Quantum Dynamics Course

Numerical Project

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The Shin-Metiu model system

The Shin-Metiu model system I

The system comprises donor and acceptor ions which are fixed at a distance $L = 19.0a_0$, and a proton and an electron that are free to move in one dimension along the line connecting the donor-acceptor complex (see Fig. 4). This model is very flexible and, based on the parameter regime chosen, can give rise to a number of challenging situations where electron-nuclear correlations play a crucial role in the dynamics.

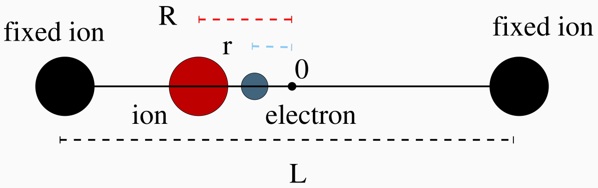


Figure 1: Schematic representation of the Shin-Metiu model. Two ions are fixed (in black) and a third one (in red) and an electron (in blue) are free to move in one dimension.

The Shin-Metiu model system II

The total Hamiltonian for the system is,

$$\hat{H}(r,R) = -\frac{1}{2m}\frac{\partial^2}{\partial r^2} - \frac{1}{2M}\frac{\partial^2}{\partial R^2} + \hat{W}(r,R), \tag{1}$$

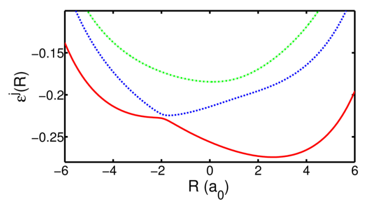
where m is the electron mass, and M is the proton mass. The coordinates of the electron and the mobile ion are measured from the center of the two fixed ions, and are labeled r and R, respectively. The full electron-nuclear potential is depicted in Fig. (**??**) and reads:

$$\begin{aligned}\hat{W}(r,R) = \frac{1}{|\frac{L}{2}-R|} + \frac{1}{|\frac{L}{2}+R|} \quad &- \quad \frac{\mathrm{erf}\left(\frac{|R-r|}{R_f}\right)}{|R-r|} \\ &- \quad \frac{\mathrm{erf}\left(\frac{|r-\frac{L}{2}|}{R_r}\right)}{|r-\frac{L}{2}|} - \frac{\mathrm{erf}\left(\frac{|r+\frac{L}{2}|}{R_l}\right)}{|r+\frac{L}{2}|}, \end{aligned} \tag{2}$$

where erf() represents the error function.

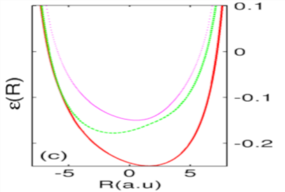
Parameter regime I

1. ($R_f = 5a_0$, $R_l = 4a_0$, $R_r = 3.1a_0$, and $t_{end} = 30$fs). In this parameter regime the ground BOPES, $\epsilon_{BO}^{(1)}$, is strongly coupled to the first excited adiabatic state, $\epsilon_{BO}^{(2)}$, around $R_{ac} = -2a_0$. The coupling to the rest of the BOPESs is negligible.
2. We suppose the system to be initially uncorrelated, as if prepared by a short laser pulse, in the first excited BO electronic state, $\epsilon_{BO}^{(2)}$, while the initial nuclear wave function is a Gaussian wavepacket, with $\sigma = 1/\sqrt{2.85}$, centered on the equilibrium geometry of the ground BO state, at $R = -4.0a_0$.



Parameter regime II

1. ($R_f = 7a_0$, $R_l = 4.4a_0$, $R_r = 3.1a_0$, and $t_{end} = 20$fs). In this parameter regime the ground BOPES $\epsilon_{BO}^{(1)}$ is strongly coupled to the first excited adiabatic state, $\epsilon_{BO}^{(2)}$, within an extended region defined by $R < 4a_0$. In addition, there is a moderate coupling between the second BOPES, $\epsilon_{BO}^{(2)}$, and the third BOPES, $\epsilon_{BO}^{(3)}$, for $R > 2a_0$. The coupling to the rest of the BOPESs is negligible.
2. We suppose the system to be initially uncorrelated, as if prepared by a short laser pulse, in the first excited BO electronic state, $\epsilon_{BO}^{(2)}$, while the initial nuclear wave function is a Gaussian wavepacket, with $\sigma = 1/\sqrt{2.85}$, centered on the equilibrium geometry of the ground BO state, at $R = -7.0a_0$.



Static properties

- Calculate the full interaction potential:

$$\hat{W}(r, R) \tag{3}$$

- Calculate the BOPESs and adiabatic electronic states:

$$\hat{\mathcal{H}}_{el}(r; R)\Phi_\gamma(r; R) = E^{el}_\gamma(R)\Phi_\gamma(r; R) \tag{4}$$

- Calculate also the second order non-adiabatic couplings

$$\mathcal{S}_{\gamma\zeta}(R) = \int dr\ \Phi^*_\zeta(r; R)\left[-\sum_A \frac{\hbar^2}{2M_A}\nabla^2_A\right]\Phi_\gamma(r; R) \tag{5}$$

Dynamical properties

- Calculate the adiabatic populations:

$$P_m(t) = \int dR |\chi^{(m)}(R,t)|^2 \tag{6}$$

- Calculate the decoherence dynamics:

$$D_{nm}(t) = \int dR |\chi^{(m)}(R,t)|^2 |\chi^{(n)}(R,t)|^2 \tag{7}$$

- Calculate the reduced nuclear and electronic probability densities:

$$\rho(R,t) = \int dr |\Psi(t)|^2 \tag{8}$$

$$\rho(r,t) = \int dR |\Psi(t)|^2 \tag{9}$$

For help

1. Parameter regime I: PHYS. REV. MAT. 3, 023803 (2019)
2. Parameter regime II: PHYS. REV. LETT. 113, 083003 (2014)