2D spectroscopy of coupled electronic-nuclear motion

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We theoretically investigate the photon-echo spectroscopy for a model [1] which involves the coupled (c) quantum dynamics of an electron and a nucleus. This model serves to illustrate the limiting cases of an adiabatic and a diabatic motion [2]. In the first case, an interpretation of the two-dimensional (2D) spectra is feasible using the Born-Oppenheimer (BO) approximation is feasible. It is then possible to identify pure vibrational coherences in fixed electronic states. For the case of strong non-adiabatic coupling, i.e., a diabatic motion, the 2D-spectra reveal a complicated structure which is related to the breakdown of the BO-approximation. The spectra are then dominated by vibronic coherences.

Hamiltonian

\[ \hat{H} = \frac{1}{2M} \ddot{R}^2 + V(r, R) + \hat{W}(R, r, t) \]

\[ W(R, r, t) = -\left( -\xi + R \right) E^2(t) \]

Born-Oppenheimer treatment

\[ \hat{H} = \left( \begin{array}{cc} V(r, R) & \hat{W}(R, r, t) \hat{W}^*(R, r, t) \hat{W}(R, r, t) \end{array} \right) \]

\[ \hat{T} = \left( \begin{array}{cc} \hat{T}_1 & \hat{T}_2 \end{array} \right) \]

Calculation of 2D spectra

Third-order polarization (\( -\chi_k + k_x + \chi_k \cdot \text{direction} \))

\[ p_{P}^{(3)}(t, r) = \sum_{n=1}^{N} \langle \phi^{(m-1)} | | \phi^{(n+1)} \rangle \langle \phi^{(n+1)} | | \phi^{(n)} \rangle \langle \phi^{(n)} | | \phi^{(n-1)} \rangle \langle \phi^{(n-1)} | \rangle \]

\[ p_{P}^{(3)}(t, r) = \langle \phi^{(n)} \rangle \langle \phi^{(n-1)} \rangle | \phi^{(n)} \rangle \langle \phi^{(n-1)} \rangle \langle \phi^{(n)} | | \phi^{(n-1)} \rangle \langle \phi^{(n-1)} | \rangle \]

2D spectrum

\[ S_\gamma(E_x, E_y) = \int dt \int d\tau e^{-i \omega_{\chi} t - i E_y \tau} p_{P}^{(3)}(t, r) \]

\[ (\phi^{(n)} \phi^{(n-1)}, t) \]

\[ (\phi^{(n)} \phi^{(n+1)}, t) \]

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\[ (\phi^{(n)} \phi^{(n+1)}, t) \]

\[ (\phi^{(n)} \phi^{(n-1)}, t) \]

Conclusion

Vibrational coherences in fixed electronic states can be identified if the Born-Oppenheimer approximation is valid. This is no longer possible in the case of strong non-adiabatic coupling.

References