Model for Ionization with Stark Shift Matlab Code

The Weinacht Group

March 21, 2016

Since we are interested in the Stark shifts of and the populations transferred into various ionic states, the model contains the ground neutral state and several ionic states. The energies and the transition dipole moments (TDM) of these states are usually from an *ab initio* electronic structure calculation. In addition to the IR pulse which is used in experiment, an artificial weak VUV pulse is introduced to couple the neutral to the ground ionic state since we do not model the actual ionization process. The model does not include any nuclear dynamics.

1 Pulses

Use 2 pulses, IR and VUV, to model the laser pulse in the lab:

$$E_{IR} = \mathcal{E}_{IR}(t)\frac{(e^{i\omega_{IR}t} + c.c.)}{2} = \mathcal{E}_{IR}(t)cos(\omega_{IR}t) \tag{1}$$

$$E_{VUV} = \mathcal{E}_{VUV}(t)\frac{(e^{i\omega_{VUV}t} + c.c.)}{2} = \mathcal{E}_{VUV}(t)cos(\omega_{VUV}t) \tag{2}$$

For a Gaussian temporal envelope, $\mathcal{E}(t) = \mathcal{E}e^{-\frac{t^2}{2T^2}}$, $FWHM_{field} = 2\sqrt{2ln2}\ T$ and $FWHM_{intensity} = 2\sqrt{ln2}\ T$.

For a cosine square temporal envelope, $\mathcal{E}(t) = \mathcal{E}cos^2(\frac{\pi t}{T})$, $FWHM_{field} = \frac{T}{2}$ and $FWHM_{intensity} = 2acos(0.5^{0.25})\frac{T}{\pi} \approxeq 0.364T$.

In the following, we distinguish two different cases depending on whether the spin-orbit coupling is included in the ab initial calculation the states' energies (compare equations (4) and (16)):

2 Diabatic Basis

The total Hamiltonian consists of 3 parts, the bare Hamiltonian H_0, the spin-orbital coupling H_{SO} and the molecule-field coupling H_{MF}.

$$H = H_0 + H_{SO} + H_{MF} \tag{3}$$

$$H_0 \left|\phi_k\right\rangle = \hbar\omega_k \left|\phi_k\right\rangle \tag{4}$$

$$H_{SO} = S\hbar, \quad \text{s.t.} \quad S_{kj} = \left\langle\phi_k\right| S \left|\phi_j\right\rangle, S_{0j} = S_{k0} = 0 \tag{5}$$

$$H_{MF} = -\vec{\mu}\cdot\vec{E} = -\mu E, \quad \mu_{kj} = \left\langle\phi_k\right| \mu \left|\phi_j\right\rangle \tag{6}$$

where $E = E_{IR} + E_{VUV}$. Write the wave function as:

$$\left|\psi(t)\right\rangle = \tilde{a_0}(t)\left|\phi_0\right\rangle + \sum_{k\neq 0}\tilde{a_k}(t)\left|\phi_k\right\rangle \tag{7}$$

where $|\phi_0\rangle$ is the neutral ground state and $|\phi_i\rangle$'s are excited/ionic states. Substitute (3) and (7) into the Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$ and apply (4) and (5):

$$i\hbar\dot{\tilde{a}}_0(t)|\phi_0\rangle + i\hbar\sum_{k\neq 0}\dot{\tilde{a}_k}(t)|\phi_k\rangle = (\hbar\omega_0 - \mu E)\tilde{a_0}(t)|\phi_0\rangle + \sum_{k\neq 0}(\hbar\omega_k - \mu E + S\hbar)\tilde{a_k}(t)|\phi_k\rangle \tag{8}$$

To project onto eigenstates by left-multiplying by eigen-bra $\langle\phi_k|$:

$$\dot{\tilde{a}}_0(t) = -i\omega_0\tilde{a}_0 + i\sum_{k\neq 0}\frac{\mu_{0k}}{\hbar}(E_{VUV} + E_{IR})\tilde{a}_k \tag{9}$$

$$\dot{\tilde{a}}_{k\neq 0}(t) = -i\omega_k\tilde{a}_k + i\frac{\mu_{k0}}{\hbar}(E_{VUV} + E_{IR})\tilde{a}_0 + i\sum_{j\neq k}\frac{\mu_{kj}}{\hbar}E_{IR}\tilde{a}_j - i\sum_{j\neq k}S_{kj}\tilde{a}_j \tag{10}$$

Now let $\tilde{a}_k(t) = a_k(t)e^{-i\omega_k t}$ (this is equivalent to going to the interaction picture) and get:

$$\dot{a}_0(t) = \frac{i}{2\hbar}\sum_{k\neq 0}\mu_{0k}[\mathcal{E}_{VUV}(t)e^{i\omega_{VUV}t} + 2\mathcal{E}_{IR}cos(\omega_{IR}t)]a_k(t)e^{-i\omega_{k0}t} \tag{11}$$

$$\begin{aligned}\dot{a}_{k\neq 0} =& \frac{i}{2\hbar}\mu_{k0}[\mathcal{E}_{VUV}(t)e^{-i\omega_{VUV}t} + 2\mathcal{E}_{IR}cos(\omega_{IR}t)]a_0(t)e^{-i\omega_{0k}t} \\ &+ \frac{i}{\hbar}\sum_{j\neq k}\mu_{kj}\mathcal{E}_{IR}cos(\omega_{IR}t)a_j(t)e^{-i\omega_{jk}t} \\ &- i\sum_{j\neq k}S_{kj}a_j(t)e^{-i\omega_{jk}t}\end{aligned} \tag{12}$$

where

$$\omega_{kj} = \omega_k - \omega_j \tag{13}$$

We have dropped fast-rotating terms, $\mathcal{E}(t)e^{\pm i\omega_{VUV}t}$, since we have set $\omega_{VUV} \approx \omega_{ko}$.

Here, states $|\phi_k\rangle$'s are eigenstates of H_0. S_{kj} is a complex matrix. The final (after the pulse) Hamiltonian is $H_0 + H_{SO}$. To obtain the populations in the final eigenstates, one first diagonalizes the final Hamiltonian $P^{-1}(H_0 + H_{SO})P = D$ to obtain matrix P, then performs a change of basis, $a \mapsto P^{-1}a$.

3 Adiabatic Basis

The total Hamiltonian consists of 3 parts, the bare Hamiltonian H_0, the spin-orbital coupling H_{SO} and the molecule-field dipole-coupling H_{MF}. Working in the eigenspace of $H_0 + H_{SO}$:

$$H = H_0 + H_{SO} + H_{MF} \tag{14}$$

$$H_{MF} = -\vec{\mu}\cdot\vec{E} \tag{15}$$

$$(H_0 + H_{SO})|\phi_i\rangle = \hbar\omega_i|\phi_i\rangle \tag{16}$$

Write the wave function as:

$$|\psi(t)\rangle = \tilde{a_0}(t)|\phi_0\rangle + \sum_{i\neq 0}\tilde{a_i}(t)|\phi_i\rangle \tag{17}$$

where $|\phi_0\rangle$ is the neutral ground state and $|\phi_i\rangle$'s are excited/ionic states. Substitute (14) and (17) into Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$ and project onto eigenstates:

$$\dot{\tilde{a}}_0(t) = -i\omega_0\tilde{a}_0 + \sum_{i\neq 0}(E_{VUV} + E_{IR})\tilde{a}_i \tag{18}$$

$$\dot{\tilde{a}}_{i\neq 0}(t) = -i\omega_i\tilde{a}_i + i\frac{\mu_{i0}}{\hbar}(E_{VUV} + E_{IR})\tilde{a}_0 + i\sum_{j\neq i}\frac{\mu_{ij}}{\hbar}E_{IR}\tilde{a}_j \tag{19}$$

Now let $\tilde{a}_i(t) = a_i(t)e^{-i\omega_i t}$ and get:

$$\dot{a}_0(t) = \frac{i}{2\hbar}\sum_{i\neq 0}\mu_{0i}[\mathcal{E}_{VUV}(t)e^{i\omega_{VUV}t} + 2\mathcal{E}_{IR}cos(\omega_{IR}t)]a_i(t)e^{-i\omega_{i0}t} \tag{20}$$

$$\begin{aligned}\dot{a}_{i\neq 0} =& \frac{i}{2\hbar}\mu_{i0}[\mathcal{E}_{VUV}(t)e^{-i\omega_{VUV}t} + 2\mathcal{E}_{IR}cos(\omega_{IR}t)]a_0(t)e^{-i\omega_{0i}t} \\ &+ \frac{i}{\hbar}\sum_{j\neq i}\mu_{ij}\mathcal{E}_{IR}cos(\omega_{IR}t)a_j(t)e^{-i\omega_{ji}t}\end{aligned} \tag{21}$$

where

$$\omega_{ij} = \omega_i - \omega_j \tag{22}$$

We have dropped fast-rotating terms, $\mathcal{E}(t)e^{\pm i\omega_{VUV}t}$, since we have set $\omega_{VUV} \approx \omega_{io}$.