Ionic Shake-Up in XUV Ionization of Molecules
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ABSTRACT

An XUV pulse incident on a molecule typically removes an electron from one of the inner valence shells. Such a process is accompanied by various relaxation effects like autoionization, auger decay. Here we describe an interface with quantum chemistry for studying these processes numerically. We present the results of its first application: transition rates for XUV photo-ionization of O_2 molecule and a short list of more applications for which we envisage to use this interface.

INTERFACE WITH QUANTUM CHEMISTRY

Consider a N electron system in which we want to study q ($q \leqslant N$) electron dynamics. An interface with quantum chemistry consists of:
- Extracting (N-q) electronic wave-function $\Psi_1(\vec{r}_1, ...\vec{r}_{N-q})$ from a quantum chemistry package.
- Attaching to it a q electron continuum wave function.
  $\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_n) = \mathcal{A}[\Psi_1(\vec{r}_1, ...\vec{r}_{N-q}) \times \Psi_2(\vec{r}_{N-q+1}, ..., \vec{r}_N)]$

We use COLUMBUS quantum chemistry package[1,2].

EXPANDING A QUANTUM CHEMISTRY WAVEFUNCTION

Expanding Configuration Interaction(CI) Wavefunction :
1. CI wavefunction: $|\psi\rangle = \sum_i c_i |CSF\rangle_i$
2. Configuration state function: $|CSF\rangle = \sum_i \alpha_i |Det\rangle_i$
3. Determinant: $|Det\rangle = \frac{1}{\sqrt{N!}} \sum_i (-1)^{p_i} P_i[\chi_1(1)\chi_2(2).....\chi_n(n)]$
4. Molecular Orbital : $\chi(\vec{r}) = \sum_i \beta_i \phi_i(\vec{r})$
5. Atomic Orbital: $\phi(\vec{r}) = \sum_i a_i G_i(\vec{r})$
where $G_i(\vec{r})$ is a gaussian function.

TRANSITION RATES FOR XUV PHOTO-IONISATION OF O_2

MOTIVATION

- Continuum states are not handled by standard quantum chemistry and evaluation of transitions rates is quite tricky as it involves evaluation of **bound-continuum matrix elements**.
- Recent experiments[3] involve interaction of XUV pulses with gases. A **large number of electronic states** present, makes it difficult to undestand the dynamics.
- An analysis of population **distribution of ionic states** is required.
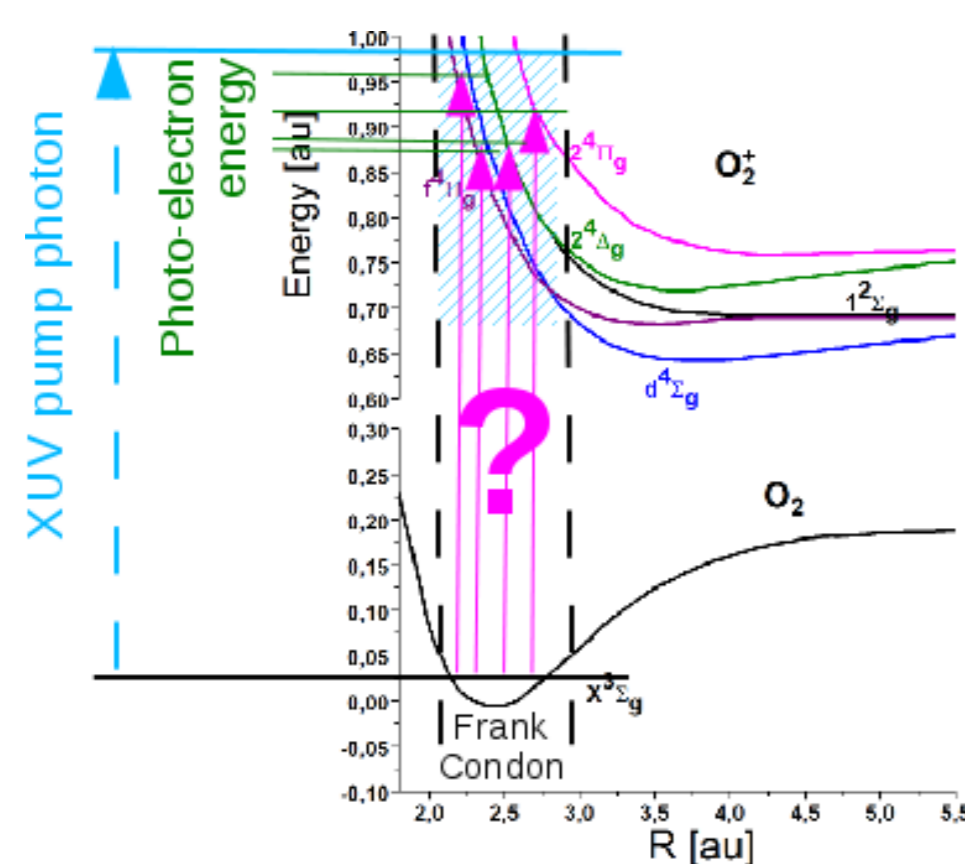
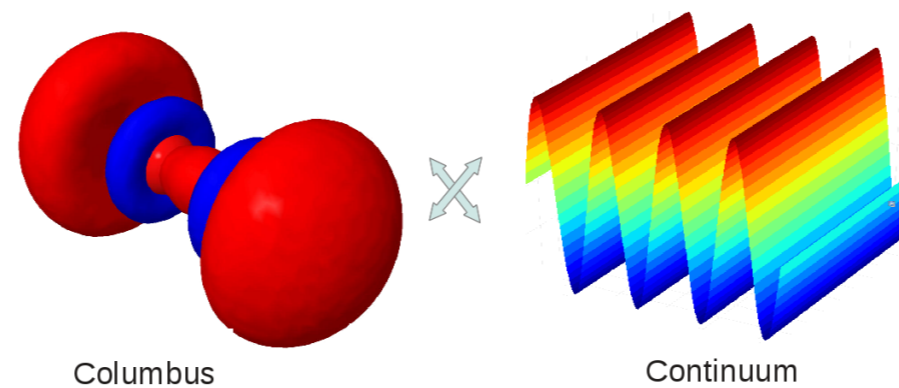## TRANSITION RATE

Given by Fermi's Golden rule:
$T_{i \to f} = \frac{2\pi}{\hbar} |\langle \psi_f | \vec{E}.\vec{r} | \psi_i \rangle|^2 \rho(\epsilon_f)$.
$\psi_i = \Psi_{O_2}(\vec{r}_1, ..., \vec{r}_{16})$
$\psi_f = \mathcal{A}[\Psi_{O_2^+}(\vec{r}_1, ..., \vec{r}_{15}) \times \chi(\vec{r}_{16})]$

PLANE WAVE APPROXIMATION

First approximation: plane wave $\chi_k(\vec{r}) \approx e^{i\vec{k}.\vec{r}}$ for ionized electron and integrate over a k-grid. $T_{i \to f} \propto \int dk^3 |\langle \Psi_{O_2} | \vec{E}.\vec{r} | \mathcal{A}[\Psi_{O_2^+} \chi_k] \rangle|^2$

Columbus   Continuum

IMPROVEMENTS

Replacing plane waves with **scattering solutions** in collaboration with Piero Decleva, Trieste.

RESULTS

Single Photo-Ionization of O_2 with 38eV XUV photon and O_2 and O_2^+ wavefunctions calculated from a cc-pvdz basis.

S.No	Ionization Energy(eV)	Symmetry	Total Transition rate
1	16.1	$^4\Pi_u$	2.36×10^{-7}
2	11.6	$^2\Pi_g$	1.51×10^{-7}
3	17.6	$^4\Sigma_g^-$	8.44×10^{-8}
4	34.3	$^2\Pi_u$	7.67×10^{-9}
5	23.5	$^2\Pi_u$	4.92×10^{-8}
6	19.9	$^2\Sigma_g^-$	4.16×10^{-8}
7	17.2	$^2\Pi_u$	1.78×10^{-8}
8	26.9	$^2\Sigma_u^-$	3.92×10^{-9}
9	24	$^4\Sigma_u^-$	3.805×10^{-9}
10	25	$^2\Pi_g$	3.71×10^{-9}
11	23.7	$^4\Pi_g$	2.91×10^{-9}
12	33.1	$^2\Sigma_u^-$	2.75×10^{-9}
13	34.9	$^2\Pi_u$	2.47×10^{-9}
14	33.01	$^2\Sigma_u^-$	1.95×10^{-9}
15	38.4	$^4\Sigma_g^-$	1.23×10^{-9}

Table 1: List of states in descending order of transition rates

CONCLUSIONS

- Plane Wave Approximation yields transition rates that can be relied upon only upto the **relative order of magnitudes** which would suffice for our purpose.
- Results in Table 1. were used to correlate some of the auto-electron peaks obtained in XUV pump-probe experiments performed by Matthias kling's group at MPQ [4].

FUTURE CALCULATIONS WITH THE INTERFACE

- Static Ionization rates for real systems- atoms and small molecules by solving Schrödinger equation in conjunction with Complex scaling [5,6].
- Single Electron dynamics in molecules.
- Double Ionization in molecules [7, **Poster by A. Zielinski**] .

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