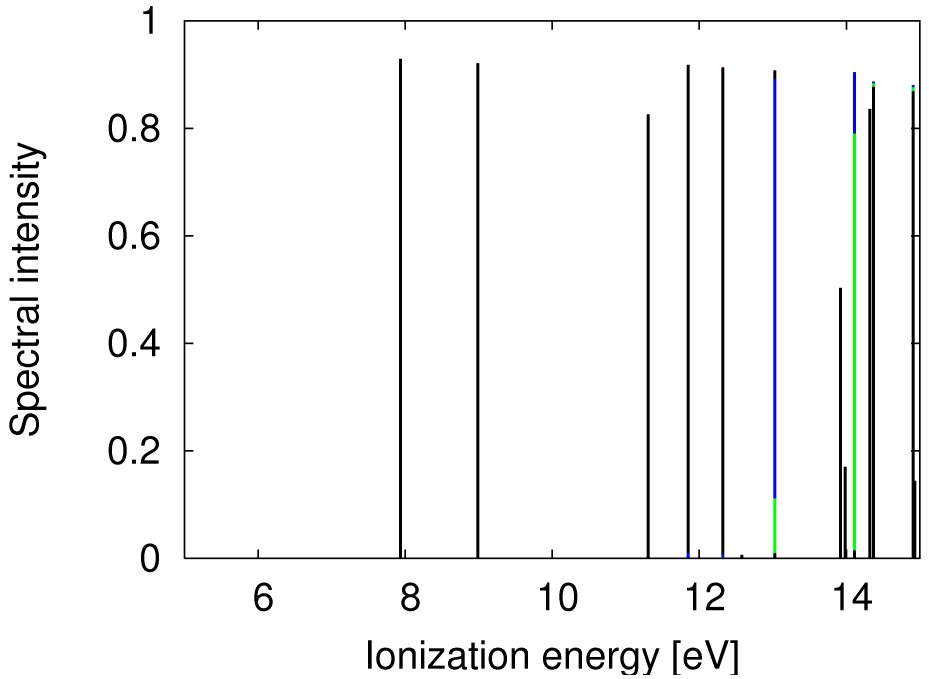
A. I. Kuleff, S. Lünnemann, and L. S Cederbaum, Chem. Phys. **414**, 100 (2013).

Examples: Inner-valence hole mixing

4-methylphenol



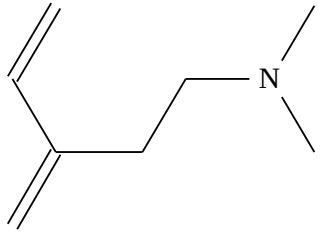


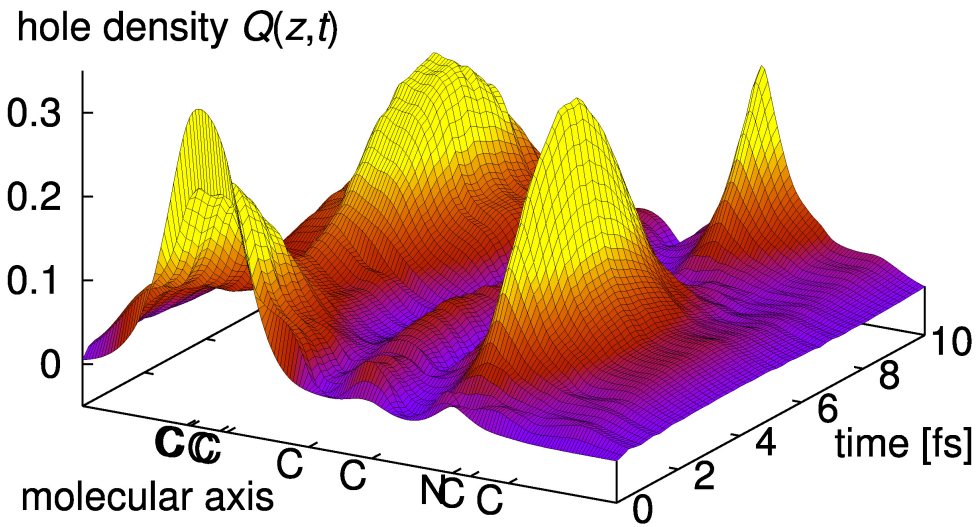


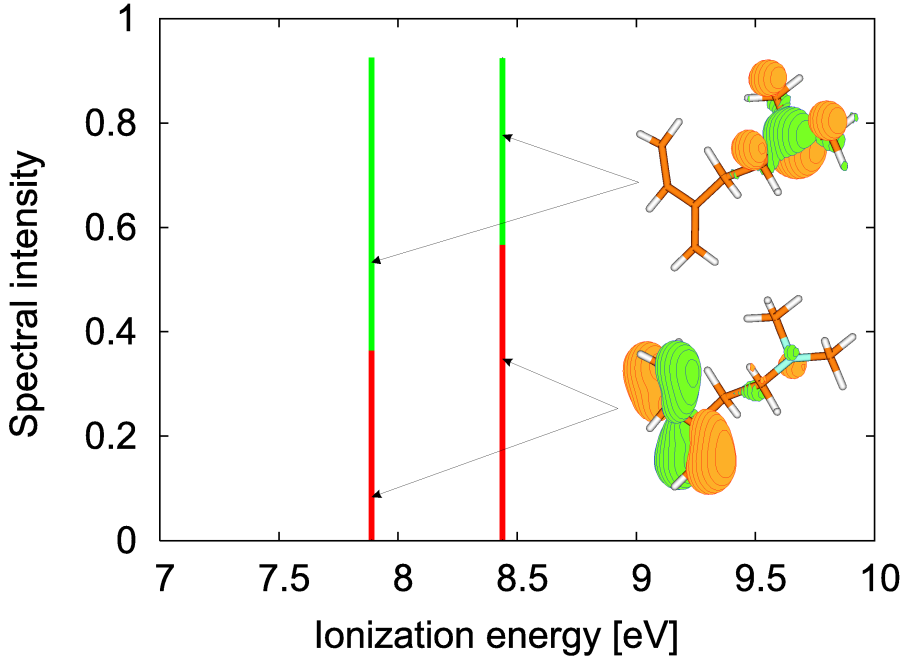
A. I. Kuleff, S. Lünnemann, and L. S Cederbaum, J. Phys. Chem. A **114**, 8676 (2010).

Examples: Outer-valence hole mixing

3-methylen-4-penten-*N*,*N*-dimethylamine (MePeNNA)







S. Lünnemann, A. I. Kuleff, and L. S. Cederbaum, J. Chem. Phys. **129**, 104305 (2008).

A. I. Kuleff and L. S. Cederbaum, Phys. Rev. Lett. **106**, 053001 (2011).

N. V. Golubev and A. I. Kuleff, Phys. Rev. A **91** 051401(R) (2015).

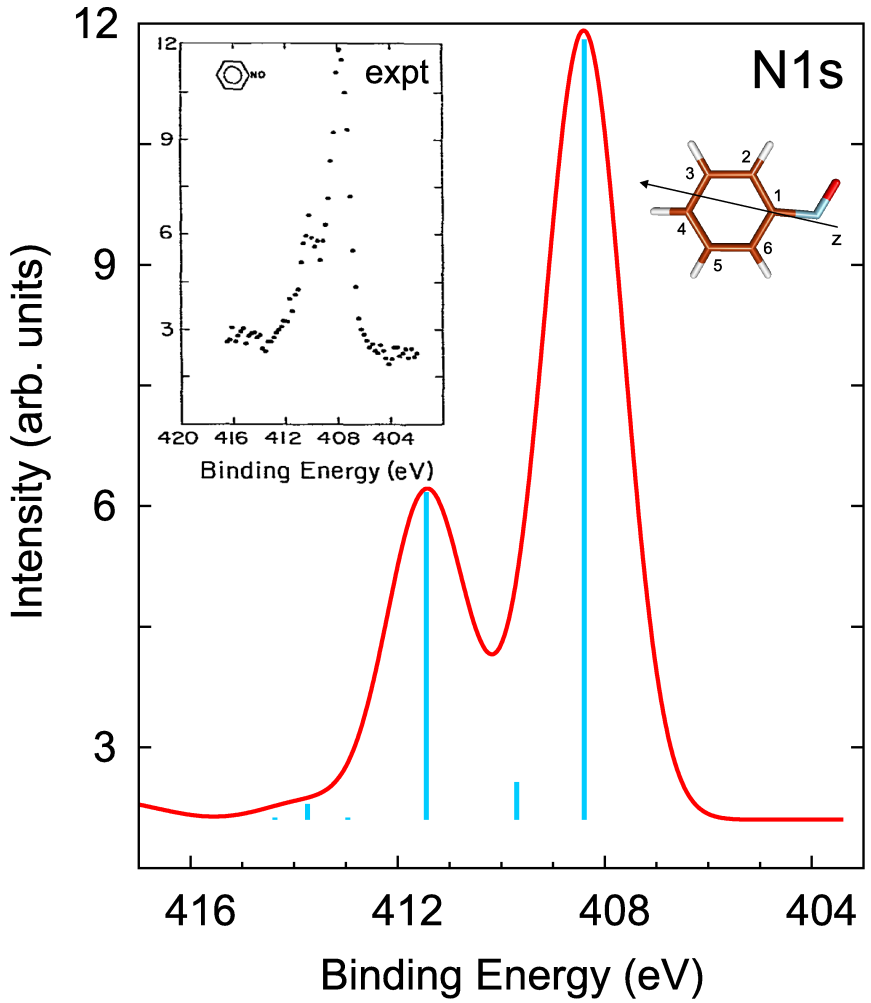
Examples: Relaxation satellite

Experiment

XPS (CPL **98**, 531 (1983))

Theory

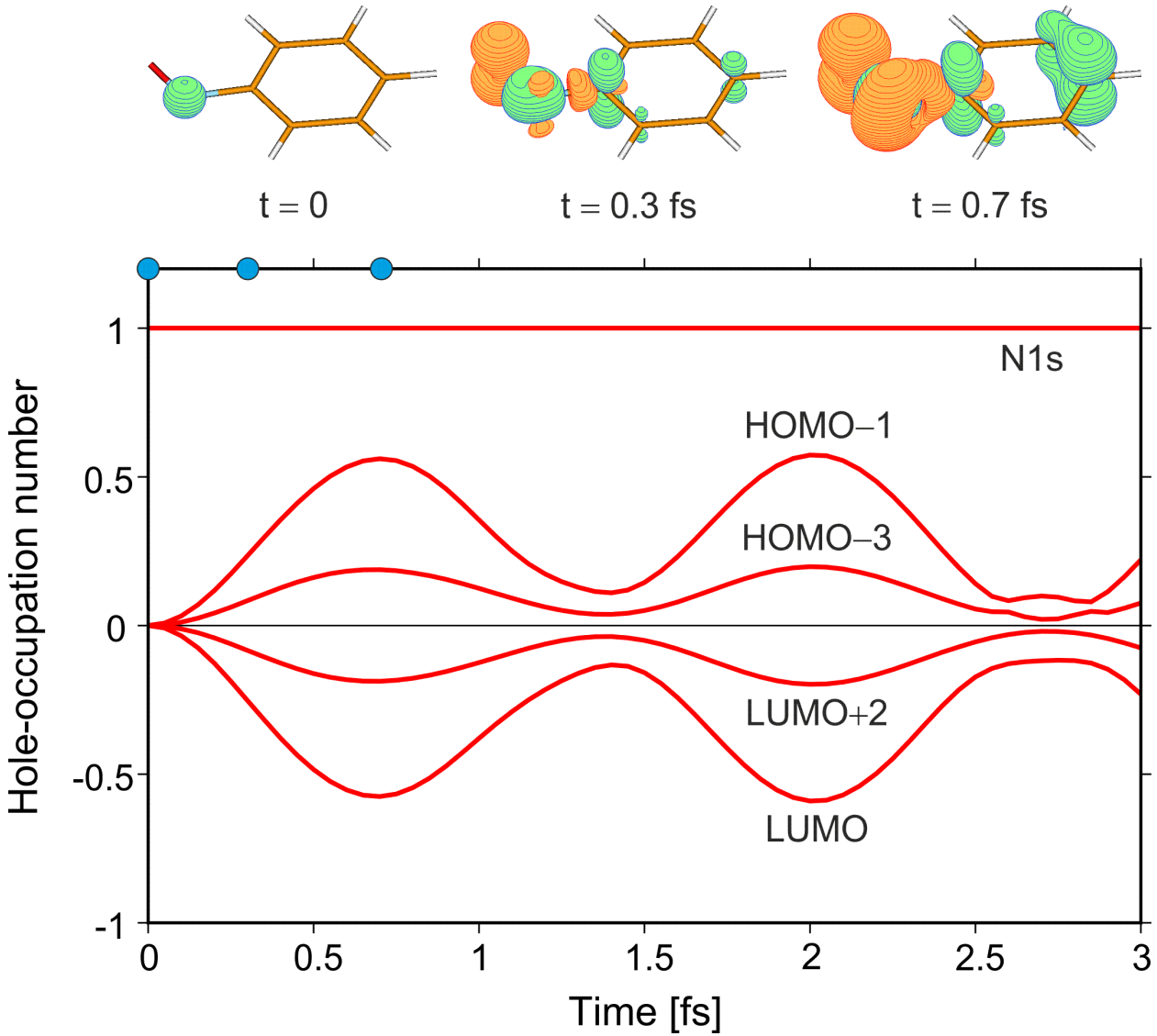
ADC(4) with core-valence separation



$$|\text{Main state}\rangle \approx -0.63|\Phi_{N1s}\rangle + 0.33|\Phi_{L,H-1,N1s}\rangle + 0.15|\Phi_{L+2,H-3,N1s}\rangle$$

$$|\text{Sat. state}\rangle \approx 0.41|\Phi_{N1s}\rangle + 0.49|\Phi_{L,H-1,N1s}\rangle - 0.15|\Phi_{L+2,H-3,N1s}\rangle$$

Examples: Relaxation satellite

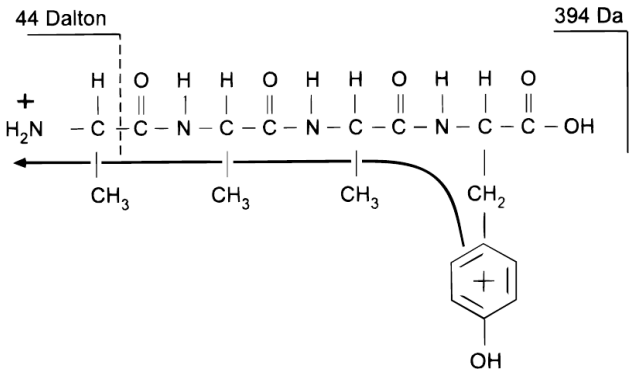


A. I. Kuleff, N. V. Kryzhevoi, M. Pernpointner, and L. S. Cederbaum, *Phys. Rev. Lett.* **117**, 093002 (2016).

Coupling to the nuclear dynamics

Charge dynamics in peptide chains

Ala-Ala-Ala-Tyr



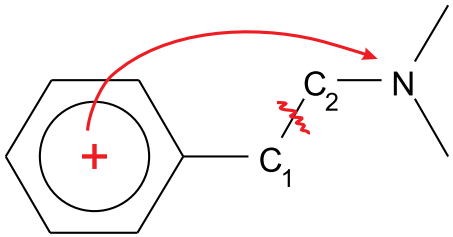
R. Weinkauf *et al.*, J. Phys. Chem. A **101**, 7702 (1997).

Charge-directed reactivity

F. Remacle, R. D. Levine, and M. A. Ratner, CPL **285**, 25 (1998).

Coupling to the nuclear dynamics

2-Phenylethyl-*N*,*N*-dimethylamine (PENNA)



CT + bond breaking is 80 ± 28 fs

L. Lehr *et al.*, JPCA **109**, 8074 (2005).

Coupling to the nuclear dynamics

S. Lünnemann *et al.*, CPL **450**, 232 (2008).

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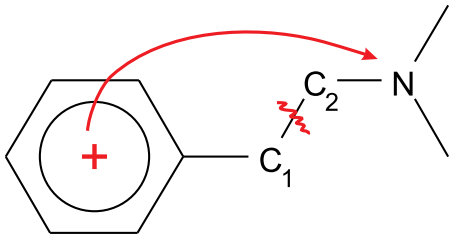

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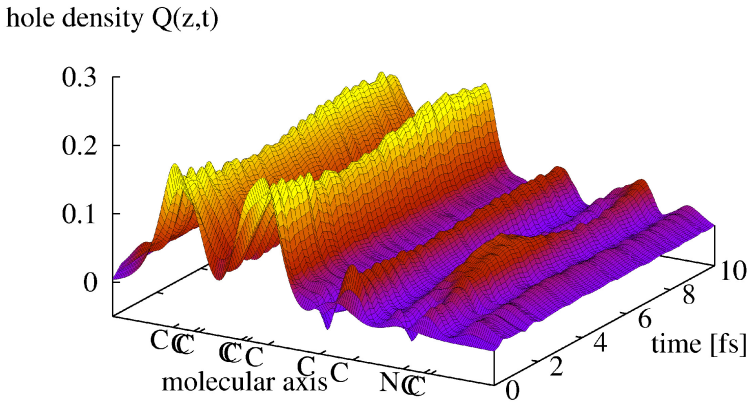
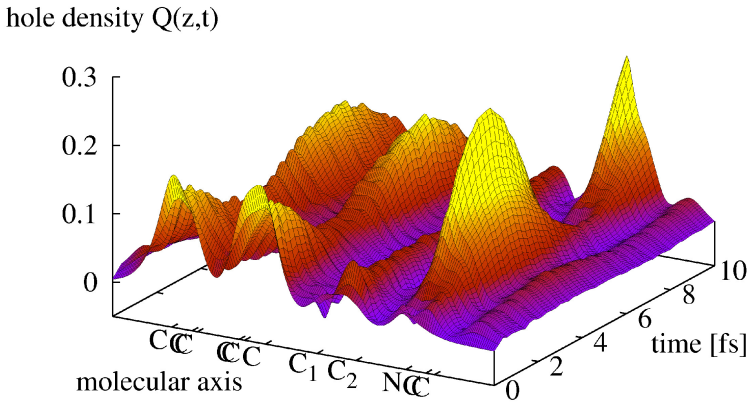


stretch +0.2



"Attochemistry"

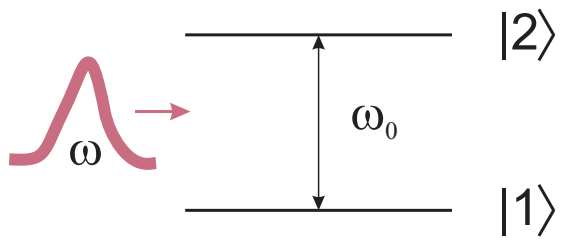
- The electronic motion governs the effective potential seen by the nuclei (BO)

- By controlling the purely electronic step we may achieve control over the charge-directed reactivity

- By appropriately tailored ultrashort laser pulses, one might be able to preselect and put the system on a particular reaction pathway at a very early stage of its quantum evolution

Controlling charge migration

Two ionic states (two-hole mixing)



$$|\Psi(t)\rangle = c_1(t)e^{-i\epsilon_1 t}|1\rangle + c_2(t)e^{-i\epsilon_2 t}|2\rangle, \qquad \vec{E}(t) = \vec{\mathcal{E}}(t)e^{-i\omega t} + \vec{\mathcal{E}}^*(t)e^{i\omega t}$$

RWA:
$$\begin{aligned} \dot{c}_1(t) &= ic_2(t)\mu\mathcal{E}^*(t)e^{i\delta t} \\ \dot{c}_2(t) &= ic_1(t)\mu\mathcal{E}(t)e^{-i\delta t} \end{aligned}$$

$$E(t) = -\frac{i}{\mu}\left(\frac{\dot{c}_2(t)}{c_1(t)}e^{-i\omega_0 t} + \frac{\dot{c}_1(t)}{c_2(t)}e^{i\omega_0 t}\right)$$

Let $|\tilde{c}_1(t)|^2 = f(t)$ then

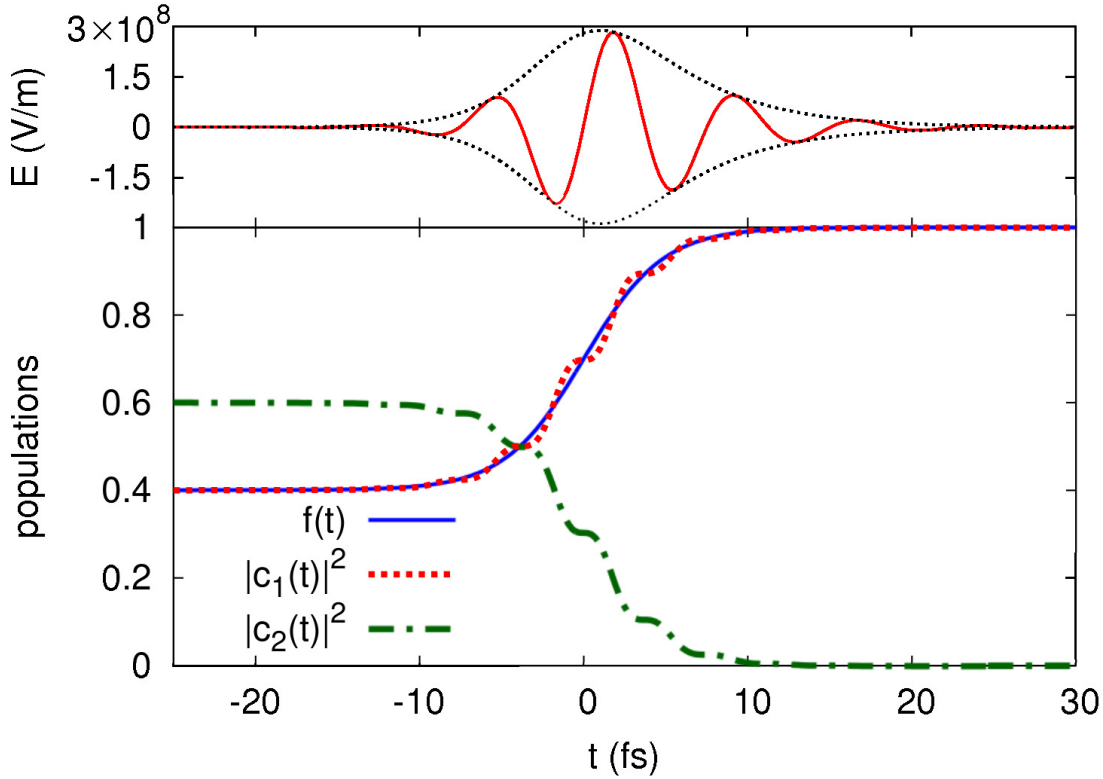
$$\boxed{E(t) = \frac{1}{\mu}\frac{\dot{f}(t)}{\sqrt{f(t)(1-f(t))}}\sin\left(\omega_0 t + \varphi\right)}$$

N. V. Golubev and A. I. Kuleff, Phys. Rev. A **90**, 035401 (2014)

Controlling charge migration

$$f(t) = a_i[1 - g(t)] + a_f g(t)$$

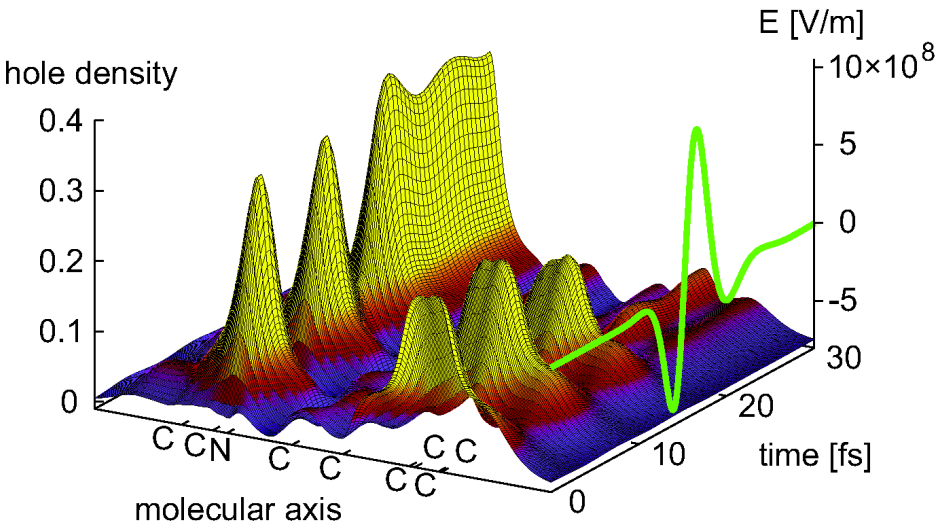
$$g(t) = \frac{1}{1 + e^{-\alpha t}}$$



N. V. Golubev and A. I. Kuleff, Phys. Rev. A **90**, 035401 (2014)

Controlling charge migration in MePeNNA

Propagation with the full Hamiltonian of the system and its coupling to the field



N. V. Golubev and A. I. Kuleff, Phys. Rev. A **91**, 051401(R) (2015)

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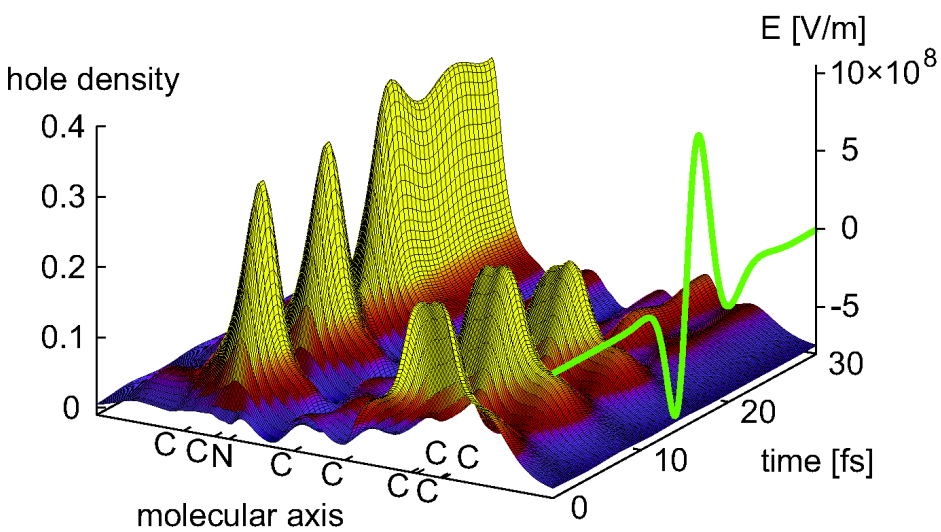
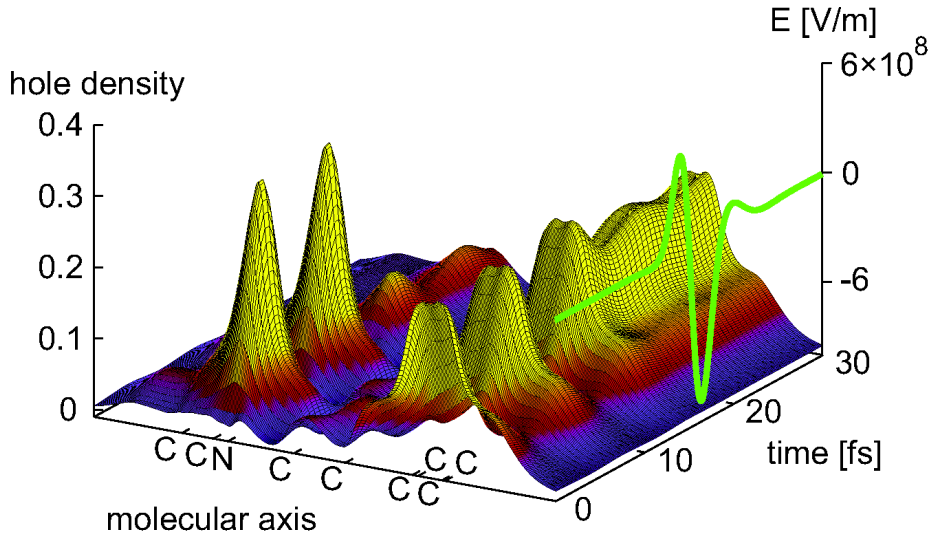
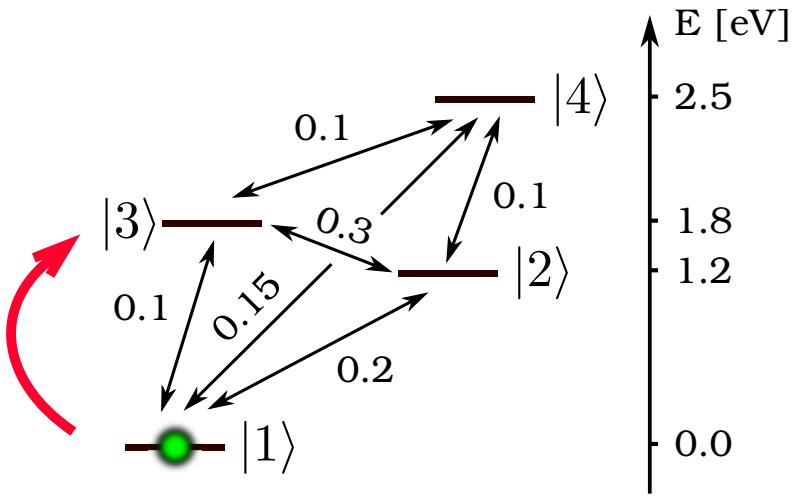




N. V. Golubev and A. I. Kuleff, Phys. Rev. A **91**, 051401(R) (2015)

Controlling by split-and-delay

Two delayed Gaussian pulses optimized using numerical algorithms (e.g. MADS)



N. V. Golubev, V. Despré, and A. I. Kuleff, J. Mod. Optics **64**, 1031 (2017)

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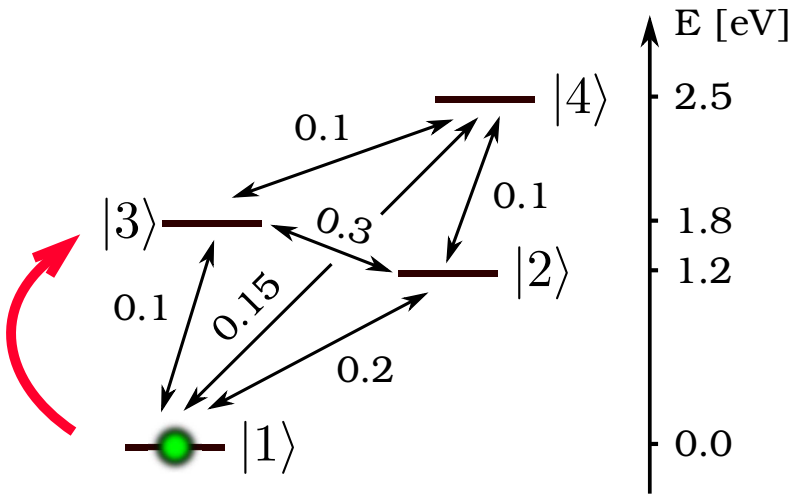
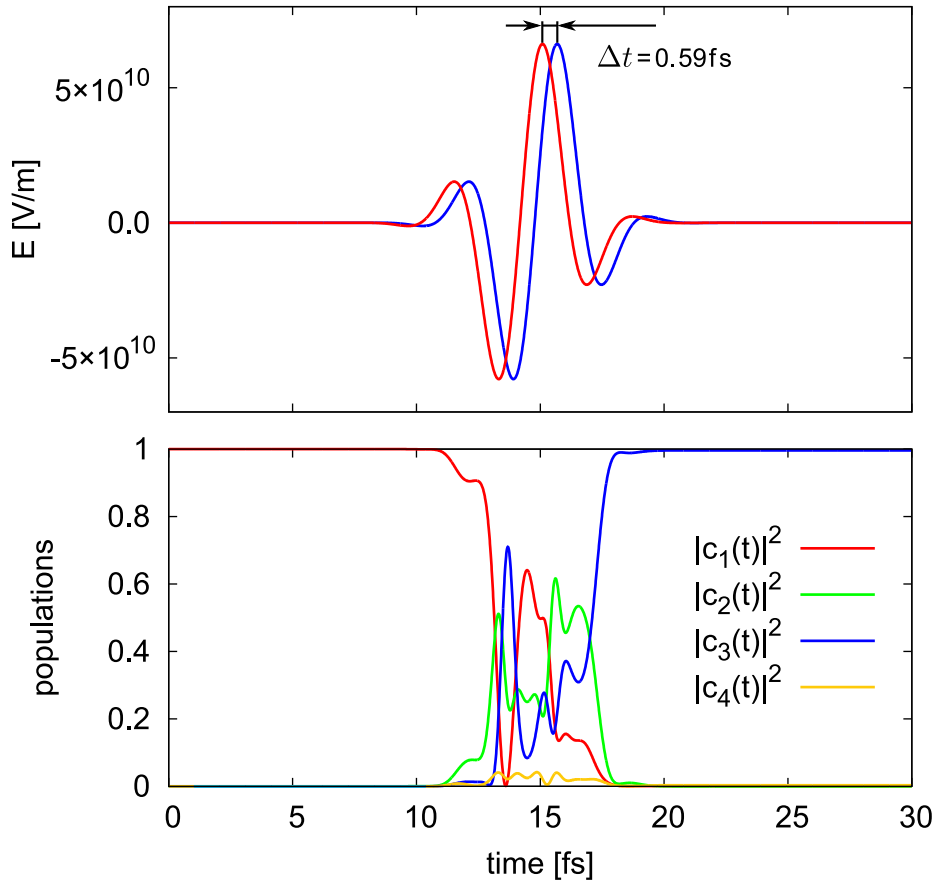
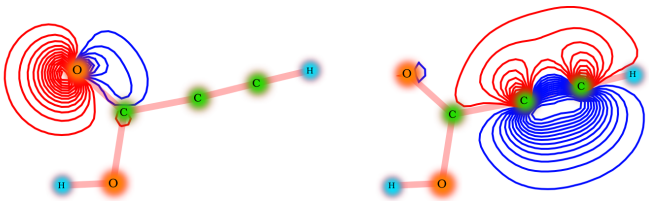
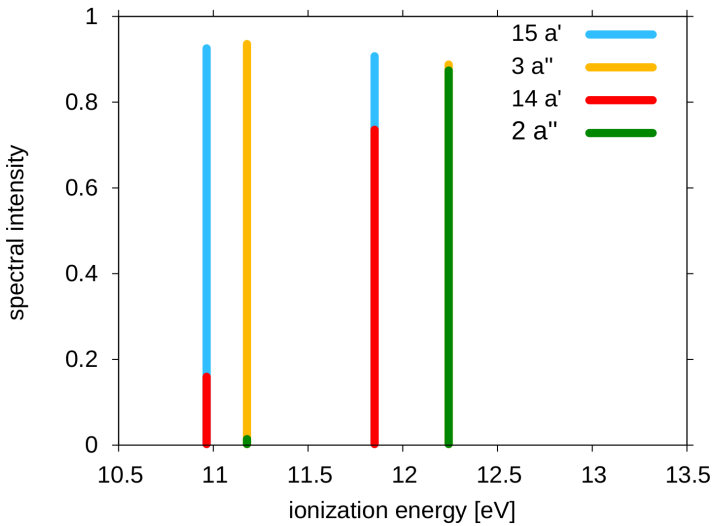




N. V. Golubev, V. Despré, and A. I. Kuleff, J. Mod. Optics **64**, 1031 (2017)

Controlling charge migration in propiolic acid





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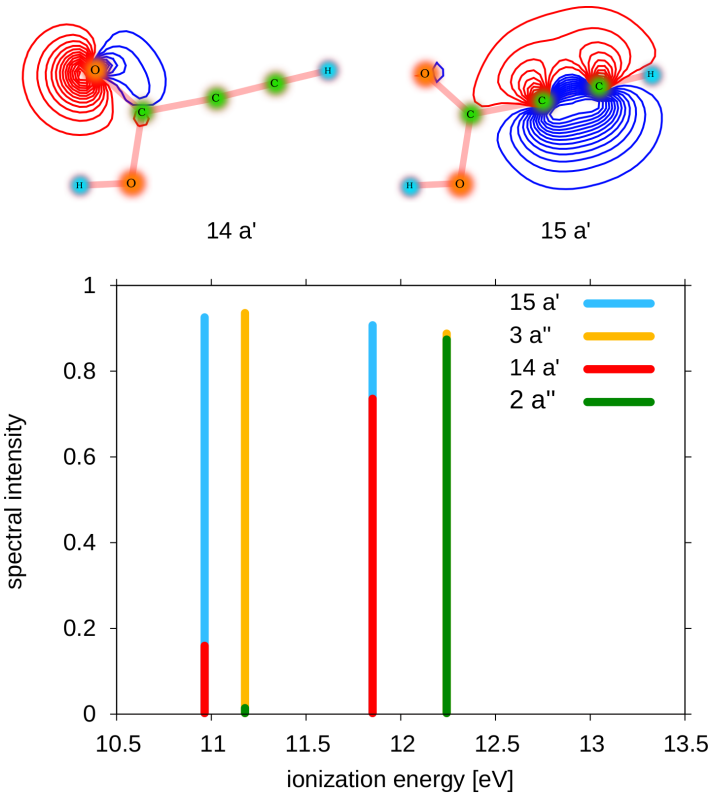

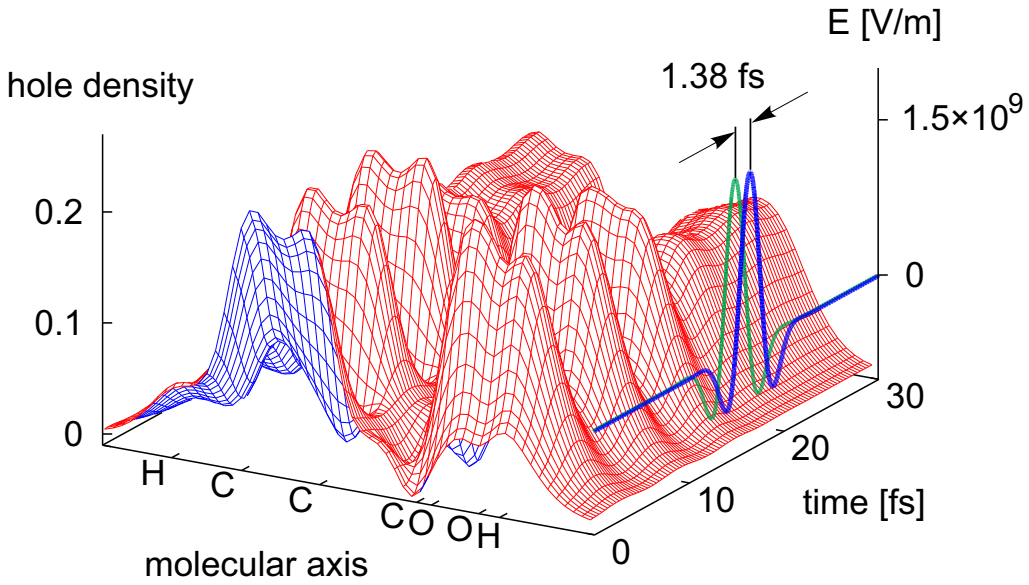

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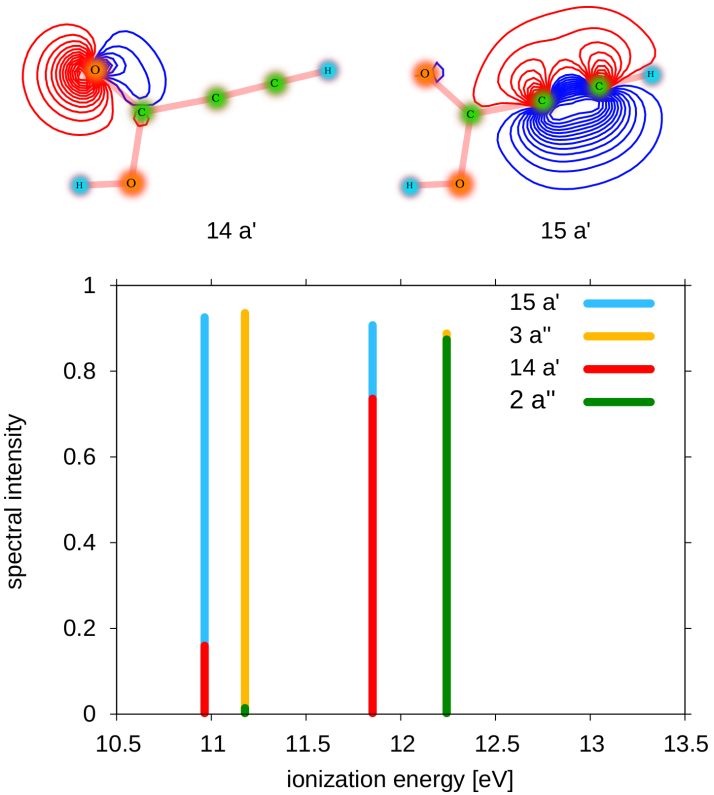

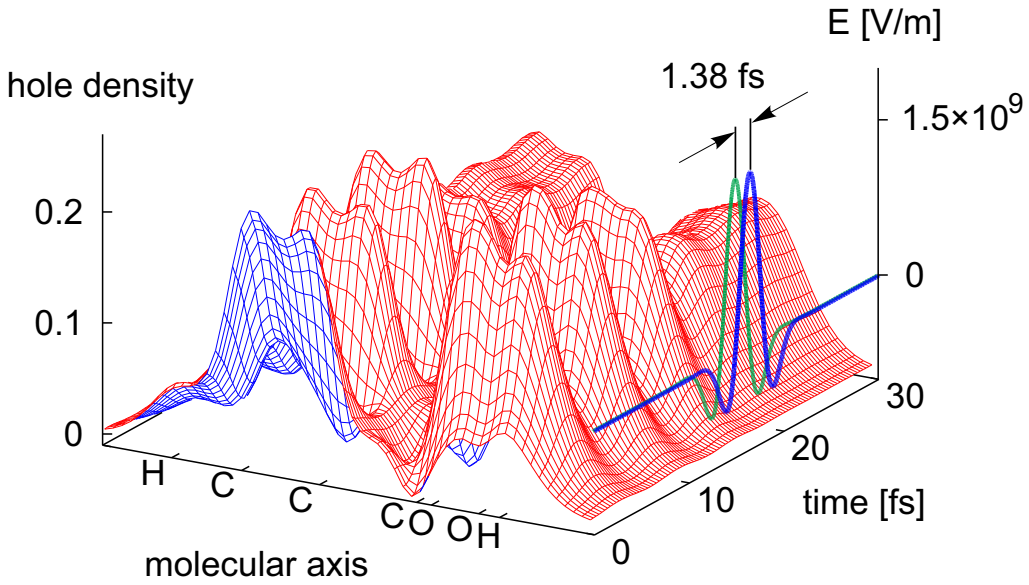

We can design ultrashort laser pulses that are able to control the electron dynamics!

N. V. Golubev, V. Despré, and A. I. Kuleff, J. Mod. Optics **64**, 1031 (2017)

Coupled electron-nuclear dynamics

- Born-Huang expansion of the molecular wave function:

$$\Psi(\underline{r}, \underline{R}, t) = \sum_i \chi_i(\underline{R}, t)\Phi_i(\underline{r}; \underline{R}),$$

where $\Phi_i(\underline{r}; \underline{R})$ satisfy $\hat{H}_e\Phi_i(\underline{r}; \underline{R}) = V_i(\underline{R})\Phi_i(\underline{r}; \underline{R})$ (**adiabatic states**).

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- Diabatization and construction of a vibronic-coupling Hamiltonian:

$$\hat{H}_{VC} = \hat{T}_n + V_0 + \sum_k \kappa_k^{(i)} q_k + \frac{1}{2}\sum_{k,l} \gamma_{k,l}^{(i)} q_k q_l + ...$$

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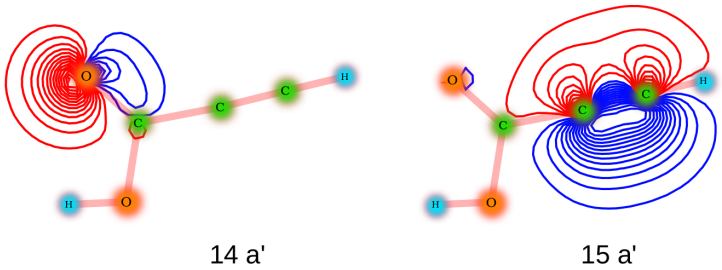
- Constructing the density:

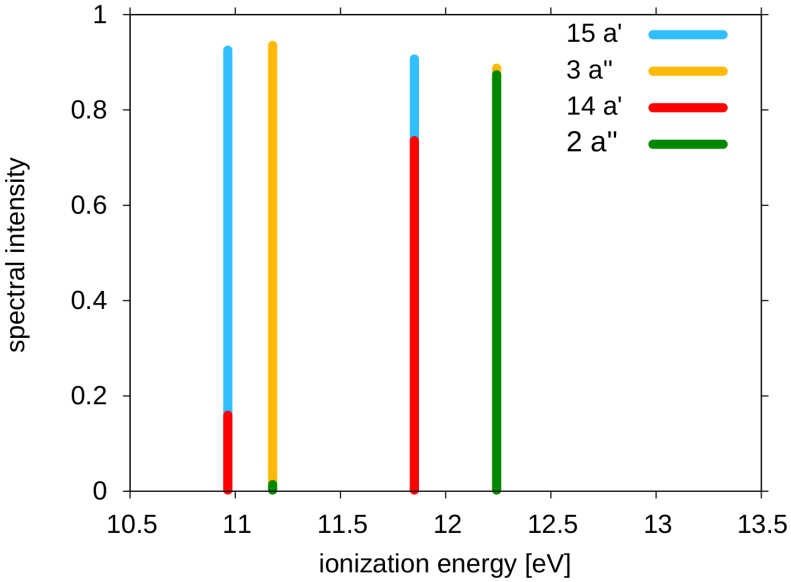
$$\rho(\vec{r}, t) = \sum_{i,j} \langle \chi_i(\underline{R}, t)\Phi_i(\underline{r}; \underline{R})|\hat{\rho}(\underline{r})|\Phi_j(\underline{r}; \underline{R})\chi_j(\underline{R}, t)\rangle_{\underline{r}-1,\underline{R}}$$

$$\rho(\vec{r}, t) = \sum_{i,j} \langle \chi_i(\underline{R}, t)|\rho_{ij}(\vec{r}, \underline{R})|\chi_j(\underline{R}, t)\rangle_{\underline{R}}$$

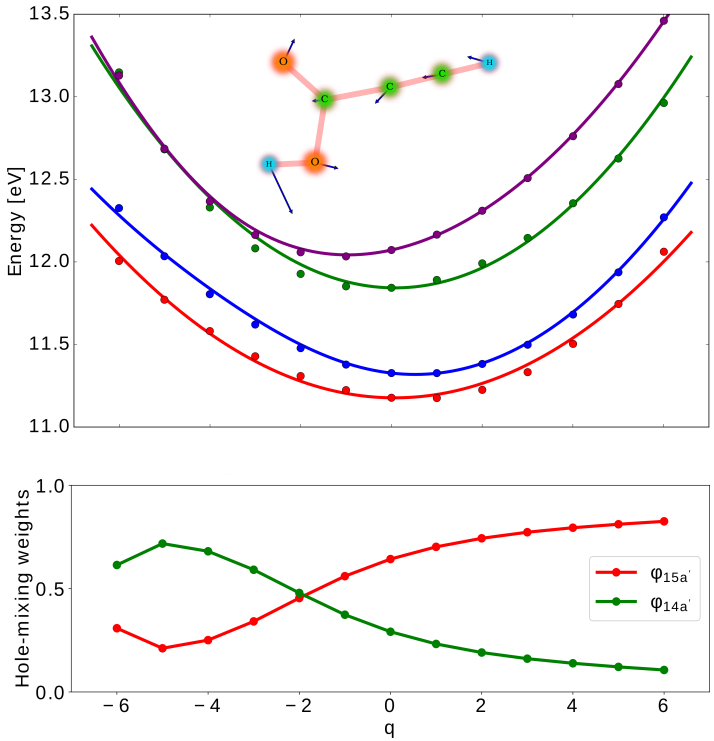
$$\rho_{ij}(\vec{r}, \underline{R}) \approx \rho_{ij}(\vec{r}) \quad \Rightarrow \quad \boxed{\rho(\vec{r}, t) = \sum_{i,j} \chi_{ij}(t)\rho_{ij}(\vec{r})}$$

Electron-nuclear dynamics in propiolic acid





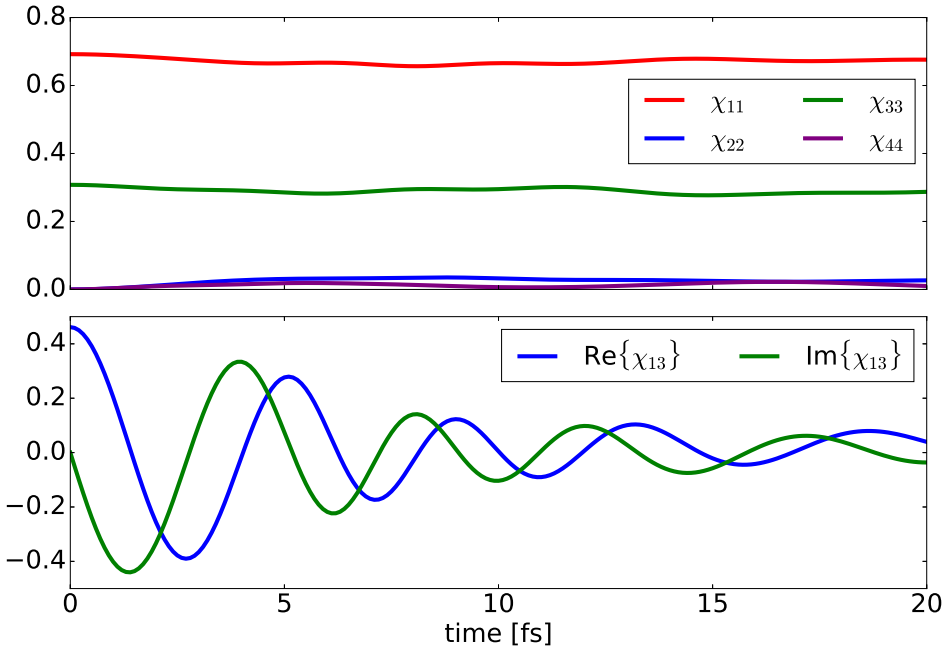
V. Despré, N. V. Golubev, and A. I. Kuleff, PRL **121**, 203002 (2018).



- ADC(3)/dzp calculations along all 15 normal modes of the system
- The VC Hamiltonian was constructed by least-square fit to the *ab initio* data
- The initial WPs were constructed using the hole-mixing parameters

Electron-nuclear dynamics in propiolic acid

Decoherence of charge migration by nuclear dynamics



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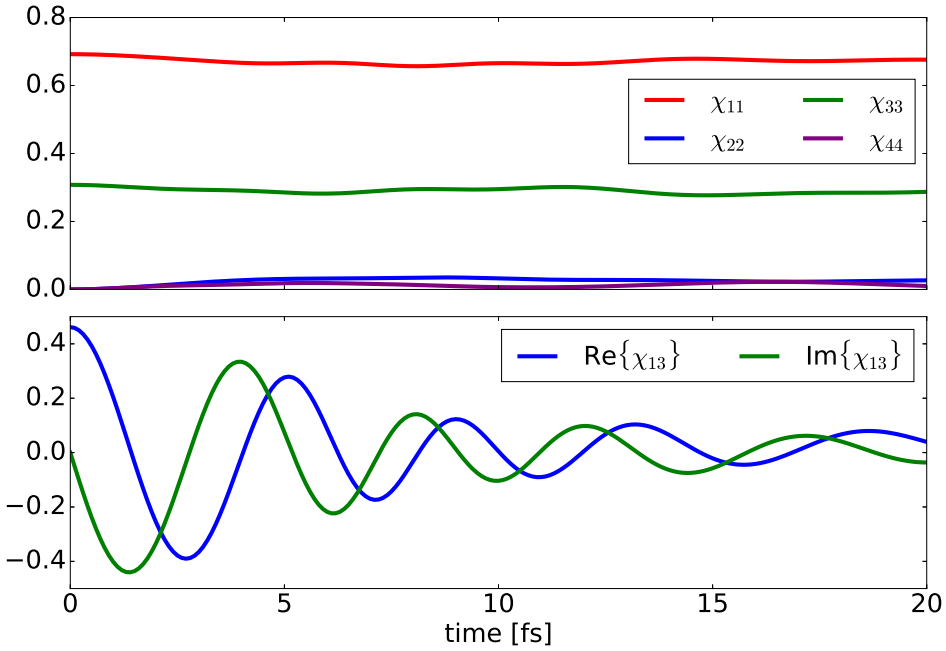

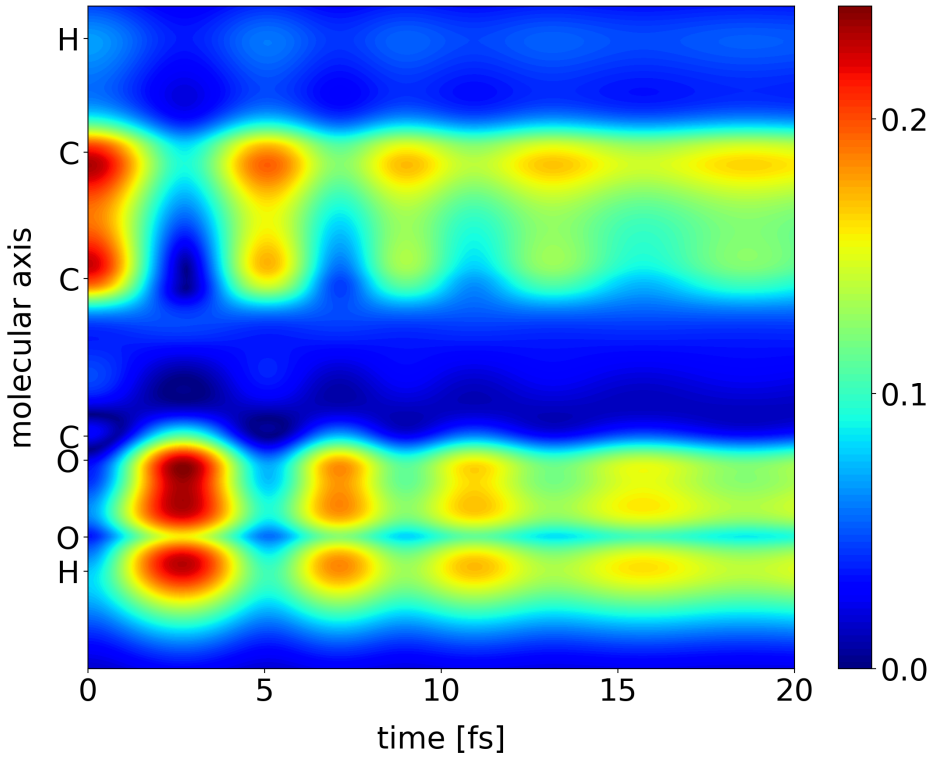

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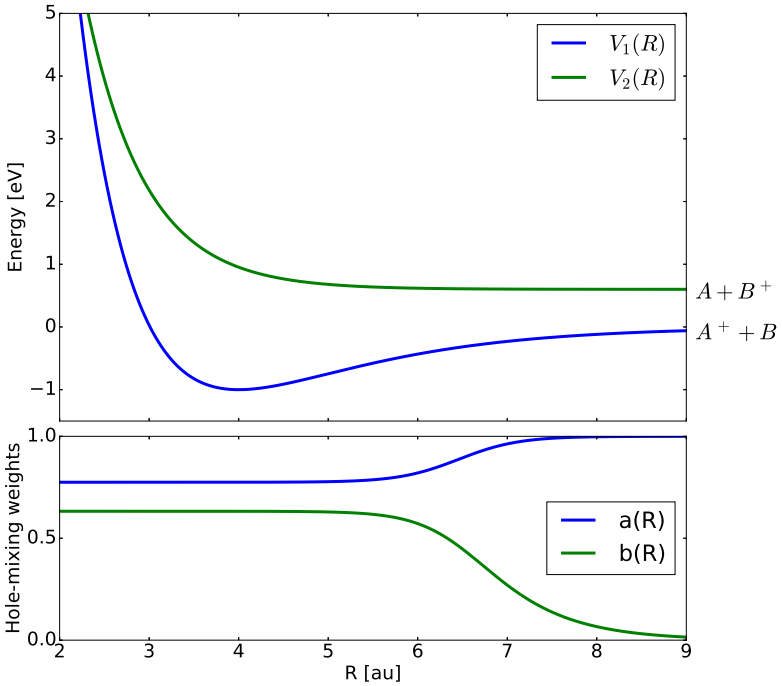
Laser control of charge-directed reactivity



$$\Phi_1(\vec{r}, R) = a(R)\varphi_L(\vec{r}) + b(R)\varphi_R(\vec{r})$$
$$\Phi_2(\vec{r}, R) = a(R)\varphi_L(\vec{r}) - b(R)\varphi_R(\vec{r})$$

$$|\Psi(0)\rangle = a(R)\chi(R)|\Phi_1\rangle + b(R)\chi(R)|\Phi_2\rangle$$

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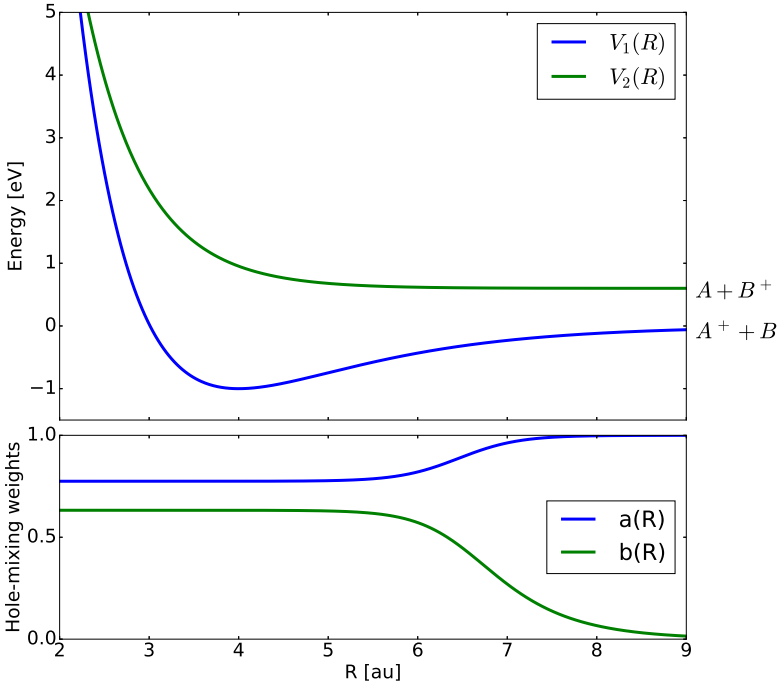

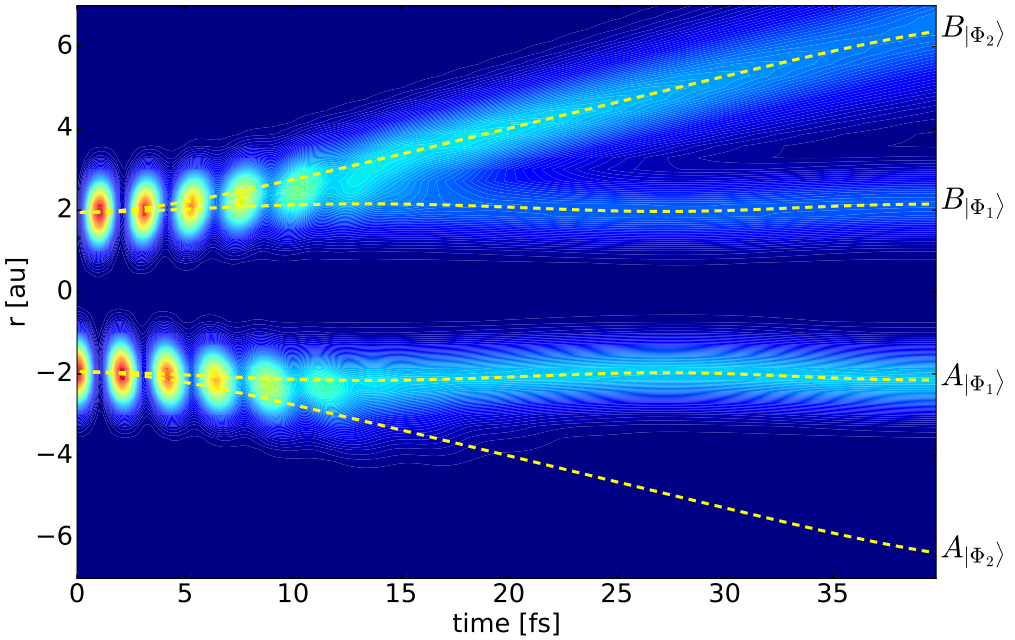

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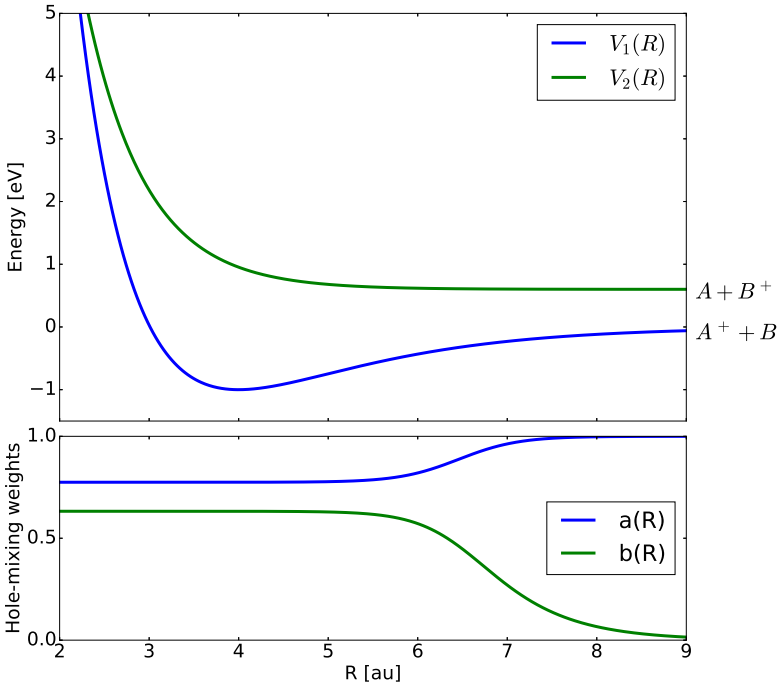

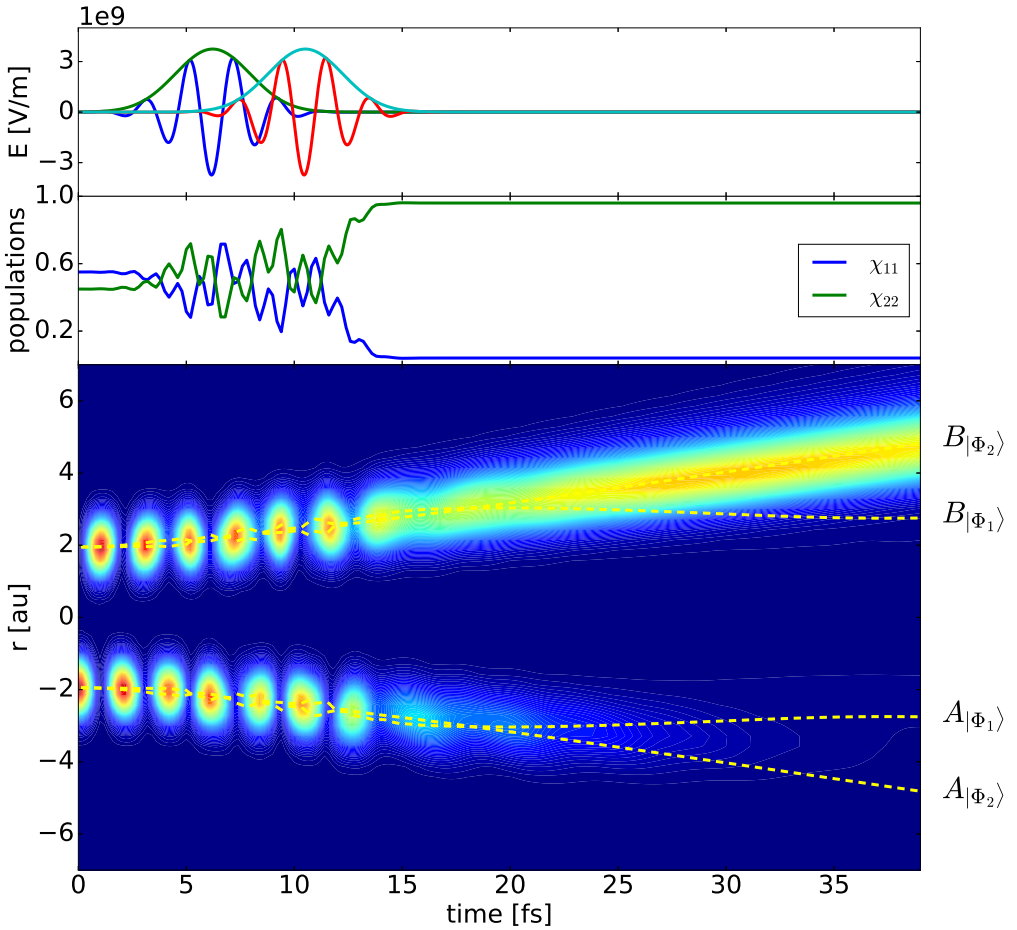

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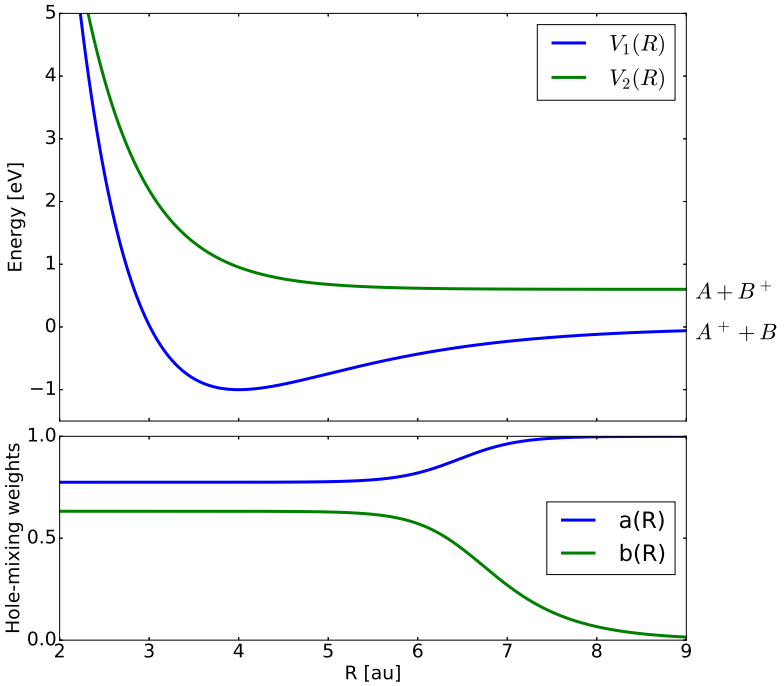

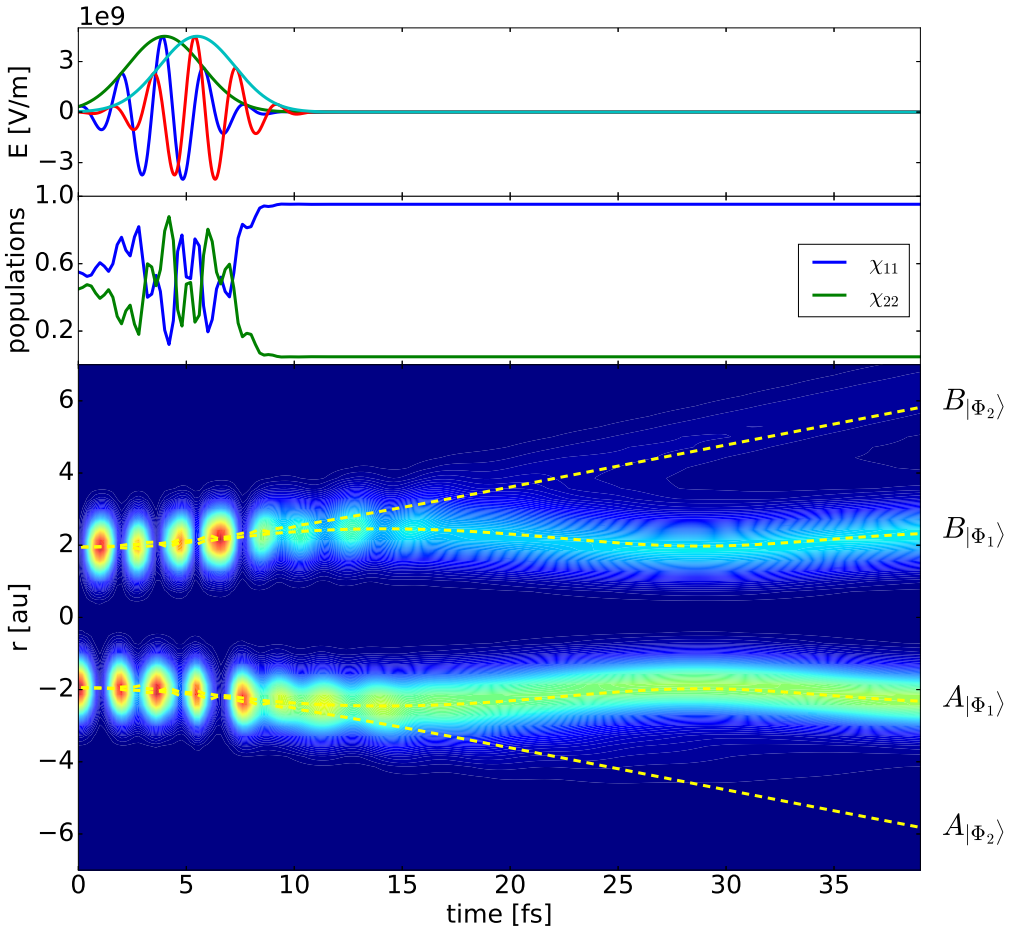

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- The dream of attochemistry may be a reality! We might be able to control a chemical reaction by manipulating only the electron coherence