Multiple orbital contribution in multiphoton ionization of H_2O in intense ultrafast laser fields

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Abstract

We present all-electron time-dependent density-functional theory (TDDFT) investigation of multiphoton ionization (MPI) of H_2O in intense ultrafast linearly-polarized laser pulses with arbitrary molecular orientation.

A new time-dependent Voronoi-cell finite difference (TDVFD) method featuring highly adaptive molecular grids and an efficient time propagator is applied for accurate TDDFT solutions, taking into account the detailed electronic structure and responses in multiple orbital dynamics.

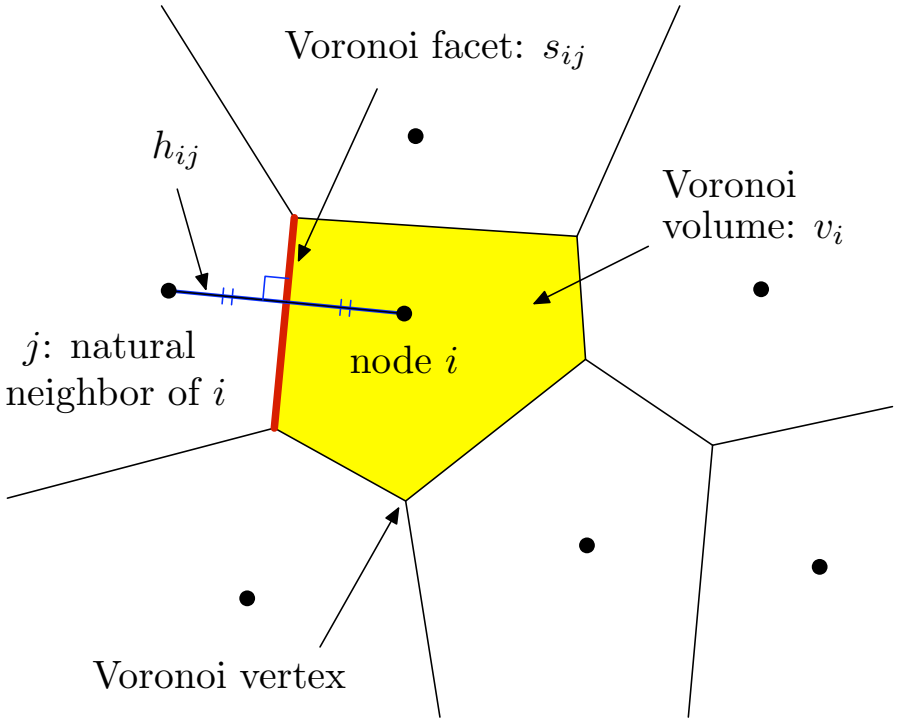
Our results demonstrate that the inner orbital dominantly contributes to the overall orientation dependence of H_2O MPI.

Voronoi-cell finite difference

- Based on Voronoi diagram and natural neighbors
- Laplacian operator at each grid evaluated by Voronoi volume, area, and distance
- Simple like FD, adaptive like FE, formulated like FV
- Direct solution of the Schrödinger, Kohn-Sham, and Poisson equations on *unstructured* grids
- Extensible to time-dependent problems

Background picture adopted from http://en.wikipedia.org/wiki/Voronoi_diagram

Discrete Laplacian in VFD



Voronoi diagram:

$$T_i = \{\mathbf{x} \in \mathbb{R}^n : d(\mathbf{x}, \mathbf{x}_i) < d(\mathbf{x}, \mathbf{x}_j) \text{ for } \forall j \neq i\}$$

Laplacian definition from Gauss's theorem

$$\nabla^2 \varphi = \lim_{\int_V d\tau \to 0} \frac{\int_S \nabla\varphi \cdot \mathbf{n}\, d\sigma}{\int_V d\tau}$$

Discrete Laplacian after Voronoi discretization

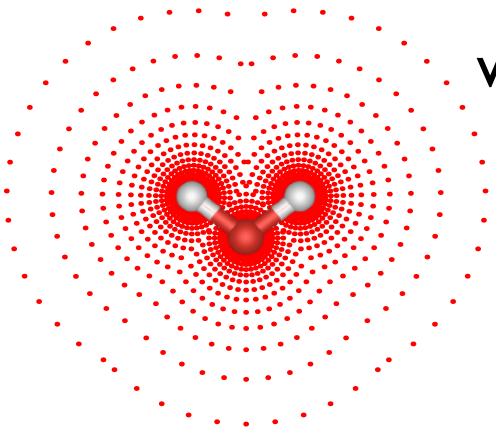
$$\left(\nabla^2 \varphi\right)_i = \frac{1}{v_i} \sum_{j}^{\text{natural neighbors}} \frac{\varphi_j - \varphi_i}{h_{ij}} s_{ij}$$

Symmetric Laplacian matrix

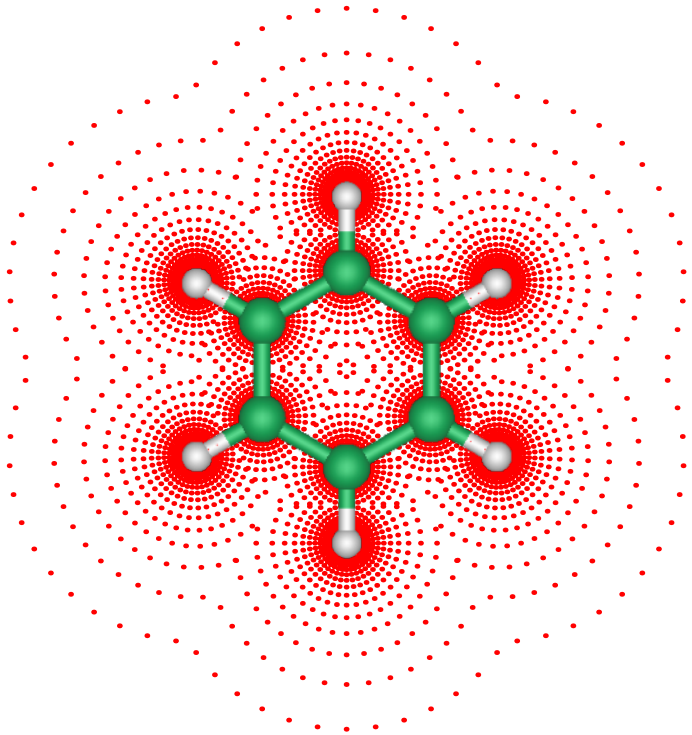
$$\tilde{L}_{ij} = \begin{cases} -\dfrac{1}{v_i} \displaystyle\sum_{k}^{\text{neighbors}} \dfrac{s_{ik}}{h_{ik}} & (i = j) \\ \dfrac{1}{\sqrt{v_i v_j}} \dfrac{s_{ij}}{h_{ij}} & (i,\ j\text{: neighbors}) \\ 0 & (\text{otherwise}) \end{cases}$$

Sukumar and Bolander, *CMES* **4**, 691 (2003)
Sukumar, *Int. J. Numer. Meth. Engng* **57**, 1 (2003)
Son (unpublished)

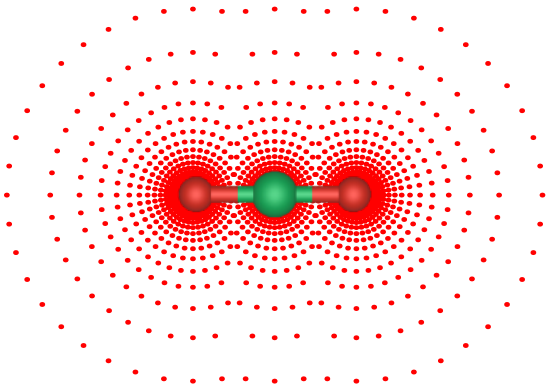
VFD on molecular grids



water: H_2O



carbon dioxide: CO_2



benzene: C_6H_6

- *Unstructured*: capable of any types of grid distribution
- *Non-uniform*: denser grids near nuclei, sparser grids in long distances
- Intuitively constructed by a combination of atomic spherical grids

TDDFT solved by TDVFD

Time-dependent Kohn-Sham equation for *N*-electron system in laser fields

$$i\frac{\partial}{\partial t}\psi_{i\sigma}(\mathbf{r},t) = \left[-\frac{1}{2}\boldsymbol{\nabla}^2 + u_{\mathrm{eff},\sigma}(\mathbf{r},t)\right]\psi_{i\sigma}(\mathbf{r},t),$$

$$(i = 1, 2, ..., N_\sigma).$$

$$u_{\mathrm{eff},\sigma}(\mathbf{r},t) = u_{\mathrm{ne}}(\mathbf{r}) + u_{\mathrm{h}}(\mathbf{r},t) + u_{\mathrm{xc},\sigma}^{\mathrm{LB}\alpha}(\mathbf{r},t) + \mathbf{F}(t)\cdot\mathbf{r}$$

The split-operator technique in the energy representation

$$\psi(\mathbf{r},t+\Delta t) = e^{-i\hat{U}(\mathbf{r},t)\frac{\Delta t}{2}}\psi(\mathbf{r},t)e^{-i\hat{H}_0(\mathbf{r})\Delta t}e^{-i\hat{U}(\mathbf{r},t)\frac{\Delta t}{2}}\psi(\mathbf{r},t) + O(\Delta t^3)$$

$$\hat{H}_0(\mathbf{r}) = -\tfrac{1}{2}\boldsymbol{\nabla}^2 + u_{\mathrm{eff},\sigma}(\mathbf{r},0),$$

$$\hat{U}(\mathbf{r},t) = \mathbf{F}(t)\cdot\mathbf{r} + \left[u_{\mathrm{xc},\sigma}^{\mathrm{LB}\alpha}(\mathbf{r},t) - u_{\mathrm{xc},\sigma}^{\mathrm{LB}\alpha}(\mathbf{r},0)\right] + \left[u_{\mathrm{h}}(\mathbf{r},t) - u_{\mathrm{h}}(\mathbf{r},0)\right],$$

- $H_0(\mathbf{r})$ is accurately solved within VFD; $\exp[-iH_0(\mathbf{r})\Delta t]$ is solved by the spectral decomposition.
- $U(\mathbf{r},t)$ is diagonal in VFD; thus $\exp[-iU(\mathbf{r},t)\Delta t/2]$ is trivial.

Tong & Chu, *Phys. Rev. A* **57**, 452 (1998) / Son & Chu, *Chem. Phys.* (submitted)

Electronic structure calculations

Orbital binding energies (in eV)

Molecule	Orbital	LSDA FD	LSDA LCAO	LSDA VFD	LBα GPS	LBα VFD	EXP
N_2	$3\sigma_g$	10.3	10.4	10.4	15.5	15.5	15.5
	$1\pi_u$	11.2	11.9	11.9	16.9	16.9	16.8
	$2\sigma_u$	14.8	13.4	13.5	18.5	18.5	18.6
	$2\sigma_g$	28.5	28.2	28.2		33.0	37.3
	$1\sigma_u$	407.0	380.0	380.1		402.8	409.9
	$1\sigma_g$	407.1	380.1	380.2		402.8	409.9
CO_2	$1\pi_g$	10.4	9.3	9.4		14.7	13.8
	$1\pi_u$	14.0	13.0	13.0		18.2	17.6
	$3\sigma_u$	12.4	12.8	12.8		18.2	18.1
	$4\sigma_g$	12.4	13.8	13.8		19.2	19.4
	$2\sigma_u$	25.8	28.2	28.1		33.3	36.9
	$3\sigma_g$	26.4	29.1	29.1		34.2	38.0
	$2\sigma_g$	244.9	271.1	271.1		291.7	297.5
	$1\sigma_u$	429.3	508.6	508.9		533.7	540.8
	$1\sigma_g$	429.3	508.6	508.9		533.7	540.8
H_2O	$1b_1$	7.6	7.4	7.4		12.5	12.6
	$3a_1$	9.3	9.4	9.4		14.5	14.8
	$1b_2$	13.3	13.3	13.3		18.2	18.7
	$2a_1$	24.4	25.2	25.2		30.1	32.4
	$1a_1$	488.0	506.4	506.6		531.0	539.7

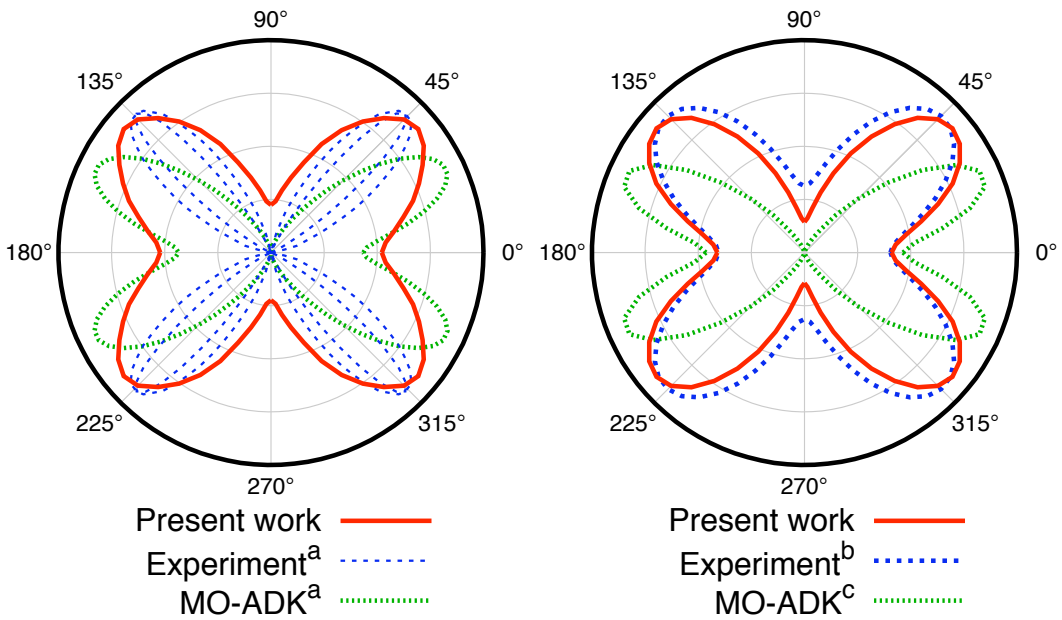
Son & Chu, *Chem. Phys.* (submitted)

FD parameters: 4th-order scheme, Δx=0.1 a.u. and r_{max}=10 a.u.
LCAO parameters: aug-cc-pVQZ
VFD parameters: N_r=300, L=0.5 a.u., l_{max}=25, and r_{max}=20 a.u.

LBα parameters: α=1.19 and β=0.01
GPS: Telnov & Chu, *PRA* **79**, 041401(R) (2009)

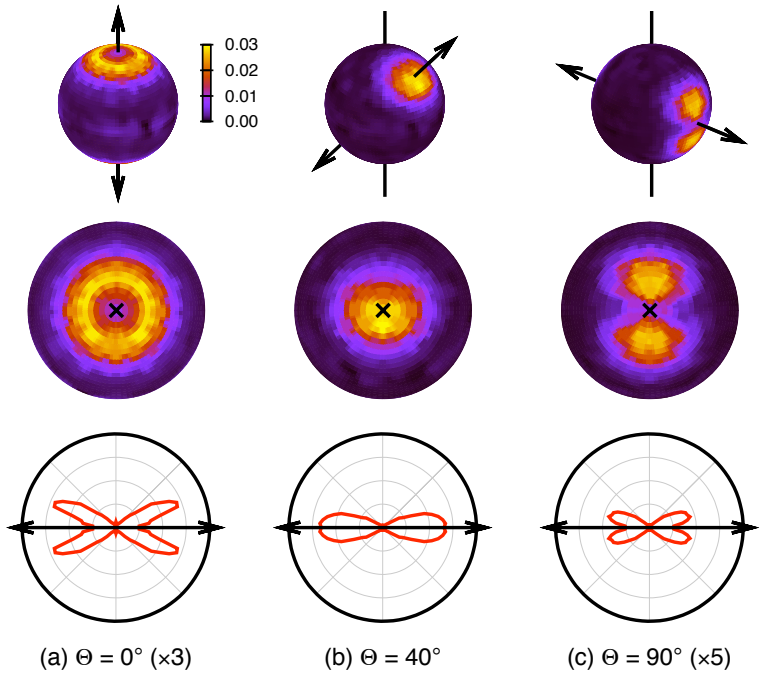
CO_2 MPI

Orientation-dependent plots



Photoelectron angular distribution

820 nm, 1.1×10^{14} W/cm^2

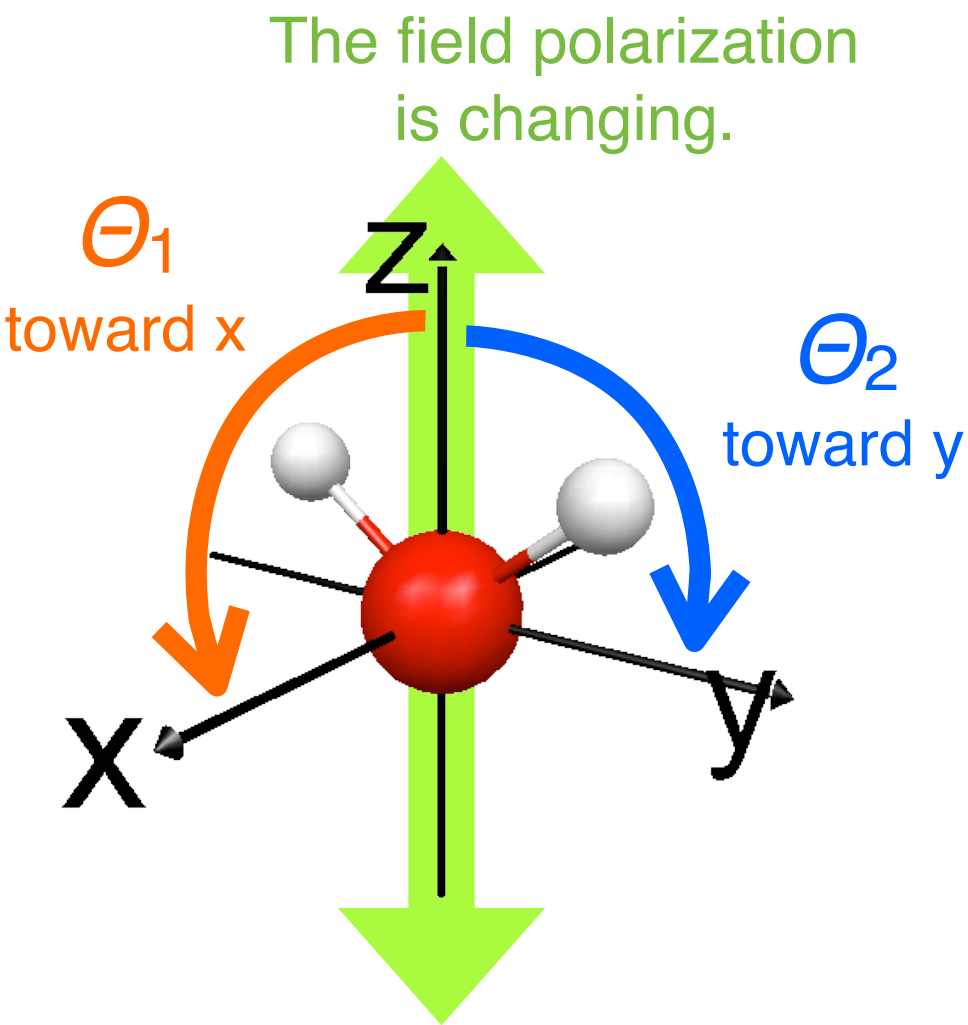


The TDDFT results agree well with recent experiments of CO_2 MPI.

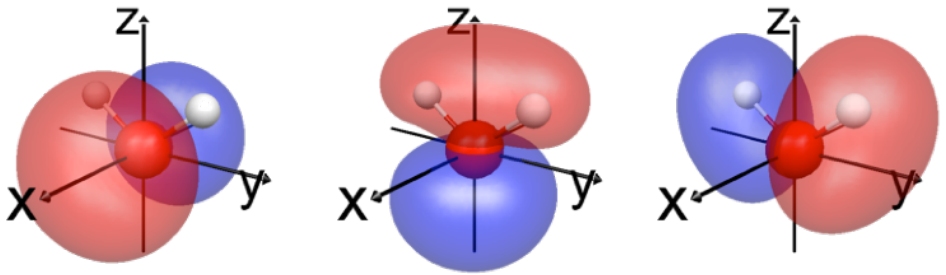
[a] Pavičić *et al.*, *Phys. Rev. Lett.* **98**, 243001 (2007)
[b] Thomann *et al.*, *J. Phys. Chem. A* **112**, 9382 (2008)
[c] Le *et al.*, *J. Mod. Opt.* **54**, 967 (2007)

Present work:
Son & Chu, *Phys. Rev. A* **80**, 011403(R) (2009)

Orientation effect on H_2O MPI



H_2O is contained in the *yz*-plane.



HOMO ($1b_1$) –12.6 eV

HOMO–1 ($3a_1$) –14.8 eV

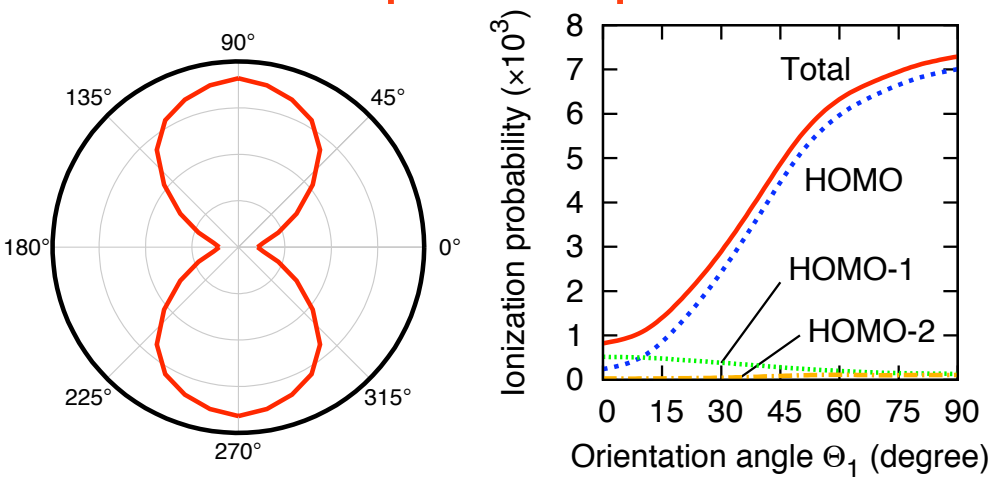
HOMO–2 ($1b_2$) –18.7 eV

- Increasing Θ_1 toward x
  - Maximize MPI of HOMO
  - Minimize MPI of HOMO–1
  - No effect on MPI of HOMO–2
- Increasing Θ_2 toward y
  - No effect on MPI of HOMO
  - Minimize MPI of HOMO–1
  - Maximize MPI of HOMO–2

Multiple orbital contribution in H_2O MPI

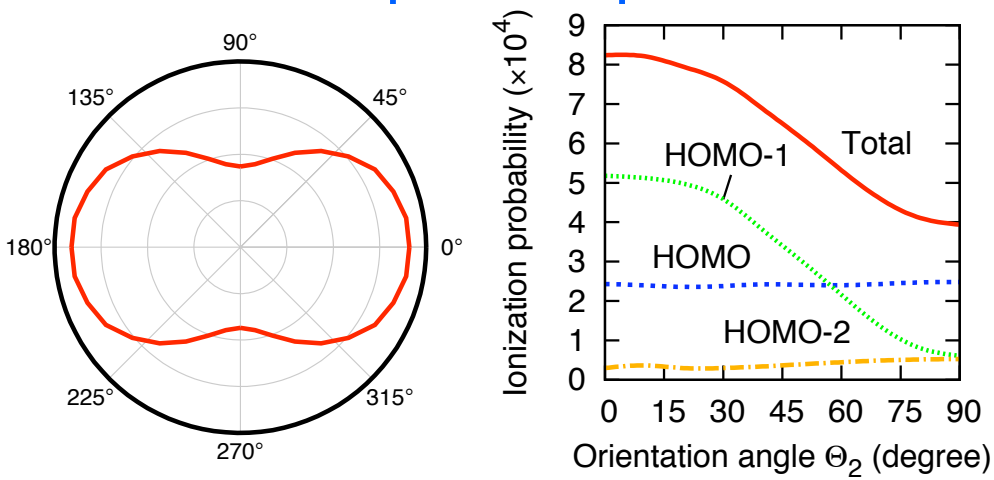
H_2O at 800 nm, 5×10^{13} W/cm^2

orientation-dependent plot w.r.t. Θ_1



H_2O at 800 nm, 5×10^{13} W/cm^2

orientation-dependent plot w.r.t. Θ_2



- HOMO is dominant to the orientation-dependent MPI pattern when Θ_1 changes.

- The change of Θ_2 in the *yz*-plane does not affect HOMO ionization because HOMO has a nodal plane of the *yz*-plane.
- HOMO–1 shows dominant contribution to the overall pattern when Θ_2 changes.

Son & Chu, *Chem. Phys.* (submitted)

Conclusion

- TDDFT is a promising tool to investigate attosecond electronic dynamics of many-electron systems in strong laser fields.
- TDVFD provides accurate TDDFT solutions for polyatomic molecules on highly adaptive molecular grids.
- Detailed electronic structure and responses in multiple orbital dynamics are important in strong-field electronic dynamics.
- For MPI of aligned H_2O, the inner orbital (HOMO–1) shows dominant contribution to the ionization process when the field is applied in a specific direction w.r.t. the molecular alignment.
- It will be possible to selectively probe individual orbitals in strong-field electronic dynamics.

References

- N. Sukumar, *Int. J. Numer. Meth. Engng* **57**, 1 (2003)
- N. Sukumar & J. E. Bolander, *CMES* **4**, 691 (2003)
- S.-K. Son & S. I. Chu, *Phys. Rev. A* **80**, 011403(R) (2009)
- S.-K. Son & S. I. Chu, *Chem. Phys.* (submitted)