Coupled electron-nuclear quantum dynamics through and around a conical intersection

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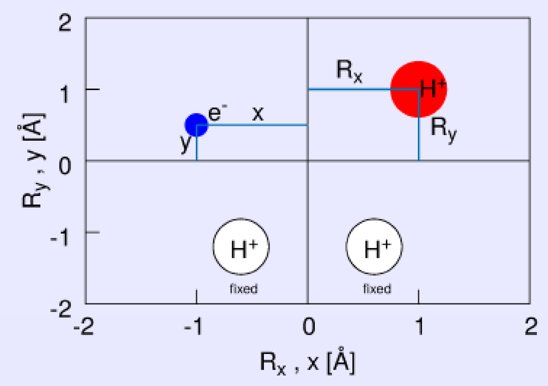
Abstract

In solving the time-dependent Schrödinger equation for a coupled electron-nuclear system, we study the motion of wave-packets in a model which exhibits a conical intersection (CoIn) of two adiabatic potential energy surfaces. Two different situations are studied. In the first case, an efficient non-adiabatic transition takes place while the wave packet passes the region of the CoIn. It is demonstrated that during these times, the nuclear probability density retains its Gaussian shape and the electronic density remains approximately constant. Secondly, a dynamics is regarded where non-adiabatic transitions do not take place, and the nuclear dynamics follows a circle around the location of the CoIn. During this motion the electronic density is shown to rotate. The comparison to the Born-Oppenheimer nuclear dynamics reveals the geometrical phase being associated with the circular motion. This phase is clearly revealed in the time-dependence of autocorrelation functions and the resulting spectra obtained from the two calculations.

2D Shin-Metiu-Model[1]

$$\hat{H}(\mathbf{R},\mathbf{r}) = \frac{\hat{\mathbf{p}}_r^2}{2} + \frac{\hat{\mathbf{P}}_R^2}{2M} - \frac{1}{\sqrt{a+|\mathbf{r}-\mathbf{R}|}} - \frac{1}{\sqrt{a+|\mathbf{r}-\mathbf{R}_1|}} - \frac{1}{\sqrt{a+|\mathbf{r}-\mathbf{R}_2|}} + \frac{1}{\sqrt{b+|\mathbf{R}_1-\mathbf{R}_2|}} + \frac{1}{\sqrt{b+|\mathbf{R}-\mathbf{R}_1|}} + \frac{1}{\sqrt{b+|\mathbf{R}-\mathbf{R}_2|}} + \left(\frac{R}{R_0}\right)^4$$



Dynamics

coupled electron-nuclear motion

$$i\frac{\partial}{\partial t}\Psi(x,y,R_x,R_y,t) = \hat{H}(x,y,R_x,R_y)\,\Psi(x,y,R_x,R_y,t)$$

initial condition

$$\Psi(x,y,R_x,R_y,t_0) = N\,\underbrace{e^{-\beta(R_y-R_{y0})^2}e^{-\beta(R_x-R_{x0})^2}}_{Gaussian} \cdot \underbrace{e^{-iPR_x}}_{Momentum} \cdot \underbrace{\varphi_n(x,y;R_x,R_y)}_{adiabatic\ state}$$

$$\rho_{nuc}(\mathbf{R},t) = \int |\psi(\mathbf{r},\mathbf{R},t)|^2\, d\mathbf{r}$$

$$\rho_{el}(\mathbf{r},t) = \int |\psi(\mathbf{r},\mathbf{R},t)|^2\, d\mathbf{R}$$

$$V(\mathbf{r},t) = V(\mathbf{r},\underline{\mathbf{R(t)}})$$

BO approx. nuclear motion

$$i\frac{\partial}{\partial t}\psi_n(R_x,R_y,t) = \hat{H}_n(R_x,R_y)\,\psi_n(R_x,R_y,t)$$

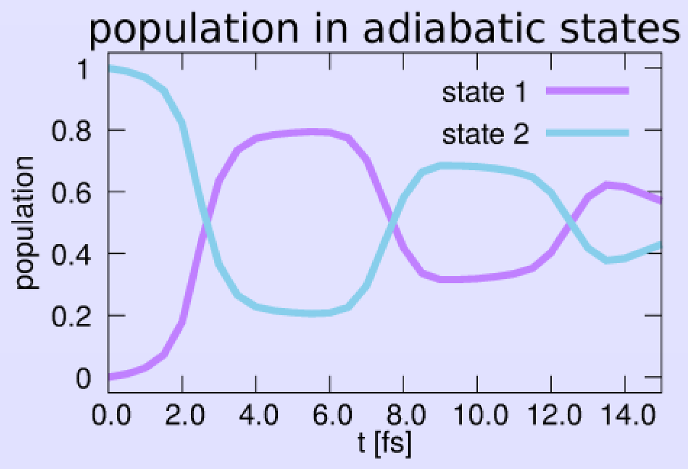
$$\hat{H}_n(x,y,R_x,R_y) = \hat{T}(R_x,R_y) + V_n(R_x,R_y)$$

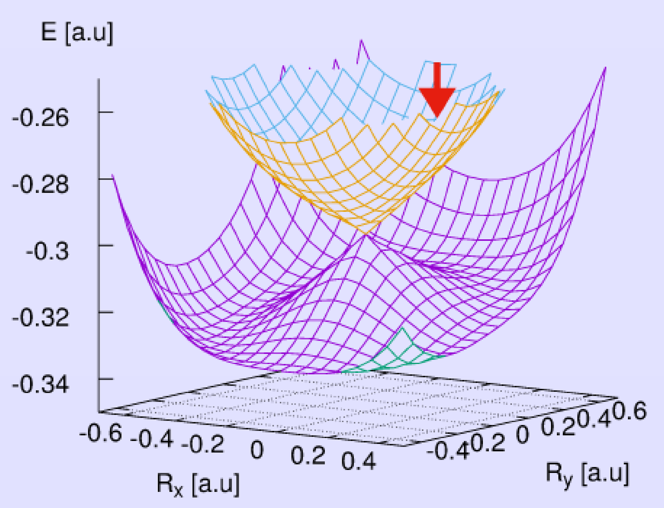
initial condition

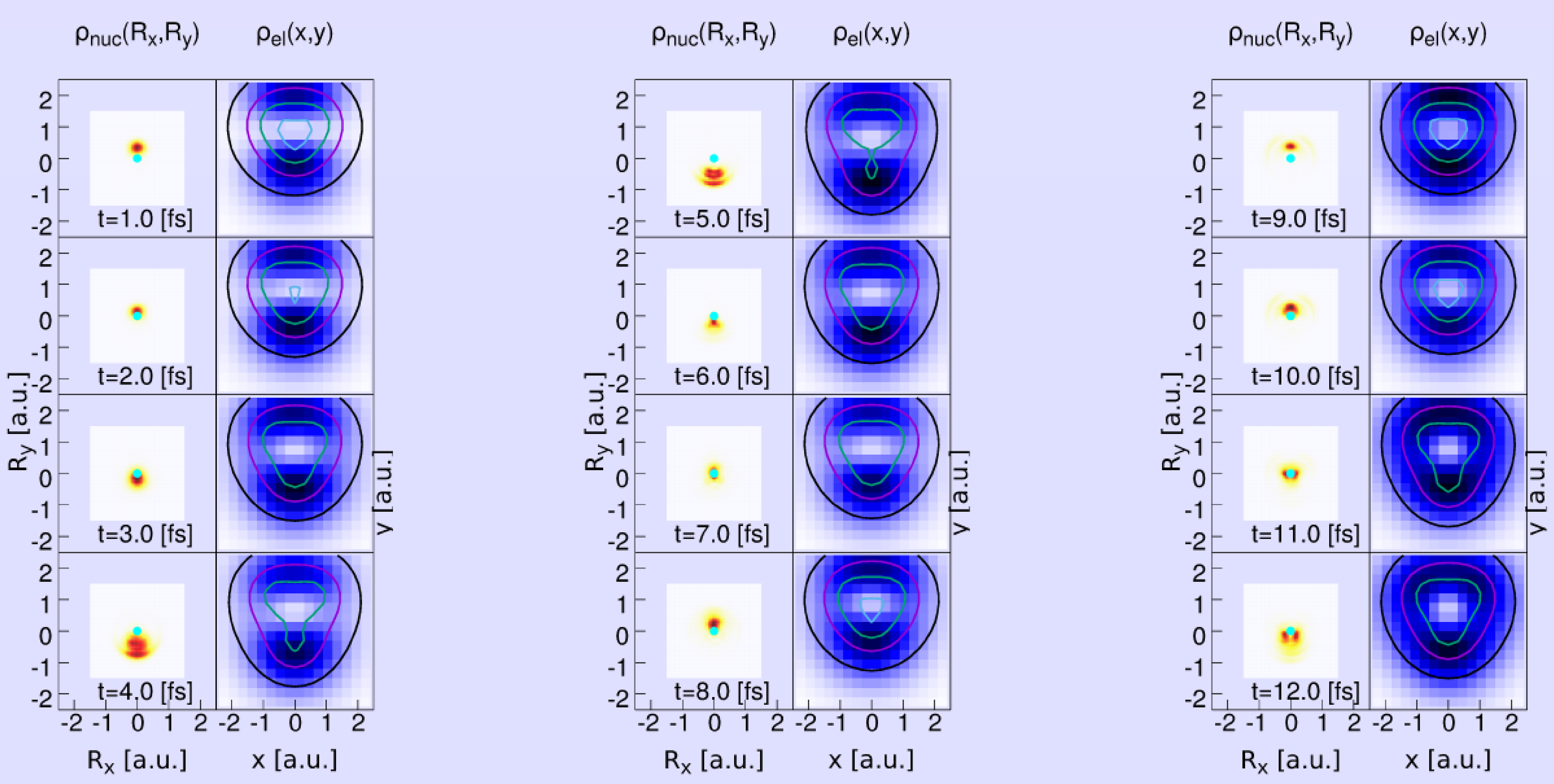
$$\psi_n(R_x,R_y,t_0) = N\,\underbrace{e^{-\beta(R_y-R_{y0})^2}e^{-\beta(R_x-R_{x0})^2}}_{Gaussian} \cdot \underbrace{e^{-iPR_x}}_{Momentum}$$

$$\varrho_n(\mathbf{R},t) = \int |\psi(\mathbf{r},\mathbf{R},t)|^2\, d\mathbf{r}$$

Diabatic Motion: Passing the CoIn

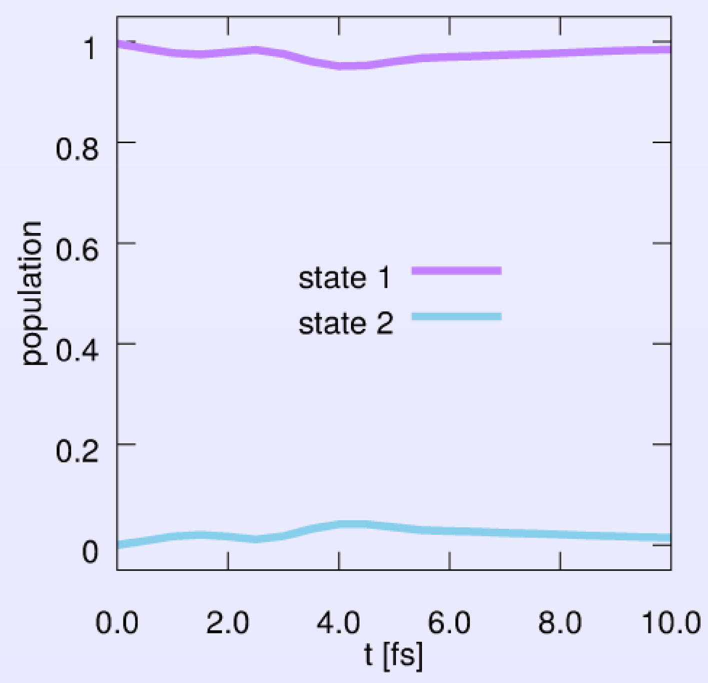


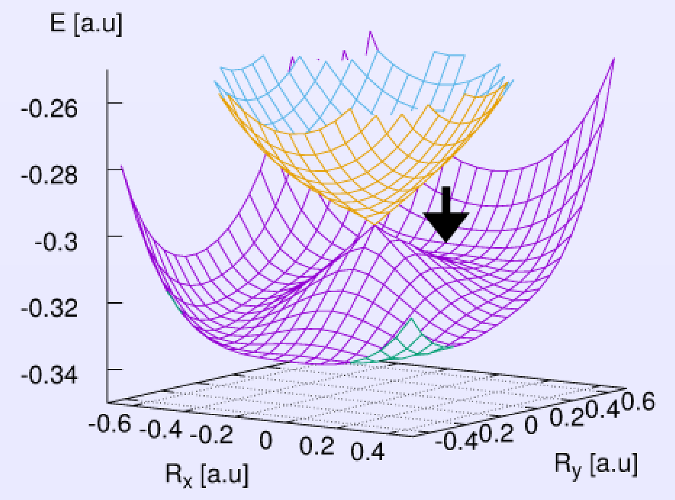


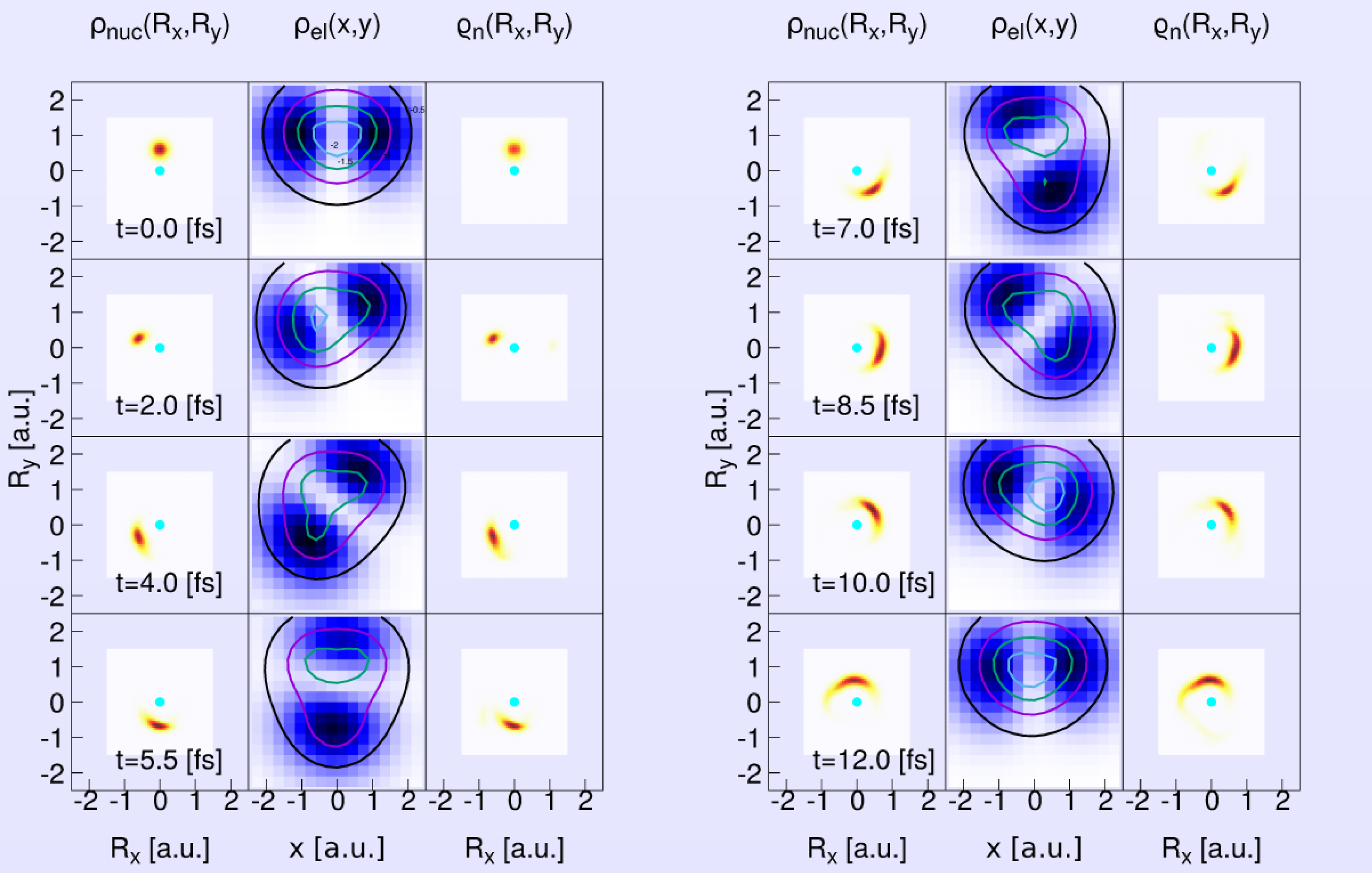


- **Diabatic motion: Electronic density stays stationary.**
- **Passing the region of the CoIn the nuclear Gaussian wave-packet retains it's shape.**
- **Efficient population transfer between adiabatic electronic states in the region of CoIn.**

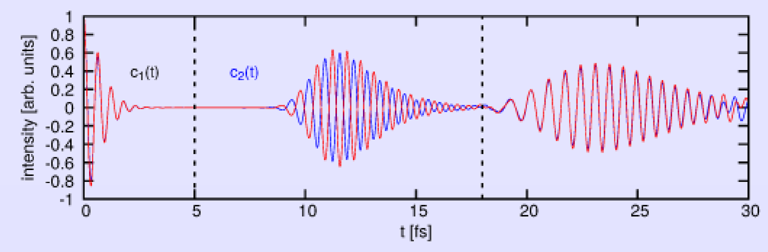
Adiabatic Motion Around CoIn







- **0 - 5.5 fs: Nuclear wave packet circles CoIn. Electronic density rotates as nuclear density rotates around CoIn. Electronic density shows a change in character from p_x to p_y-type.**
- **7 - 12 fs: Nuclear wave packet continues to circles CoIn. Electronic density rotates further and shows a change in character from p_y to $-p_x$-type again.**
- **BO-density is identical to exact density.**



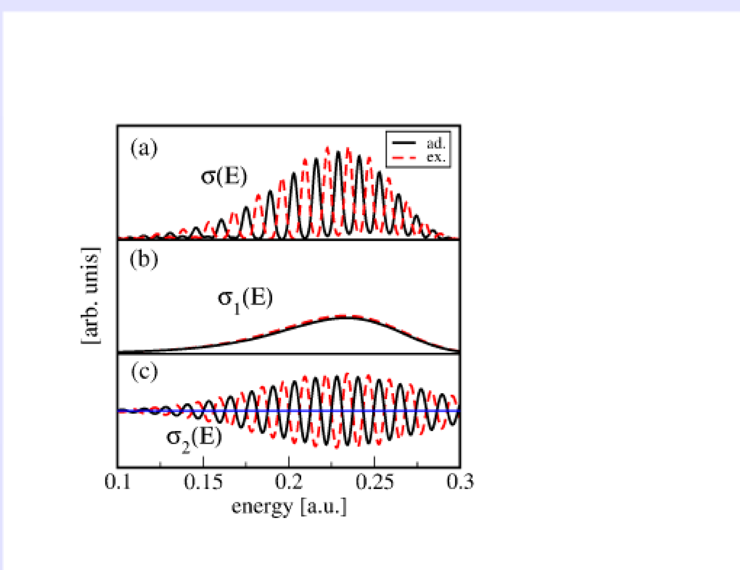
(f) Autocorrelation functions

$$c^{(ex)}(t) = \langle \Psi(x,y,R_x,R_y,t=0)\,|\,\Psi(x,y,R_x,R_y,t)\rangle$$

$$c^{(ex)}(t) = \langle \psi_1(x,y,R_x,R_y,t=0)\,|\,\psi_1(x,y,R_x,R_y,t)\rangle$$

$$T_1 \approx 0\,fs: \quad c_1^{(ad)}(t) = c_1^{(ex)}(t)$$

$$T_2 \approx 12\,fs: \quad c_2^{(ad)}(t) = -c_2^{(ex)}(t) \rightarrow \text{phase}$$



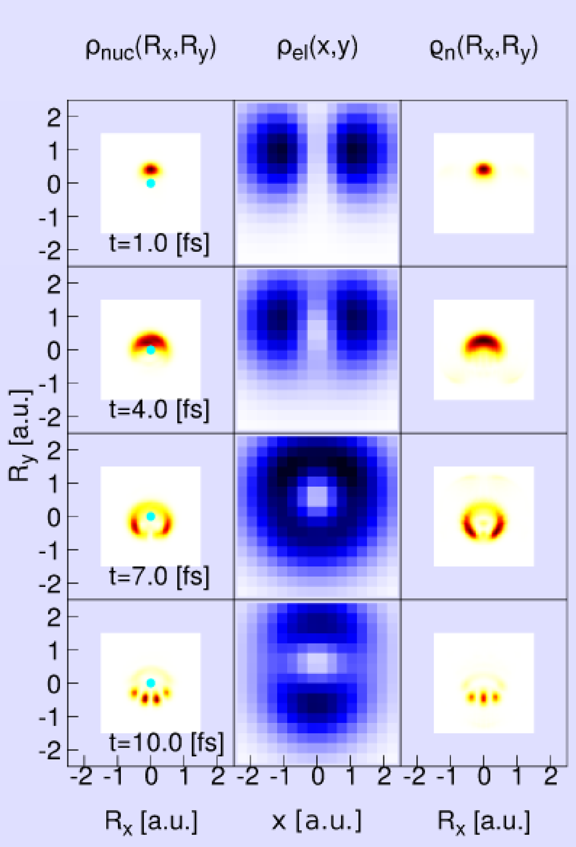
(g) Spectra

$$\sigma^j(E) = \int dt\, e^{iEt}\, c^{(j)}(t)$$

$$\sigma^{(ex)}(E) = \sigma_1(E) + \sigma_2(E)$$

$$\sigma^{(ad)}(E) = \sigma_1(E) - \sigma_2(E)$$

$\rightarrow$ spectral shift



(h) Adiabatic dynamic around CoIn

Conclusion

- For multiple passages of a nuclear wave packet through a CoIn neither the electronic nor the nuclear density exhibit substantial changes.
- For a surrounding of a CoIn by a nuclear wave packet, where no population transfer takes place, the electronic density rotates in phase with the nuclear motion but only with half of the angular frequency. This leads to a geometrical phase.

Acknowledgement

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References

[1] Min S. K., Abedi A., Kim K. S., Gross E.K.U. *Phys. Rev. Lett.* 113, 263004 (2014).