

Introduction to Beyond the Born-Oppenheimer Approximation: Ultrafast Time-Dependent Electronic and Nuclear Dynamics

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Beyond the Born-Oppenheimer Approximation: Ultrafast Time-Dependent Molecular Dynamics

F. Remacle^{a,b} and R. D. Levine^{b,c}

a. Theoretical Physical Chemistry, UR MolSys, B6c, Université de Liège, B4000 Liège, Belgium

b. Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

c. Department of Molecular and Medical Pharmacology, David Geffen School of Medicine and Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095

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In the post Born Oppenheimer regime the fast and light electrons in a molecule do not instantaneously adjust to the positions of the atoms nor are they in a stationary state. It is a regime that is complementary to high resolution spectroscopy. Events are resolved in time and not in the frequency domain and interference of states is central. We derive and compute the force between the atoms taking the interference of electronic states into full consideration. The new regime is made possible by the availability of few femtoseconds and attosecond laser pulses. It is robust with respect to random initial orientations. We introduce the theoretical methodologies and the new concepts used to describe and compute the novel chemical processes driven by attosecond electronic excitation and to compact the results. We examine how to initiate, probe and control using dynamics on a grid with special reference to state selectivity and specificity, stereodynamics, entanglement, singular value decomposition and to quantum computing.

Introduction

The post Born Oppenheimer regime is a new regime in chemical physics. It is made possible by tremendous technical developments¹⁻⁸ that opened up an ultrashort, attosecond, time span that is complementary to high resolution spectroscopy. One follows the system in time and does not resolve it in the frequency domain. AttoPhotoChemistry is a post Born Oppenheimer chemistry where, immediately after the ultrafast perturbation, the atoms do not move and the dynamics of the electrons is the subject of study.⁹ In this brief time interval we create an electronic non-stationary wave packet – a coherent superposition of electronic states. After a very short time interval the nuclei begin to respond to this unusual coherent dynamics. In this new PhotoChemistry we seek to understand and explore how the non-stationary electronic state can tune and guide the subsequent motion of the nuclei.¹⁰

In this chapter we review the basic tools that are currently available to a theoretical dynamicist working in this challenging area. The first to respond to an atto- or few femto-seconds laser pulse are the electrons. Since the nuclei had no time to effectively move, the electrons are in a state that is not in equilibrium with the location of the nuclei. So a possible first need is a description of the wave function of the electrons in their intrinsic, time evolving, state. Alternatively one can seek a strictly post Born-Oppenheimer approach, for example treating the motion of the electrons and the nuclei on equal footing. As an approach that seeks a high accuracy this is realistic only for very few body systems such as LiH where there is one nuclear coordinate and two valence electrons¹¹⁻¹³. As a practical proposition, using Gaussian wave functions as a basis set for *both* electrons and nuclei, NEO (nuclear-electronic orbitals), has proved to be a very promising tool¹⁴. An intermediate description that is especially useful for polyatomic molecules combines a self-consistent approach to the dynamics of the vibrations¹⁵ and a configuration interaction for the electronic states, MCTDH (multiconfiguration time-dependent Hartree).^{16, 17} A more recently proposed approach^{18, 19} seeks to define an analog of a classical probability of the electronic density at a given nuclear positions $\mathbf{R}$ and time t . One defines an electronic wave function that satisfies $\int d\mathbf{r} |\phi_{\mathbf{R}}(\mathbf{r}, t)|^2 = 1$, where $\mathbf{r}$ is the set of electronic coordinates. The total wave function is written as $\psi(\mathbf{r}, \mathbf{R}, t) = \phi_{\mathbf{R}}(\mathbf{r}, t)\chi(\mathbf{R}, t)$ and because of the normalization of the electronic part, $|\chi(\mathbf{R}, t)|^2 = \int d\mathbf{r} |\psi(\mathbf{r}, \mathbf{R}, t)|^2$, the nuclear density $|\chi(\mathbf{R}, t)|^2$ has thereby the interpretation of the probability density to find the nuclei at about $\mathbf{R}$ at the time t . This elegant approach has however the significant consequence that the nuclei move in a time dependent

potential energy, the expectation value of the electronic Hamiltonian in the time dependent electronic state $\phi_{\mathbf{R}}(\mathbf{r}, t)$. Born and Oppenheimer used a time independent electronic basis. They wrote a stationary wave function, sometimes known as the Born-Huang form²⁰ as $\psi(\mathbf{r}, \mathbf{R}) = \varphi(\mathbf{r}; \mathbf{R})\chi(\mathbf{R})$. The key point is that $\varphi(\mathbf{r}; \mathbf{R})$ is an *adiabatic* electronic state, the ground state stationary solution of the Schrödinger equation for the electronic Hamiltonian, H_{el} , at a fixed nuclear configuration $\mathbf{R}$, $H_{el}\varphi(\mathbf{r}; \mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r}; \mathbf{R})$. It is this stationary equation that allows us to say that the electrons instantaneously adjust to the local position of the nuclei. By substituting the form of the wave function in the full Schrödinger equation, the $\mathbf{R}$ -dependent eigenvalue $E(\mathbf{R})$ is then found to be the potential for the motion of the nuclei. Actually, there is a small extra term in the potential due to the dependence of the electronic wave function on the nuclear coordinates, $\mathcal{T}(\mathbf{R}) = \langle \varphi(\mathbf{r}; \mathbf{R}) | T_{nuc} | \varphi(\mathbf{r}; \mathbf{R}) \rangle$ where T_{nuc} is the kinetic energy operator of the nuclei. In higher precision work, including this term or not can make a real difference.²¹ By the identification of a potential that depends on the nuclear configuration, a potential that can have local, possibly deep, minima, Born and Oppenheimer showed how quantum mechanics, that favors delocalization in order to minimize the kinetic energy, can describe the localized shape of molecules in their ground state. When an adiabatic approximation is valid the potential can also account for stereochemistry, in particular the preferential cone of approach of reactants.²²

The adiabatic approximation can be valid also for an excited electronic state provided that its potential energy $E(\mathbf{R})$ is well separated from the potential of any other state in the region of interest in the configuration space of the nuclei. This can and does happen but quite often it does not. Early on, Landau and Zener and then Teller have shown that there can be localized regions where, for electronically excited states, the adiabatic approximation fails completely.^{20, 23, 24} The adiabatic approximation can also fail between the ground state and an excited state that gets close in energy. The coupling between different adiabatic electronic states is the off-diagonal matrix elements of the kinetic energy operator of the nuclei, $\mathcal{T}_{nm}(\mathbf{R}) = \langle \varphi_n(\mathbf{r}; \mathbf{R}) | T_{nuc} | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$, where the integration in the matrix element is over the electronic coordinates. The corresponding stationary state is the Born-Huang form^{20, 25} $\psi(\mathbf{r}, \mathbf{R}) = \sum_n \varphi_n(\mathbf{r}; \mathbf{R})\chi_n(\mathbf{R})$, where the different electronic states are eigenstates of the electronic Hamiltonian, H_{el} , $H_{el}\varphi_n(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R})\varphi_n(\mathbf{r}; \mathbf{R})$ and as such are orthogonal. The terms in the expansion are coupled by the non-adiabatic matrix element above.

Our introduction is a primer of the next stage, an overview of the time dependent wave function and its implications when two or more electronic states are coupled. Of course, we build on the highly developed technology of electronic structure theory as introduced and elaborated in other chapters in this volume. The adiabatic electronic states will continue to serve for us as a central basis for the description of excited electronic states. We will also use the often convenient basis of diabatic electronic states. Strictly mathematically²⁶ such states are not easy to define or compute. The pragmatic truth is that one often uses them on a more intuitive basis. The non-adiabatic coupling is strong when the electronic wave function varies rapidly with the changes in the position of the nuclei. So a practical diabatic state is a state that changes smoothly. As an example consider NaI, the molecule for which Zewail²⁷ could demonstrate experimentally the localized region of effective non-adiabatic coupling. The two diabatic states are the ionic Na^+I^- and the strictly covalent NaI state. The adiabatic ground state is a coherent superposition of these two states, with the ionic state contributing more near the equilibrium position and the covalent state increasing in contribution as the bond is extended. The ground state adiabatically dissociates into neutral atoms. Vice versa for the adiabatic excited state.

We will discuss a generalization of the Born-Huang approach for non stationary states. In other words we will discuss a quantum dynamical approach. It is important however to emphasize that a semiclassical approach to describing the dynamics of the nuclei has many potential advantages and indeed it has been very extensively developed and applied. One reason why, is the very localization in space of the region of effective non-adiabatic coupling. Local has a classical ring to it. So the simple classical picture is that of the atoms moving along a classical trajectory. As the atoms approach a localized region of coupling one estimates the probability that they will undergo a non-adiabatic transition or ‘hop’ onto a trajectory moving on a different adiabatic state. The probability of such a hop can be estimated by the Landau-Zener formula²⁸ or its refinements²⁹. A complete picture³⁰ of such surface hopping requires averaging over an ensemble of trajectories so as to sample a distribution of initial conditions. Heller^{31, 32} has shown how to approximate the quantum mechanical dynamics by representing the motion of the atoms as a Gaussian wave packet whose center moves along a classical trajectory. One can keep the width of the wave packet constant or, better, enable it to adjust to the local curvature of the potential. Using a Gaussian wave packet for the nuclear wave function³³ allows accounting for the finite width of the transition region, for recrossing and coherence and isotope effects³⁴. A major and

practical refinement is to allow quantum dynamics to determine where and when to spawn a new Gaussian on the other adiabatic state³⁵. This allows for multiple spawning events and it can be interlaced effectively with ab-initio electronic structure computations³⁶.

There are many clear advantages for working in an adiabatic basis for the electronic states. Of course, computing the non-adiabatic coupling requires a direct differentiation of the electronic states with respect to the nuclear displacements or an analytical gradient method³⁷. One practical way of avoiding a numerical differentiation is the use of the, so called, hypervirial theorem. To determine $\langle \varphi_n(\mathbf{r}; \mathbf{R}) | \partial / \partial R | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$ where the integration in the matrix element is over the electronic coordinates we compute $\langle \varphi_n(\mathbf{r}; \mathbf{R}) | [\partial / \partial R, H_{el}] | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$. This matrix element can be computed in two ways. One is to compute the commutator itself leading to $\langle \varphi_n(\mathbf{r}; \mathbf{R}) | (\partial H_{el} / \partial R) | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$. After analytically differentiating the electron-nuclear, one electron terms in H_{el} , this matrix element can be computed by the methods of quantum chemistry. The second computation is by writing the commutator as a difference between two terms, leading to $(E_m(\mathbf{R}) - E_n(\mathbf{R})) \langle \varphi_n(\mathbf{r}; \mathbf{R}) | (\partial / \partial R) | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$. The derivative coupling is therefore particularly large when the two adiabatic energies are near to one another. As already mentioned, when the non-adiabatic coupling is not weak it may be advantageous to work in a diabatic electronic basis where the electronic states do not vary appreciably with the nuclear displacements. A recent example³⁸ is the lowest optically single photon accessible excited electronic states of N₂. From the ground state one accesses excited singlet adiabatic states that are strongly coupled. It is therefore convenient to use diabatic states, two are low Rydberg-like and one is a valence excited state^{39, 40}. The diabatic states diagonalize, at least to a high degree, the nuclear kinetic energy. But they are coupled by the electronic Hamiltonian, a smoothly varying function of the nuclear coordinates.

2. Photoinduced Quantum Molecular Dynamics on Several Coupled Electronic States

To introduce the dynamics of the nuclei in a multi-electronic wave function we will use the simple case of one nuclear coordinate. We aim to use an approach that mimics the classical picture of propagating along this coordinate in time. Of course, we use a quantum mechanical approach so that the wave function is properly delocalized but the basis states are localized just like the Gaussians mentioned above. However, unlike the Gaussians we will use basis states that are orthogonal to one another. We take a clue from the, so called, Discrete Value

Representations⁴¹⁻⁴³, DVR, or from grid methods^{44, 45} in that we divide the interval of interest along the coordinate to small, equally spaced, segments of width a . Typically at a not large internuclear distance the electronic states are no longer effectively coupled. This enables us to define an end point of the interval and, see details below, to ‘absorb’ the wave function beyond that end point.

On each segment of the grid we place a gate shaped basis function of width a and height $1/a$. These orthonormal states are our basis. In principle the nuclear kinetic energy operator couples many such states⁴². In practice only close neighbors are coupled. To infer a reasonable value for the width a consider the change in a function $f(x)$ between the two ends of the interval

$$f(x \pm a) = f(x) \pm a \left. \frac{\partial f}{\partial x} \right|_{x=a} + \frac{a^2}{2} \left. \frac{\partial^2 f}{\partial x^2} \right|_{x=a} \pm \frac{a^3}{6} \left. \frac{\partial^3 f}{\partial x^3} \right|_{x=a} + a^4 \dots \quad (1)$$

The kinetic energy operator correct to order a^4 is obtained by adding the two expressions with a suitable strength factor where m is the reduced mass for the motion of the nuclei:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(x) = -\frac{\hbar^2}{2ma^2} (f(x+a) - 2f(x) + f(x-a)) \quad (2)$$

The kinetic energy can be estimated as $\hbar^2 k^2 / 2m$ where k is the wave vector. The approximation is therefore reasonable when $(\hbar^2 k^2 / 2m) > (\hbar^2 / 2ma^2)$ or $a < 1/k$ or, since $1/k$ is the wavelength of the nuclear motion, the nuclear wave function must not vary too much over the interval. The adiabatic or diabatic potential for the nuclear motion also varies. But for higher excited states or states of the continuum the range of variation of the potential is smaller. A limiting factor can be the rapid variation of the non adiabatic coupling terms so using a diabatic basis for the electronic states can be advantageous. For a better numerical accuracy one can use a fifth order interpolation or even a seventh order. The momentum and kinetic energy operations to fifth order are

$$-i\hbar \frac{\partial}{\partial x} f(x) = -\frac{i\hbar}{12a} (f(x-2a) - 8f(x-a) + 8f(x+a) - f(x+2a)) \quad (3)$$

and

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(x) = \\ -\frac{\hbar^2}{24ma^2} (-f(x-2a) + 16f(x-a) - 30f(x) + 16f(x+a) - f(x+2a)) \end{aligned} \quad (4)$$

with a reduced strength parameter.

In a diabatic basis the kinetic energy operator T is diagonal in the electronic state index. The kinetic energy operator correct to order a^4 can shift the wave function from an interval around x to the two near neighboring intervals, on the right and left, it is non diagonal in the state index

$$T_{nd}f(x) = -\frac{\hbar^2}{2ma^2}(f(x+a) + f(x-a)) \quad (5)$$

But there is also a diagonal part

$$T_d f(x) = \frac{\hbar^2}{ma^2} f(x) \quad (6)$$

The non diagonal operator correct to order a^6 can shift the wave function for two adjacent intervals on either side, see equation (4).

The grid method can be effectively combined with a kinetic energy computed via a Fourier transform to the momentum space^{44, 45}. It is equivalent to using the entire range of values of the internuclear distance. A discrete transform does also depend on choosing a realistic value of the span parameter a .

We proceed to setting up an equation of motion for the wave function. Our example will be the lowest manifold, Π symmetry, three electronic states, of one photon excited states of N_2 that can be accessed from the ground state. There are two and at higher excitation three dissociation channels. It is reported experimentally⁴⁶ that the branching between different channels depends non monotonically on the vibrational state that is excited. It is further reported⁴⁷ that the branching is different for different isotopes. To properly describe the initial state we need to use a pulse of long enough duration, hundreds of fs's so that its spread in frequency is below a vibrational spacing in the excited states, often less than a thousand wave numbers³⁹. It is therefore necessary to fully include the optical pulse in the Hamiltonian and one needs to integrate over time for duration of many vibrational periods.

For an excitation by a laser pulse polarized perpendicularly to the bond, there is a minimum of four electronic states that need to be included, the ground state and three singlet excited electronic states of $^1\Pi$ symmetry. In a diabatic scheme, one is a valence excited state and two are low Rydberg-like states often denoted as b and c and o.

The wave function describing both electronic and nuclear dynamics is, at time t and grid interval i , has four components, (more, if more electronic states are included)

$$\Psi_i(t) = \begin{pmatrix} C_{gi}(t)\Theta_i \\ C_{bi}(t)\Theta_i \\ C_{ci}(t)\Theta_i \\ C_{oi}(t)\Theta_i \end{pmatrix} \quad (7)$$

Θ_i is a gate function on interval i . These functions are normalized and orthogonal when on different intervals. Because the kinetic energy operator acts as a shift between cells, for example equation (2), there is no problem with their discontinuities. $C_{gi}(t)$ is the amplitude of the nuclear wave function of electronic state g on interval i . We will set up a differential matrix set of equations for the time propagation of these amplitudes. In the problem of interest at the earliest time only the electronic ground state is populated. The $C_{gi}(0)$'s as a function of i can be determined by a numerical integration, e.g., Numerov, of the Schrödinger equation for vibrational wave function on the potential of the electronic ground state.

The wave function $\Psi_i(t)$ describes the system at interval i . We need to propagate it in time for describing the dynamics. We need to propagate it all the way to the outermost interval where the interelectronic coupling becomes negligible. This is the onset of the region of the products. Of course, we must not have the wavefunction reflected back at the last interval. So beyond that point in space we switch on a non-reflective absorbing potential^{48, 49}. To propagate in time, we start with the time-dependent Schrödinger equation, TDSE, $(i\hbar\partial\Psi_i(t)/\partial t) = H\Psi_i(t)$ multiply on the left by a gate function and integrate over the space coordinate. The orthonormality of the gate functions leads to

$$i\frac{d}{dt}\begin{pmatrix} C_{gi}(t) \\ C_{bi}(t) \\ C_{ci}(t) \\ C_{oi}(t) \end{pmatrix} = \begin{bmatrix} T_d + V_{gg}(i) & -\mathbf{E}(t)\boldsymbol{\mu}_{gb}(i) & -\mathbf{E}(t)\boldsymbol{\mu}_{gc}(i) & -\mathbf{E}(t)\boldsymbol{\mu}_{go}(i) \\ -\mathbf{E}(t)\boldsymbol{\mu}_{gb}(i) & T_d + V_{bb}(i) & V_{bc}(i) & V_{bo}(i) \\ -\mathbf{E}(t)\boldsymbol{\mu}_{gc}(i) & V_{cb}(i) & T_d + V_{cc}(i) & V_{co}(i) \\ -\mathbf{E}(t)\boldsymbol{\mu}_{go}(i) & V_{ob}(i) & V_{oc}(i) & T_d + V_{oo}(i) \end{bmatrix} \begin{pmatrix} C_{gi}(t) \\ C_{bi}(t) \\ C_{ci}(t) \\ C_{oi}(t) \end{pmatrix} +$$

$$T_{nd}\begin{pmatrix} C_{gi-1}(t) \\ C_{bi-1}(t) \\ C_{ci-1}(t) \\ C_{oi-1}(t) \end{pmatrix} + T_{nd}\begin{pmatrix} C_{gi+1}(t) \\ C_{bi+1}(t) \\ C_{ci+1}(t) \\ C_{oi+1}(t) \end{pmatrix} \quad (8)$$

$\hbar = 1$ is used throughout. The diagonal terms $V_{gg}, V_{bb}, V_{cc}, V_{oo}$ are the potential energy curves of the ground Σ_g^+ state and the three excited $^1\Pi_u$ states. In the diabatic basis, the $^1\Pi_u$ states are coupled by the potential terms V_{bc} , V_{bo} , and V_{oc} which are local in the gate basis. In Eq. (8) and in the rest of this chapter, the interaction with the laser pulse is described in the dipole approximation, $-\mathbf{E}(t)\cdot\boldsymbol{\mu}$, where $\boldsymbol{\mu}$ is the dipole moment of the molecule and $\mathbf{E}(t)$ the time

profile of the electric field of the laser pulse, confined in a Gaussian envelope: $\mathbf{E}(t) = -d\mathbf{A}(t)/dt$, $\mathbf{A}(t) = -(\hat{\mathbf{e}} E_0 / \omega) \exp\left(\frac{-(t-t_0)^2}{2\sigma^2}\right) \sin(\omega(t-t_0) + \phi)$, to ensure $\mathbf{E}(\omega) = 0$ for few cycle pulses:

$$\mathbf{E}(t) = \hat{\mathbf{e}} E_0 \exp\left(\frac{-(t-t_0)^2}{2\sigma^2}\right) \left[\cos(\omega(t-t_0) + \phi) - \frac{(t-t_0) \sin(\omega(t-t_0) + \phi)}{\omega\sigma^2} \right] \quad (9)$$

Where ω is the carrier frequency, $\hat{\mathbf{e}}$ the polarization direction and E_0 the strength of the electric field, t_0 is the mean of the Gaussian envelope and σ its width, with the full width at half maximum, $\text{FWHM} = 2\sqrt{2 \ln 2} \sigma \sim 2.35 \sigma$. ϕ is the carrier envelope phase, defined as the phase difference between the maximum of the electric field and the maximum of the Gaussian envelope.

Working in the diabatic basis of electronic states requires to diabaticize the adiabatic states, which may become computationally heavy when more than a few electronic states are coupled. In the adiabatic basis, the coupling between the electronic states is driven by the kinetic energy terms, $T_{nm}(\mathbf{R}) = \langle \varphi_n(\mathbf{r}; \mathbf{R}) | T_{nuc} | \varphi_m(\mathbf{r}; \mathbf{R}) \rangle$, that are neglected in the BO approximation. After integrating over electronic coordinates, one gets the following explicit expression^{25, 26, 50, 51} :

$$\langle \theta_{in}(\mathbf{R}) | T_{nuc} | \theta_{jm}(\mathbf{R}) \rangle = -\frac{1}{2m} \left[\langle \theta_{in}(\mathbf{R}) | \nabla_R^2 + 2\boldsymbol{\tau}(R) \cdot \nabla_R + \nabla_R \boldsymbol{\tau}(R) + \boldsymbol{\tau}(R) \cdot \boldsymbol{\tau}(R) | \theta_{jm}(\mathbf{R}) \rangle \right] \quad (10)$$

In Eq. (10), the first term is the kinetic energy of the nuclei on each electronic state, as in the diabatic basis. The next three terms describe the non-adiabatic coupling between the electronic states. They are non-diagonal in the electronic index. The terms $2\boldsymbol{\tau}(R) \cdot \nabla_R$ and $\nabla_R \boldsymbol{\tau}(R)$ are non-local in the grid points. In computing quantum dynamics, the last two terms in Eq. (10) are often very small compared to the $2\boldsymbol{\tau}(R) \cdot \nabla_R$ term and are neglected.

In addition to the non-adiabatic coupling, adiabatic electronic states of different total spin can be coupled by spin orbit interactions. We illustrate this point taking as an example the manifold of excited singlet and triplet states of Σ_u and Π_u spatial symmetry of the homonuclear diatomic molecule N_2 which belongs to the group $D_{\infty h}$. The ground state of N_2 is $\tilde{X}^1\Sigma_g^+$. Upon an optical excitation, spin is conserved and a one photon dipole allowed transition involves a parity change leading to ungerade $^1\Sigma_u^+$ and $^1\Pi_u$ states. Here we assume that the molecule is aligned along the Z axis of the Cartesian frame and the pulse polarized along the Z direction, so that only the

$^1\Sigma_u^+$ states can be optically excited. The spin orbit interactions couple these states to other ‘ungerade’ states of higher multiplicity. The spin-orbit integrals have three components, along the X, Y, and Z axes of the molecular frame. The coupling between the orbital (L) and spin (S) angular momentum has components along the three Cartesian axis, X, Y and Z. The LSZ coupling between two interacting electronic states conserves the magnetic quantum number, $\Delta m_s = 0$. For the LSX and LSY coupling, the selection rule is $\Delta m_s = \pm 1$. Therefore the LSX and LSY spin-orbit interactions couple the $^1\Sigma_u^+$ singlet states to the $^3\Pi_u$ states but only the $\Delta m_s = \pm 1$ components of the triplet states can be populated. The $^1\Sigma_u^+$ states are also coupled to the $^3\Sigma_u^+$ states with the selection rule $\Delta m_s = 0$. Taking all three couplings between adiabatic states into account, dipole, non-adiabatic and spin-orbit, the TDSE takes the form :

$$\begin{aligned}
i\hbar \frac{dC_{gn}(t)}{dt} = & (T_d + V_{gn} - iV_{cap,g})C_{gn}(t) + \sum_{q=1}^2 T_{nd}^q (C_{g+q,n}(t) + C_{g-q,n}(t)) \\
& - \sum_{k=1}^{N_e} 2\tau_{g,nk} \sum_{q=1}^2 p^q (C_{g+q,k}(t) + C_{g-q,k}(t)) \\
& - \sum_{k=1}^{N_e} \left(E(t)\mu_{g,nk} + \frac{1}{2m} \sum_{l=1}^{N_e} \tau_{g,nl} \cdot \tau_{g,lk} - H_{g,nk}^{SO} \right) C_{gk}(t)
\end{aligned} \tag{11}$$

In Eq. (11), the first two terms on the rhs correspond to the kinetic energy of the nuclei computed by finite difference as in Eq. (4). An absorbing potential, V_{cap} is added on the edges of the grid for the dissociative electronic states. The second line correspond to the derivative, $2\boldsymbol{\tau}(R) \cdot \nabla_R$, non adiabatic coupling between electronic states where the momentum, ∇_R , is computed by finite difference using Eq. (3). The third line gathers the dipole term and the term $\boldsymbol{\tau}(R) \cdot \boldsymbol{\tau}(R)$ of the NAC that is important for N_2 . The term $\nabla_R \boldsymbol{\tau}(R)$ is neglected.

The diabatic and adiabatic potentials of three lowest excited singlet Σ states of N_2 are plotted in Figure 1. The curves of the non adiabatic coupling between states of same multiplicities and of the spin-orbit coupling between singlet, triplet and quintet states can be found in ref.³⁸

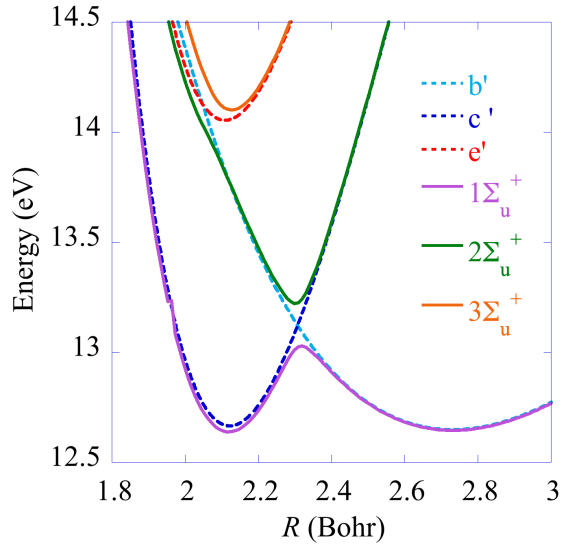


Figure 1. Schematic of the three lowest one photon accessible, dipole allowed, singlet excited states of N_2 . b' , c' and e' are the diabatic states and the corresponding adiabatic states are $1\Sigma_u^+$, $2\Sigma_u^+$, $3\Sigma_u^+$. For more discussion and details see refs.^{34, 38, 39}

3. Entanglement between electronic and nuclear degrees of freedom resulting from a short optical pulse excitation

The rather long 10 femtosecond (fs) or more laser pulses used in femtochemistry have an energy bandwidth narrow enough to excite a single electronic state. In this case, the dynamics is typically computed for this excited electronic state for which, in the absence of coupling with other excited states, the wave function is separable and written as a product of an electronic wave function and a nuclear one, i.e. there is a single term in the Born-Huang expansion

$\Psi(\mathbf{r}, \mathbf{R}) = \varphi_n(\mathbf{r}; \mathbf{R})\chi_n(\mathbf{R})$. When this is the case, considering the molecule as a bipartite system made of electronic and nuclear degrees of freedom, one says that the electronic and nuclear degrees of freedom are not entangled, and the, so called, Schmidt rank of the wave function is equal to 1. The general definition of a Schmidt rank is given below. The situation is qualitatively different when few fs or atto second (as) optical pulses are used because they are short enough to excite coherently several electronic states in polyatomic molecules. Then the wave function is a superposition of several electronic states during the excitation and also after the pulse is over : $\Psi(\mathbf{r}, \mathbf{R}) = \sum_n \varphi_n(\mathbf{r}; \mathbf{R})\chi_n(\mathbf{R})$. After the pulse is over, both in the long and short pulse cases, non adiabatic coupling and spin orbit coupling between electronic states can

give rise to entanglement in the case of a long pulse-single state excitation while in the case of the short one, the entanglement built at the excitation step will be modulated by these coupling terms. A broad-in-energy pulse entangles the electronic and nuclear degrees of freedom already at the excitation step while for a narrow-in-energy pulse, the entanglement between electronic and nuclear degrees of freedom occurs only later and typically occurs for a pair of electronic states. The entanglement resulting from the excitation by the short pulse can be controlled by the pulse parameters, see Eq. (9), its polarization, duration, carrier envelope phase and carrier wave length, which in turn, can be used to control the dynamics.

Entanglement is often, as in quantum computing,⁵² used for (two or more) identical systems that are coupled. It is a strictly quantum phenomena.⁵²⁻⁵⁴ The early example was two entangled photons emitted from the same source.^{55, 56} In general, the two systems need not be identical. Vibrational modes in a polyatomic molecule can be entangled,⁵⁷ or scattering channels in chemical reactions.^{58, 59} Entanglement between the electronic and nuclear degrees of freedom was previously studied for stationary eigenstates of vibronic Hamiltonians^{60, 61} and also for time-dependent vibronic wave functions.^{12, 62-64} The entanglement of the electronic and nuclear degrees of freedom discussed here is physically complementary to the Born-Oppenheimer separation discussed in the Introduction.

We propose to quantify the entanglement between electronic and nuclear degrees of freedom resulting from the excitation of the molecule by a short few fs and atto pulse and to follow its evolution during the dynamics, after the pulse is over.^{65, 66} To do so, we use a Singular Value Decomposition^{67, 68} (SVD) of the wave function $\Psi(\mathbf{r}, \mathbf{R}) = \sum_n \varphi_n(\mathbf{r}; \mathbf{R}) \chi_n(\mathbf{R})$. When written in function of grid points for the nuclear geometries and adiabatic electronic states:

$$\Psi(t) = \sum_g^{N_g} \sum_n^{N_e} C_{gn}(t) |g\rangle |n\rangle \quad (12)$$

The first step of the SVD analysis is to rearrange the vector of the amplitudes, $C_{gn}(t)$, into an $N_g \times N_e$ matrix $\mathbf{A}$ with typically $N_g \gg N_e$:

$$\mathbf{A}(t) = \begin{pmatrix} C_{11}(t) & \dots & C_{1N_e}(t) \\ \vdots & \vdots & \vdots \\ C_{N_g,1}(t) & \dots & C_{N_g N_e}(t) \end{pmatrix} \quad (13)$$

Then SVD is applied to $\mathbf{A}$ to bring to the form:

$$\mathbf{A}(t) = \mathbf{U}(t) \mathbf{\Sigma}(t) \mathbf{V}^\dagger(t) = \sum_{v=1}^{N_e} \sigma_v(t) \mathbf{U}_v(t) \otimes \mathbf{V}_v^\dagger(t) = \sum_{v=1}^{N_e} \sigma_v(t) \mathbf{A}_v(t) \quad (14)$$

In Eq. (14), $\mathbf{U}$ is a $N_g \times N_e$ matrix whose columns are the nuclear (right) singular vectors $\mathbf{U}_v(t)$ that depend on the grid index g only. $\mathbf{V}$ is the $N_e \times N_e$ matrix whose columns are the electronic (left) $\mathbf{V}_v(t)$ vectors that depend on the electronic index, n , only.

$$|U_v(t)\rangle = \sum_{g=1}^{N_g} u_{gv}(t)|g\rangle \text{ and } |V_v(t)\rangle = \sum_{n=1}^{N_e} v_{nv}(t)|n\rangle \quad (15)$$

$\mathbf{\Sigma}$ is the $N_e \times N_e$ diagonal matrix of the singular values, $\sigma_v(t)$. The maximum number of singular values of the matrix $\mathbf{A}$ is given by N_e , its smallest dimension. In terms of the principal components, the full density matrix takes the form :

$$\begin{aligned} \rho(t) = |\Psi(t)\rangle\langle\Psi(t)| &= \sum_{v,v'}^{N_e} \sigma_v(t)\sigma_{v'}(t) |U_v(t)\rangle\langle V_{v'}(t)| \langle U_{v'}^\dagger(t)| \\ &= \sum_{v,v'}^{N_e} \sigma_v(t)\sigma_{v'}(t) \rho_{v,v'}(t) \end{aligned} \quad (16)$$

The norm of the density matrix is given by

$$Tr[\rho(t)] = \sum_{v=1}^{N_e} \sigma_v^2(t) \quad (17)$$

In summary, the right hand side of Eq. (14) corresponds to the exact decomposition of the matrix $\mathbf{A}$ as a sum of maximum N_e separable terms given by a product of a nuclear vector and an electronic vector. Therefore the maximum Schmidt rank of the matrix $\mathbf{A}$ is N_e , a number considerably smaller than the number of separable terms in the Born-Huang expansion given in Eq. (12).

From the SVD of the matrix $\mathbf{A}$ one can readily obtain reduced electronic, $\overline{\rho_{el}}$, and nuclear, $\overline{\rho_{nucl}}$ density matrices defined as:

$$\overline{\rho_{el}(t)} = Tr_{nucl}[|\Psi\rangle\langle\Psi|] = \mathbf{A}^\dagger \mathbf{A} = \sum_{n=1}^{N_e} \sigma_v^2 \left| V_v(t) \right\rangle\langle V_v^\dagger(t) \quad (18)$$

$$\overline{\rho_{nucl}(t)} = Tr_{el}[|\Psi\rangle\langle\Psi|] = \mathbf{A} \mathbf{A}^\dagger = \sum_{n=1}^{N_e} \sigma_v^2 \left| U_v(t) \right\rangle\langle U_v^\dagger(t) \quad (19)$$

The singular values, $\sigma_v(t)$, and the corresponding nuclear $\mathbf{U}_v(t)$ and electronic $\mathbf{V}_v(t)$ can be followed as a function of time and provide a quantitative measure of the entanglement between electrons and nuclei during the pulse and as the dynamics unfolds after the pulse is over.

Typically, the magnitude of the singular values decreases sharply as a function of the index v ,⁶⁵ as is shown in Figure 2 for the non-adiabatic dynamics initiated by a short 2-3 fs pulse used for exciting the three lowest singlet $^1\Sigma_u^+$ states, $^1\Sigma_{1u}^+$, $^1\Sigma_{2u}^+$ and $^1\Sigma_{3u}^+$ of the N_2 molecule³⁴ and the six lowest Σ states, Σ_1 , Σ_2 , Σ_3 , Σ_4 , Σ_5 , Σ_6 of the LiH molecule.⁶⁹ The potentials energy curves (PEC) are shown on Figure 2 a and b respectively. In N_2 , $^1\Sigma_{1u}^+$ is a shallow valence state while

$^1\Sigma_{2u}^+$ and $^1\Sigma_{3u}^+$ are Rydberg states, all three states are bound for the 13.62 eV carrier frequency of the 3 fs (FWHM) pulse, see Eq. (9). In LiH, Σ_1 is shallow and bound, 3 eV above the ground state. The Σ_2 , Σ_3 , Σ_4 states are dissociative with very shallow wells. They are higher in energy, in the 4.5 to 6 eV range and resonant with the 2fs (FWHM) pulse of carrier frequency 5.5 eV. The energy bandwidth of these two pulses are 1.18 and 1.82 eV respectively and shown as a grey shaded area in the Franck-Condon (FC) region in Figures 2a and b.

The features of the PEC make these two molecules complementary to study the time evolution of the electron-nuclei entanglement produced at the excitation step.⁶⁵ The populations in the excited states during and after the pulse are plotted in Figure 2 c and d. In the case of N₂ (Figure 2c), the pulse populates the $^1\Sigma_{2u}^+$ Rydberg state that is strongly non adiabatically coupled to the $^1\Sigma_{1u}^+$ valence state at the exit of the Franck-Condon region. The wave packet on the shallow $^1\Sigma_{1u}^+$ state oscillates along the internuclear distance with a period of 50 fs which leads to amplitude and population transfer between the two states each time the $^1\Sigma_{1u}^+$ wave packet overlaps with the $^1\Sigma_{2u}^+$ Rydberg wave packet in the FC region. On the other hand, in the case of LiH, the pulse accesses the Σ_4 and the Σ_2 states which are strongly coupled to Σ_3 by NAC at the exit of the FC region. Because of the broad (1.82 eV) energy bandwidth of the pulse, there is also a small population in Σ_1 . The time evolution of the squares of the singular values, $\sigma_v^2(t)$, are shown in Figures 2 e and f for N₂ and LiH respectively. In both cases, one sees that a single singular value suffices to describe the dynamics until the middle of the pulse. Before the pulse, indeed, the wave function on the ground state is given by a single product $(\sum_{g=1}^{N_g} C_g |g\rangle) |GS\rangle$. During the first half of the pulse, the wave packets on the excited electronic states have not yet left the FC region and one can still describe the wave function as a single product, $|\Psi(t)\rangle = U_1(t) \otimes V_1^\dagger(t) = \left(\sum_g^{N_g} u_{g1} |g\rangle\right) \left(\sum_n^{N_e} v_{n1}^* |e\rangle\right)$ where $U_1(t)$ is localized in the FC region and $V_1(t)$ has amplitudes on several electronic states, see Figures 3 and 4 below, in particular Figure 4a for the LiH molecule. This means that the amplitudes $C_{gn}(t)$ in the Born-Huang expansion, Eq. (12), are factorizable as $C_{gn}(t) = u_{g1} v_{n1}$ and the Schmidt rank of $|\Psi(t)\rangle$ remains one. However, as soon as the wave packets on each electronic state leave the FC region, they experience different potentials and non-adiabatic interactions and do not any more fully overlap. They are entangled. The exit of the FC region corresponds to an increase of the Schmidt rank as several singular values contribute to the expansion of the wave function, Eq. (14) :

$$|\Psi(t)\rangle = \sum_{v=1}^{N_e} \sigma_v(t) \mathbf{U}_v(t) \otimes \mathbf{V}_v^\dagger(t) = \sum_{v=1}^{N_e} \sigma_v(t) \left(\sum_g^{N_g} u_{gv} |g\rangle \right) \left(\sum_n^{N_e} v_{nv}^* |e\rangle \right) \quad (20)$$

However, one can see from Figures 2 e and f that the entanglement is not maximum since the number of singular components that are effectively needed to describe the total wave function $|\Psi(t)\rangle$ is smaller than the number of electronic states. This is particularly true in the case of LiH, for which only four $\sigma_v^2(t)$ take gradually significant values as a function of time and are modulated by the non adiabatic coupling after the pulse. The second and third principal components that are localized on the excited Σ states (Figure 4 c,d,e,f) while the first component is localized on the GS after the pulse (Figure 4 a, b). In N_2 , the second component is localized on the valence $^1\Sigma_{1u}^+$ except when the wave packet on $^1\Sigma_{1u}^+$ recurs in the FC region, leading to localization of this component on the GS and $^1\Sigma_{2u}^+$ Rydberg state, Figure 3 c,d. The third component is localized in the $^1\Sigma_{2u}^+$ Rydberg state except when the $^1\Sigma_{1u}^+$ recurs in the FC region and is overlapping with the GS and $^1\Sigma_{2u}^+$. The SVD analysis therefore leads to a massive compaction of the information of the wave function by defining principal components that have weights on several electronic states and are localized in several regions of the internuclear distance. A threshold for determining the number of principal components, N_{min} , needed to describe accurately the wave function can be defined from the norm of the density matrix, $\rho_{N_{min}}$, see Eq. (17):

$$\Delta\rho_{N_{min}}(t) = 1 - \sum_{v=1}^{N_{min}} \sigma_v^2(t) \geq 0 \quad (21)$$

Or using the Frobenius norm, which also takes into account the off diagonal elements of $\rho(t)$ (Eq. (16))

$$\|F_{N_{min}}\| = \sqrt{\sum_{i,j=1}^{N_g N_e} |\rho_{ij}^{N_{min}} - \rho_{ij}|^2} \quad (22)$$

The localization of the electronic singular vectors on the adiabatic electronic states and heatmaps of the localization of the nuclear singular vectors computed for the three largest components and shown in Figure 3 for N_2 and Figure 4 for LiH. (Figure 3). $Tr[\rho_{N_{min}}]$ is plotted in Figure 5 for the three largest components of N_2 (panel a) and of LiH (panel c).

Describing more nuclear degrees of freedom requires implementing High Order SVD.⁷⁰ This was implemented to the ultrafast Jahn-teller rearrangement in the three lowest states of the methane cation, CH_4^+ , upon sudden ionization.⁶⁶ The dynamics in this case is described for two nuclear coordinates and three coupled electronic states.^{71, 72}

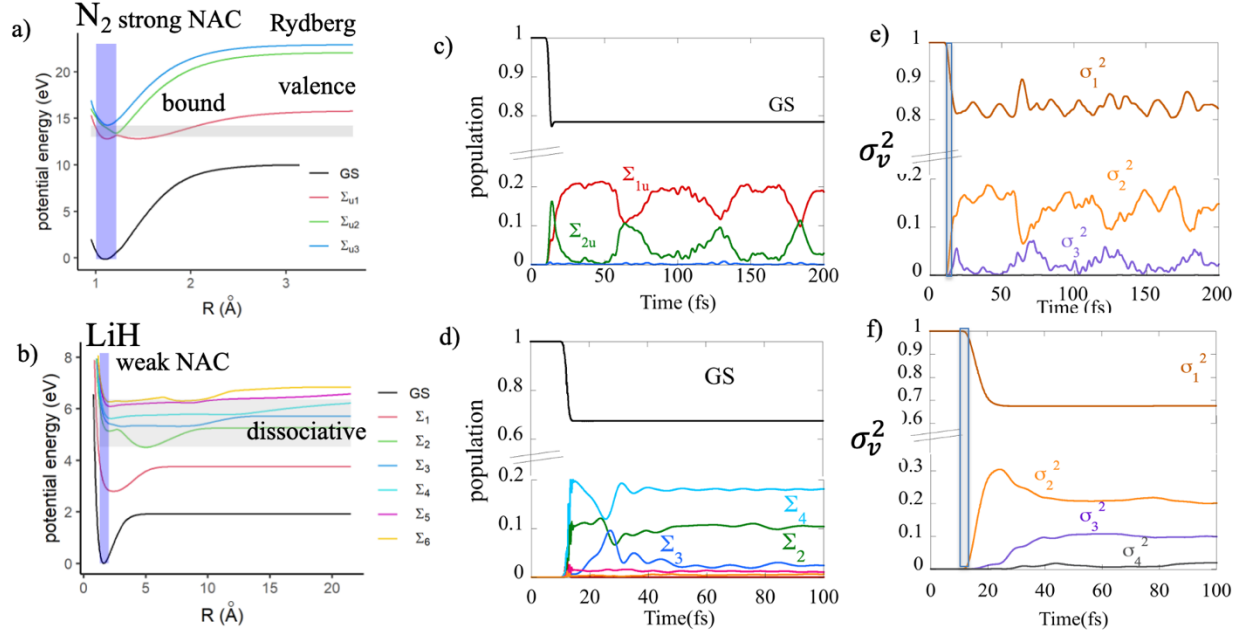


Figure 2. a) PEC of the GS and the three lowest $^1\Sigma_u^+$ states of N_2 ³⁴ and b) of LiH ⁶⁹, the FC region is shaded in violet and the energy bandwidth of the pulse in grey. Population dynamics in N_2 (c) and in LiH (d). Time evolution of the singular values in N_2 (e) and in LiH (f). See ref. ⁶⁵ for more details.

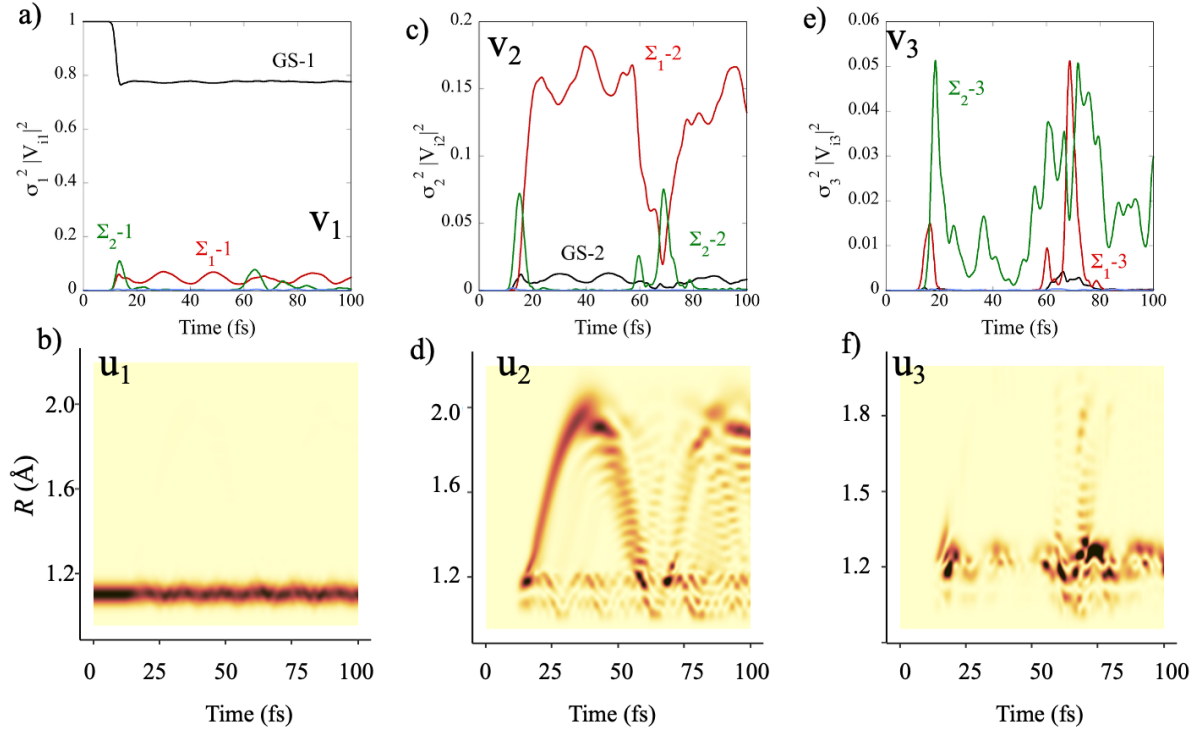


Figure 3: Localization of largest principal components of the wave functions computed for the dynamics in N_2 shown in Figure 2. Panels a, c, e show the localization of the electronic singular vectors on the adiabatic electronic states while panels b, d, f are a heatmap of the localization of the nuclear coordinates on the grid of internuclear distances. Adapted from ref. ⁶⁵

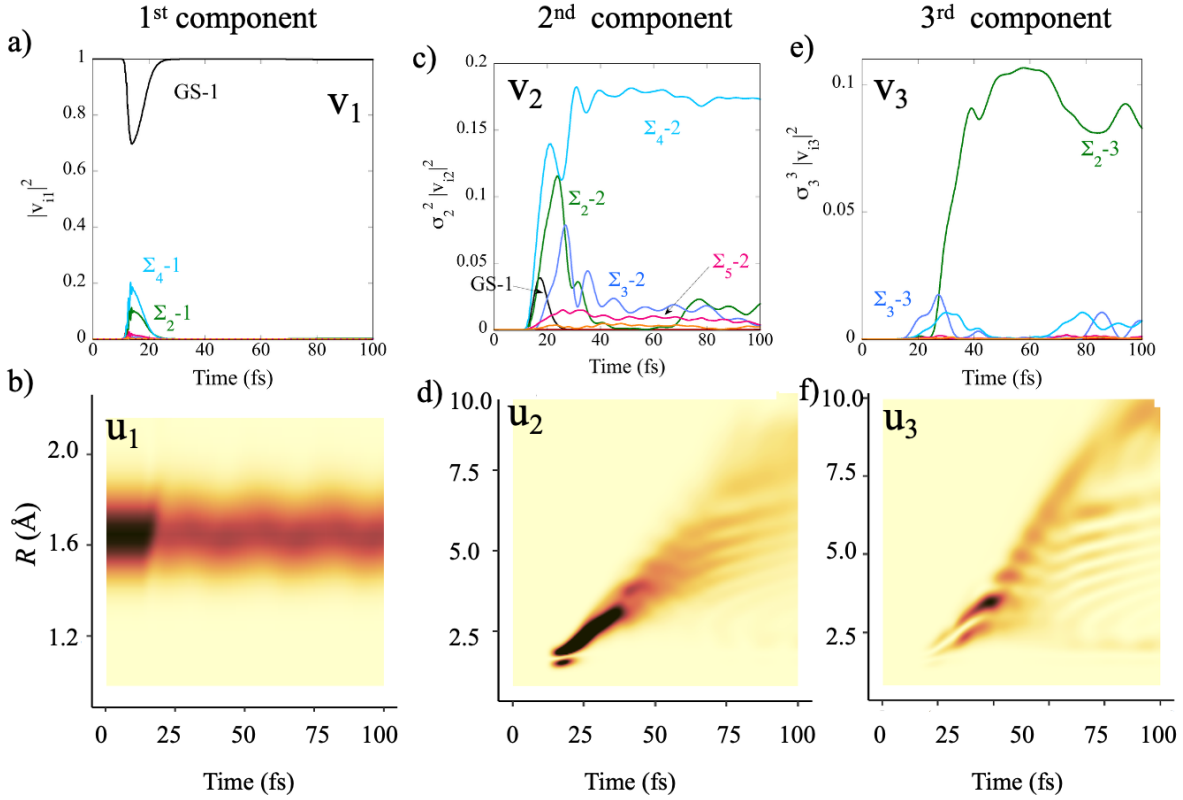


Figure 4: Localization of largest principal components of the wave functions computed for the dynamics in LiH shown in Figure 2. Panels a, c, e show the localization of the electronic singular vectors on the adiabatic electronic states while panels b, d, f are a heatmap of the localization of the nuclear coordinates on the grid of internuclear distances. Adapted from ref. ⁶⁵

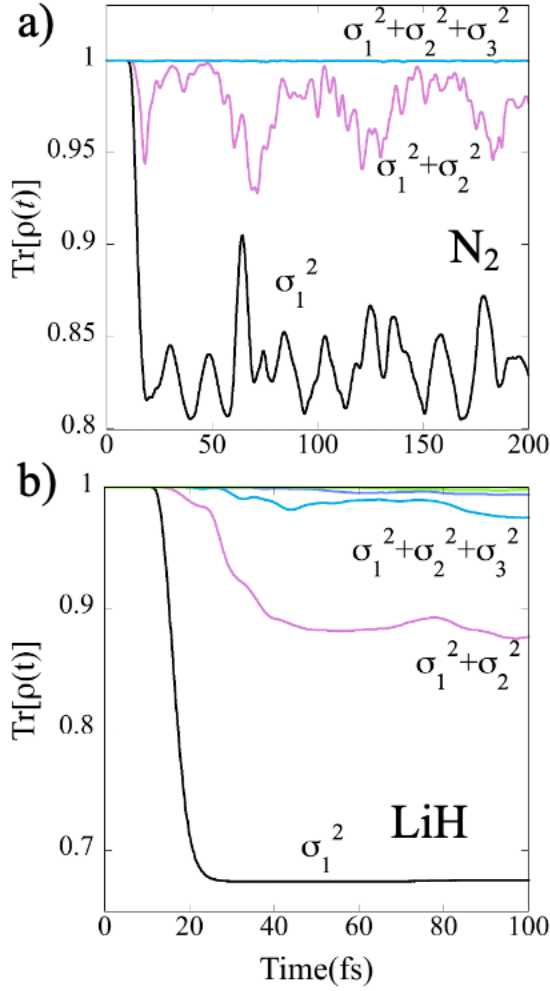


Figure 5: Norm of the density matrix, $Tr[\rho_{N_{min}}(t)]$ as a function of time for N_2 (panel a) and LiH (panel b). The green and the dark blue lines in panel b correspond to adding σ_4^2 and σ_5^2 ($N_{min} = 4$ and 5 respectively) which is seen to lead to a smaller error on the norm at longer times.

4. Force exerted on the nuclei by the entangled electronic and nuclear motions

Towards a rational design of control schemes exploiting the entanglement between electrons and nuclei made possible by exciting molecules by short-in-time-broad-in-energy atto and fs optical pulses, it is necessary to assess how this entanglement affects the force on the nuclei, so as to be able to steer nuclear motion towards the desired products by adjusting the pulse parameters.

In this section, we derive the exact expression of the quantum mechanical force exerted by a vibronic wave packet on the nuclei using the exact form of the Ehrenfest theorem. We show⁷³

that the force is composed of four terms. Two terms that depend on the features of the electric field of the pulse and that are unique to attochemistry. The other two terms depend on the features of gradients of the potentials and of the non adiabatic couplings and were derived previously.²⁵ Specifically we show that electronic coherences and electron-nuclei entanglement play a significant role in defining the force on nuclei and can be exploited to steer the chemical reaction.

Using the exact Ehrenfest theorem and the Newtonian definition of a force, the force exerted on the nuclei for a diatomic molecule is to be computed as

$$F_{tot} = d\langle \mathbf{P}_N \rangle / dt = i\langle [\mathbf{P}_N, \mathbf{H}] \rangle = -\langle [\nabla_R, \mathbf{H}] \rangle \quad (23)$$

Where bold symbols are used for the matrix representation of the operators in the basis of N_g geometries for the nuclear coordinate and N_e adiabatic states as used above. In Eq.(23), $\mathbf{P}_N$ is the nuclear momentum, and $\mathbf{H} = \mathbf{T}_N + \mathbf{H}_{el} + \mathbf{E}(t) \cdot \boldsymbol{\mu}$ where $\mathbf{T}_N$ is the kinetic energy of the nuclei, $\mathbf{H}_{el}$ the electronic Hamiltonian, $\mathbf{E}(t)$ the electric field of the pulse, and $\boldsymbol{\mu}$, the dipole operator. Computing the commutators and integrating over electronic coordinates, we get:

$$F_{tot} = -\langle (\nabla_R V) \rangle + \langle [\boldsymbol{\tau}, V] \rangle + \mathbf{E}(t) \langle (\nabla_R \boldsymbol{\mu}) \rangle - \mathbf{E}(t) \langle [\boldsymbol{\tau}, \boldsymbol{\mu}] \rangle \quad (24)$$

$$F_{tot} = F_V + F_{[\tau, V]} + F_\mu + F_{[\tau, \mu]}$$

The first two terms are defined by the potentials of the electronic states and their couplings. They are a property of the molecule. The first term is classical. It is the mean value on the potential gradients over the electronic states. The second term is non classical and depends on electronic coherences.²⁵

The next two terms in Eq. (24) define the force during the pulse and are proportional to the time profile of the pulse electric field, $\mathbf{E}(t)$, Eq.(9) . They are important for excitation by a short atto or few fs pulse sufficiently broad in energy to access several electronic states. They are non classical in the sense they depend on electronic coherences and can be shaped by adjusting the pulse parameters. In Eq. (24) the average over both electronic and nuclear degrees of freedom, which are both treated quantum mechanically by solving the TDSE, $i\hbar d\mathbf{C}/dt = \mathbf{H}\mathbf{C}$. The molecular Hamiltonian is

$$\mathbf{H} = -\frac{1}{2m} (\nabla_R^2 + 2\boldsymbol{\tau} \cdot \nabla_R + (\nabla_R \boldsymbol{\tau}) + \boldsymbol{\tau} \cdot \boldsymbol{\tau}) + V - \mathbf{E}(t) \cdot \boldsymbol{\mu} \quad (25)$$

The force defined in Eq. (24) is the instantaneous force on the nuclei and, as such, it is different from the mean field force for the motion of the classical nuclei derived in, so called, Ehrenfest dynamics, which is obtained by averaging only over the electronic wave functions, $\varphi_n(\mathbf{r}; \mathbf{R})$'s, see refs ⁷⁴⁻⁷⁶.

From the Born-Huang expansion of the total wave function, Eq. (12), one can rewrite Eq. (24) explicitly in terms of the vector $\mathbf{C}$ of the amplitudes $\{C_{gn}(t)\}$:

$$F_{tot} = -\mathbf{C}^\dagger (\nabla_R V) \mathbf{C} + \mathbf{C}^\dagger [\boldsymbol{\tau}, V] \mathbf{C} + E(t) \mathbf{C}^\dagger (\nabla_R \boldsymbol{\mu}_{nucl}) \mathbf{C} + E(t) \mathbf{C}^\dagger (\nabla_R \boldsymbol{\mu}_{el}) \mathbf{C} - E(t) \mathbf{C}^\dagger [\boldsymbol{\tau}, \boldsymbol{\mu}] \mathbf{C} \quad (26)$$

In Eq. (26), all the terms except the first one, $-\mathbf{C}^\dagger (\nabla_R V) \mathbf{C}$, and the term $E(t) \mathbf{C}^\dagger (\nabla_R \boldsymbol{\mu}_{nucl}) \mathbf{C}$, are off-diagonal in electronic states and governed by the electronic coherences and the entanglement between electrons and nuclei.

We discuss the relative importance of the terms of the force in the case of the multiphoton excitation of the LiH molecule by a one cycle, CEP controlled NIR pulse.⁷³ Two CEP values are used and the polarization of the pulse is oriented with the internuclear axis of the LiH molecule, see inset in Figure 6 where we show the dynamics of the populations in the GS and six lowest Σ states, $\Sigma_1, \Sigma_2, \Sigma_3, \Sigma_4, \Sigma_5, \Sigma_6$ for the two values of the CEP's. For the CEP = 0 the maximum of the electric field is oriented towards the Li atom, which results in a larger population in the Σ_4 and in the Σ_1 states with subsequent population transfers due to the NAC coupling to Σ_2, Σ_3 , see Figure 6 a and b for the short time and longer time population dynamics. On the other hand, the CEP = π primarily excites the Σ_1 , see Figure 6 c and d. After the pulse, Figure 6 b and d, there is a rich population dynamics between the excited Σ states, $\Sigma_2, \Sigma_3, \Sigma_4$, induced by the NAC coupling while the GS and Σ_1 remain decoupled because of the large energy difference, see Figure 2 b.

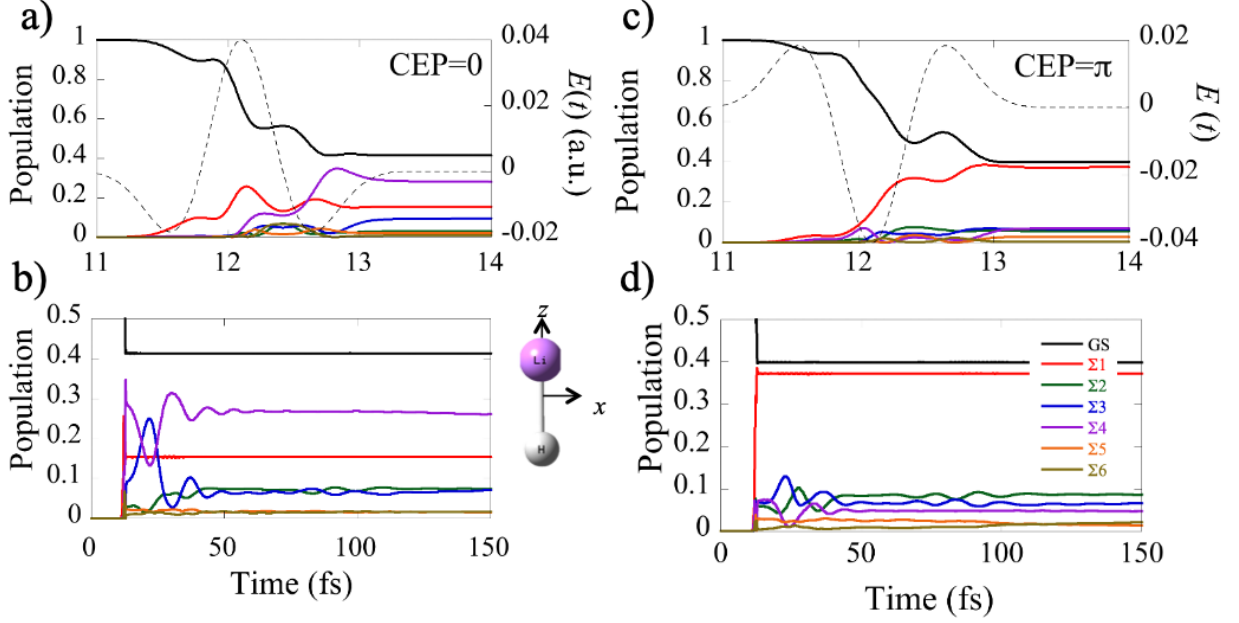


Figure 6. Dynamics of the population induced by a short one cycle NIR pulse with CEP=0 (panels a and b) and CEP= π (panels c and d). The pulse parameters are : carrier frequency of $\omega_p = 0.0633$ a.u. (720 nm), a FWHM = 0.8 fs, centered at $t_p = 12.1$ fs (500 a.u.) and a peak intensity, $|E_0|$ of 0.04 a.u..

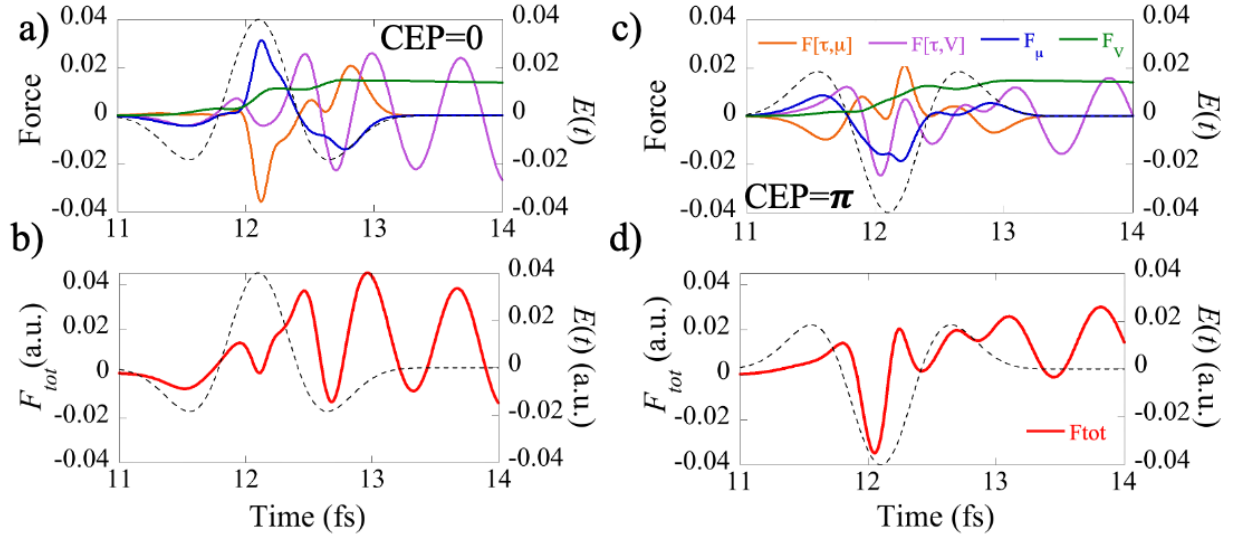


Figure 7: Dynamics of the four terms of the force (top row) and of the total force (red, bottom row) for the CEP=0 dynamics (panels a and b) and the CEP= π dynamics (panels c and d). The time profile of the electric field is shown in dashed lines.

The total force and the four terms (Eq. (24)) are plotted in Figure 7. One can see that the total force time dependence during and after the pulse is qualitatively different from the CEP=0 and the CEP= π dynamics. For the CEP=0, the total force (Figure 7b) is close to 0 at the max of the pulse, because of the opposite signs of the two dipole terms and of the two potential terms (Figure 7a). On the other hand, the total force is maximal for the CEP= π dynamics and negative (Figure 7d), because the gradient dipole term and the non-classical potential term are adding (Figure 7c). The magnitude of the force is -0.04 a.u. which corresponds to 3.28 nN (one a.u. of force = 82 nN), which is comparable to the typical strength of weak covalent bonds, as is the case in LiH.

At the end of the pulse, the dipole terms of the total force go to zero and only the two potential terms contribute to the total force. One can see from Figure 7 a and b that the value of the total force and its sign is determined by the non-classical terms, which are governed by the electronic coherences and the value of the NAC coupling. The total force is negative for the pulse at CEP=0 and positive for the CEP= π one. This means that at the end of the pulse, the mean value of the internuclear distance, $\langle R \rangle$, of the GS elongates for the CEP=0 dynamics but is decreasing for the CEP= π one. This difference of sign of the total force induces a phase difference between the oscillations of the wave packets on the GS for the CEP=0 and the CEP= π dynamics, as can be seen from Figure 8 a and b. Also note that for the non-classical NAC term of force to be finite one needs that the GS- Σ_1 electronic coherence is non zero, which occurs when the wave packet on Σ_1 revisits the FC region, every ≈ 90 fs, and the wave packets on the GS and on Σ_1 overlap. In between the revivals of the GS- Σ_1 electronic coherence, the force is dominated by the classical potential term.

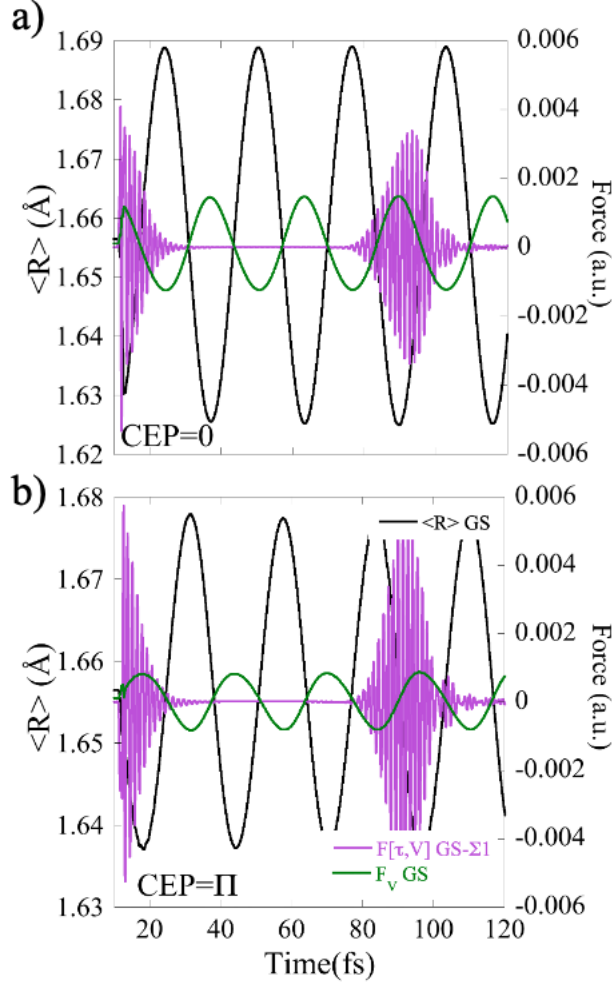


Figure 8. Time evolution of the potential terms of the force after the pulse for the CEP = 0 dynamics (a) and the CEP = π dynamics (b).

For the dissociative states, Σ_2 , Σ_3 , Σ_4 , the gradient of the potentials are small as the internuclear distance increases which results in a negligible value of the classical potential terms. Moreover these states are strongly coupled by NACs and the electronic coherences survive for a long time since their potential energy curves are parallel. As a result, for dissociative states, it is the non-classical NAC terms that dominate the total force after the pulse. We show the results for the Σ_3 state which is strongly non adiabatically coupled to the Σ_2 and Σ_4 states in Figure 9. One can see that the force on a given potential plays the role of a friction term on the motion of the wave packet. A positive total force slows down the motion of the wave packet while a negative one accelerates it.

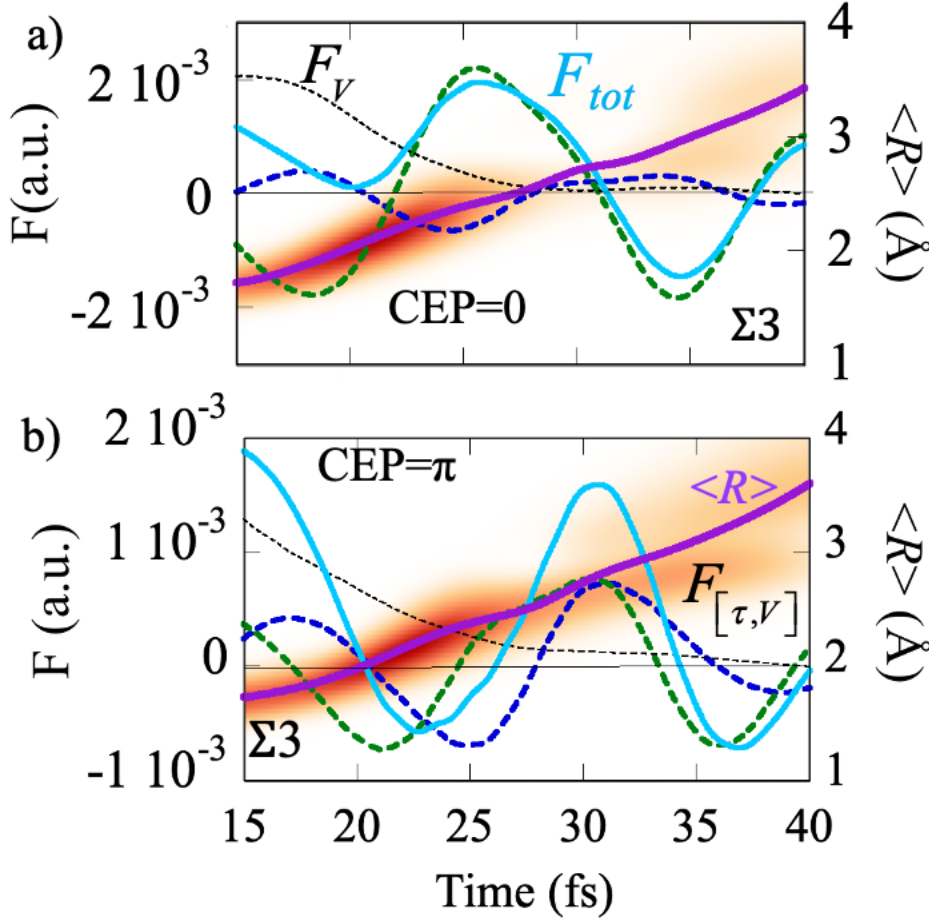


Figure 9. The contribution of the non-classical NAC terms, $\Sigma_2 - \Sigma_3$ term is plotted in green dashes and $\Sigma_3 - \Sigma_4$ one in blue and of the gradient potential classical term (black dashes) to the total force (azure thick line) for the Σ_3 state versus time after the CEP=0 pulse (panel a) and for CEP= π pulse (panel b). The value of $\langle R \rangle$ for is plotted as a thick violet line and the spreading of the wave packet as a heatmap in orange.

5. Entanglement is robust to averaging over initial random orientations

The orientation of the molecule with respect to the polarization direction of the pulse electric field is a very effective way for selecting the electronic states that will be taking part in the initial superposition built by the pulse and therefore the subsequent dynamics. For the diatomic molecules like N₂ and LiH discussed in Sections 3 and 4 above, optical selection rules allow to select electronic states of Σ or Π symmetry depending if the molecular axis is oriented parallelly or perpendicularly to the polarization direction of the electric field. For polyatomic molecules equilibrium geometries belonging to a point group, optical selection rules are broken as soon as the dynamics take the molecule out of its equilibrium geometry but trends are often still valid in the FC region, except when bright and dark electronic states are already coupled by NAC interactions in the FC region. Nevertheless, these trends can be exploited to build different initial non stationary electronic densities using the polarization direction of the pulse as a control parameter as we showed in the case of the photoisomerization of norbornadiene into quadricyclane.⁷⁷

A single or a sequence of laser pulses can be effectively used to align or orient molecules, enabling to carry out field free photoexcitation or photoionization experiments in the molecular frame.⁷⁸⁻⁸² However, not all types of molecules can be oriented and the achievable orientation is typically limited to values of $\langle \cos \theta \rangle \approx 0.7$ and $\langle \cos^2 \theta \rangle \approx 0.8$.⁸³⁻⁸⁵

A realistic description of quantum dynamics of molecules photoexcited by short atto and few fs pulses therefore requires an averaging over the initial molecular orientations with respect to the pulse polarization direction. Orientation averaging is computationally costly in computer time and storage capacity since the quantum dynamical propagation needs to be repeated as many times as the number of molecular orientations in the ensemble. Orientation averaging is still manageable computationally for the vibronic quantum dynamics of diatomic molecules but becomes out of reach for quantum dynamical simulation involving several nuclear degrees of freedom on coupled electronic states, as typical when polyatomic molecules and cations are excited by ultrashort, broad in energy atto pulses.^{77, 86-90} Moreover, for implementing control, one needs to tune the pulse parameters for an ensemble of molecular orientations.

We discuss in this section an approach for averaging quantum dynamics over random initial molecular orientations that both allow for considerable savings of computer resources and provides insights on the stereodynamics of the ensemble.⁹¹

For this purpose we use a Singular Value Decomposition (SVD) of the density matrix of the ensemble. We outlined the principles of SVD analysis applied for quantifying entanglement in section 2 above. Here the SV Decomposition identifies the principal orientations of the ensemble. It provides a measure of the entanglement between orientations and molecular degrees of freedom and insights on the stereodynamics of the ensemble. In addition, we show that the identification of the principal orientations leads to significant computer resources savings for computing the quantum dynamics of the ensemble, which makes averaging over initial molecular orientations affordable computationally.

We consider an ensemble of molecules with initial random orientations with respect to the polarization direction of the electric field of a short atto or few fs pulse. Computationally, it is advantageous to work in the molecular frame, so we numerically implement N_o random orientations of the pulse polarization with respect to the molecule in the molecular frame as shown schematically in Figure 10 for the LiH molecule.

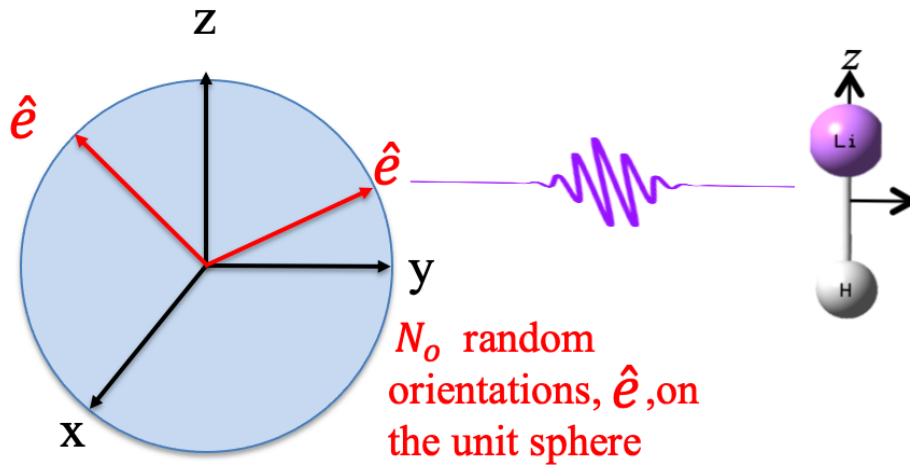


Figure 10 : Scheme for computing the quantum dynamics of N_o random orientations of the polarization direction of the pulse with respect to the LiH molecule in the molecular frame.

For each orientation of the pulse polarization, we need to solve the TDSE, $i\hbar d\mathbf{C}_o/dt = \mathbf{H}\mathbf{C}_o$ on a grid of $N_b = N_e \cdot N_g$ molecular basis functions made of products $\{|g\rangle |e\rangle\}$ of N_g molecular geometries and N_e adiabatic electronic states as explained section 1

$$\Psi_o(t) = \sum_b^{N_b} C_b^o(t) |b\rangle \geq \sum_g^{N_g} \sum_k^{N_e} C_{gk}^o(t) |g\rangle |k\rangle \quad (27)$$

The molecular Hamiltonian is given in Eq. (25). We arrange the N_o vectors $\mathbf{C}_o$ in a rectangular $N_b \times N_o$ rectangular matrix $\mathbf{A}$, typically $N_o \ll N_b$. The principal orientations of the ensemble are determined by SVD of the matrix $\mathbf{A}$

$$\mathbf{A} = \mathbf{U} \mathbf{\Sigma} \mathbf{V}^\dagger = \sum_{v=1}^{N_o} \sigma_v \mathbf{U}_v \otimes \mathbf{V}_v^\dagger = \sum_{v=1}^{N_o} \sigma_v \mathbf{A}_v \quad (28)$$

Eq. (28) is exact for N_o terms on the rhs. The matrix $\mathbf{A}$ has maximum N_o non zero eigenvalues which is the maximum entanglement between orientations and molecular degrees of freedom. Each of the N_o terms in Eq. (28) is separable in a molecular vector $\mathbf{U}_v$ that has amplitudes only on the N_b molecular basis function and an orientation vector $\mathbf{V}_v$ that have only amplitudes on the N_o randomly sampled orientations on the unit sphere.

The full density matrix of the ensemble, ρ_{ens} , of dimension $N_b N_o \times N_b N_o$ is given by the direct product $\mathbf{A} \otimes \mathbf{A}^\dagger$ and corresponds to a pure case for a photoexcitation from the ground state (GS). The molecular, $N_b \times N_b$, ρ^{mol} , and orientation, $N_o \times N_o$, ρ^{or} , reduced matrices are mixtures, given by

$$\rho^{mol} = (1/N_o) \text{Tr}_{or}[\rho_{ens}] = (1/N_o) \mathbf{A} \mathbf{A}^\dagger \quad (29)$$

And

$$\rho^{or} = (1/N_o) \text{Tr}_{mol}[\rho_{ens}] = (1/N_o) \mathbf{A}^\dagger \mathbf{A} \quad (30)$$

with

$$\text{Tr}[\rho^{mol}] = \text{Tr}[\rho^{or}] = (1/N_o) \sum_{v=1}^{N_o} \sigma_v^2 = \sum_{v=1}^{N_o} s_v, \quad s_v = \sigma_v^2 / N_o \quad (31)$$

Typically, as we show in detail below, only a few principal components, N_{min} , are needed to recover the traces of ρ^{mol} and ρ^{or} to a specified accuracy threshold, thereby leading to a lower Schmidt rank and providing a significant compaction of the matrix $\mathbf{A}$. Furthermore, when there is no additional source of entanglement between the molecular and orientation degrees of freedom after the interaction with the pulse, the dynamics of the ρ^{mol} matrix can be computed by propagating the N_{min} $\mathbf{U}_v$ molecular vectors using the TDSE, which leads to major savings of computer resources in memory and time:

$$i\hbar d\mathbf{U}_v/dt = \mathbf{H} \mathbf{U}_v, \quad v = 1, N_{min}, N_{min} \ll N_o \quad (32)$$

We demonstrate in Refs. ⁹¹ and ⁷² that for a sudden excitation or photoionization process involving several electronic states in the FC region, exactly three principal orientations are necessary, orientated along the three Cartesian axis of the molecular frame.

When the interaction with the electric field is explicitly taken into account in the TDSE, using the Hamiltonian of Eq. (25), the singular values, $\sigma_v(t)$, are time-dependent during the pulse and become constant after the pulse is over and the Hamiltonian is stationary. From this time on, one can use Eq.(32) to compute the ensemble dynamics. In summary, one needs to integrate the TDSE for the N_o during the short pulse. When it is over, it is sufficient to integrate the TDSE for the N_{min} principal orientations using Eq. (32). We illustrate the approach here for a UV excitation of the LiH molecule, with pulse parameters similar to these used in Section 3. The UV pulse has a carrier frequency, $\omega_p = 5.17$ eV, a duration $\sigma_p = 0.85$ fs, FWHM= 2fs, corresponding to an energy bandwidth = 1.82 eV, centered at $t_p = 12.5$ fs, $E_0 = 0.01$ a.u. (peak power of $3.51 \cdot 10^{12}$ W/cm²). Since the polarization of the electric field is randomly oriented in the molecular frame, this pulse not only populates the Σ_2 , Σ_3 , Σ_4 and Σ_5 states as in the example of Section 4, but also the doubly degenerate Π_1 and Π_3 ones by a one photon process (11a for the PEC). The Σ states are strongly coupled by NAC just at the exit of the FC region while the Π are essentially uncoupled, as can be seen from the longer time population dynamics, Figure 11c.

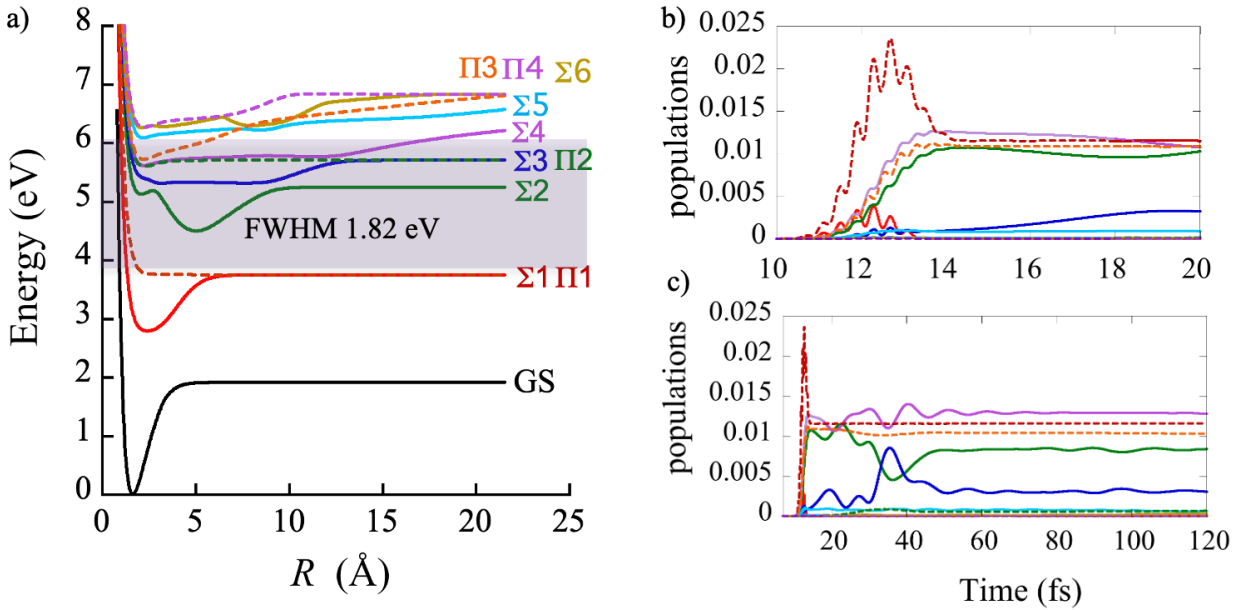


Figure 11. a) PEC for the Σ and the Π manifolds of excited electronic states in LiH that can be accessed by a 2fs deep UV pulse of 5.17 eV. The PEC of the Σ states are plotted in full line and

those of the Π states in dashes. b) Dynamics in the Σ and the Π manifolds during the pulse and just after the pulse. c) Longer time dynamics showing the population transfer between the Σ states due to NAC.

The singular values, $\sigma_v(t)$, are plotted in Figure 12a) at the maximum of the electric field and when the pulse is over as a function of the principal component index v . The corresponding error on the trace of $\text{Tr}[\rho^{mol}]$, Eq. (21), is plotted in Figure 12b, both on a logarithmic scale. One can see that the singular value magnitudes and the error on $\text{Tr}[\rho^{mol}]$ sharply decrease as a function of the index v . Only four principal orientations contribute to the dynamics of the ensemble.

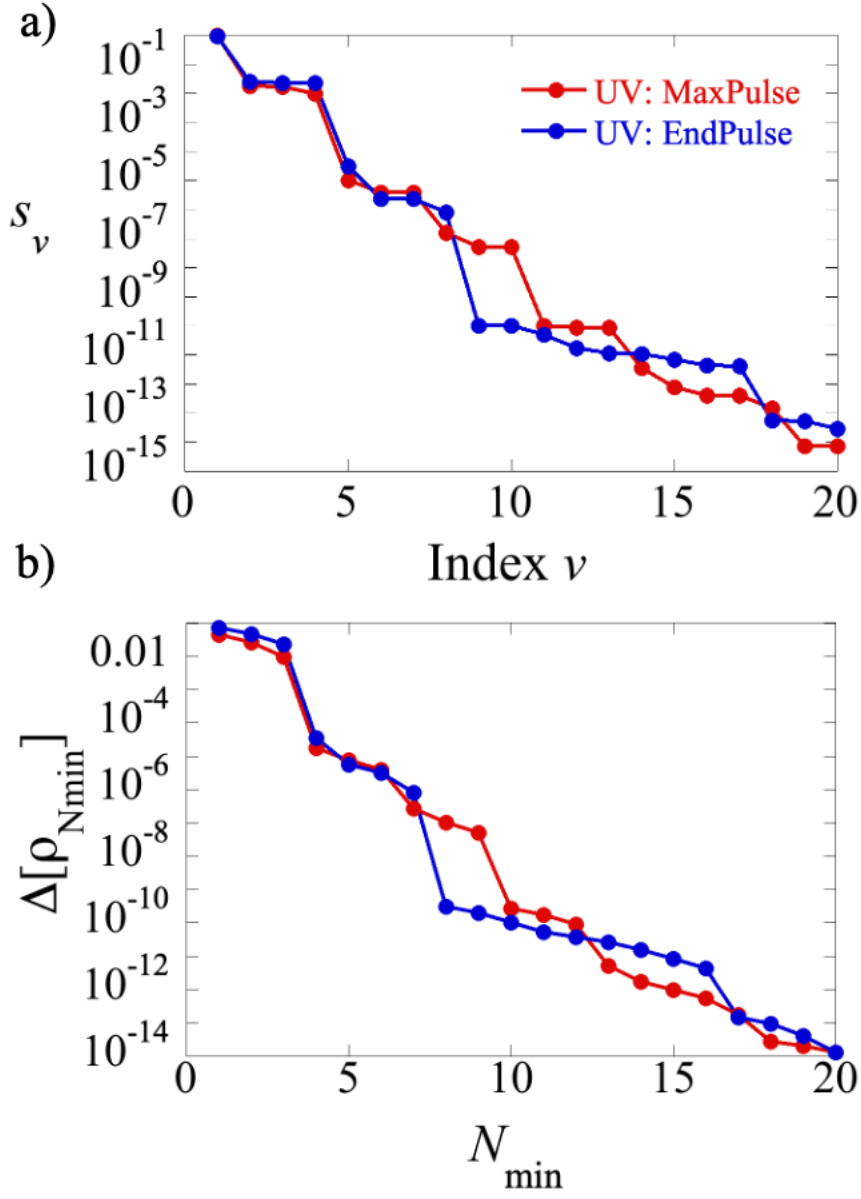


Figure 12: a) Singular values, s_v , Eq. (31), computed at the max of the electric field of the UV pulse (red) and after the pulse is over (blue) as a function of the principal orientation index v . b) error on the trace of the molecular density matrix, Eq. (21) as a function of v .

In figure 13, we show the localization of the four principal orientations on the electronic states on the grid (the $\mathbf{U}_v$ vectors) as heatmaps as well the localization of the corresponding four molecular orientations, $\mathbf{V}_v$ on the unit sphere.

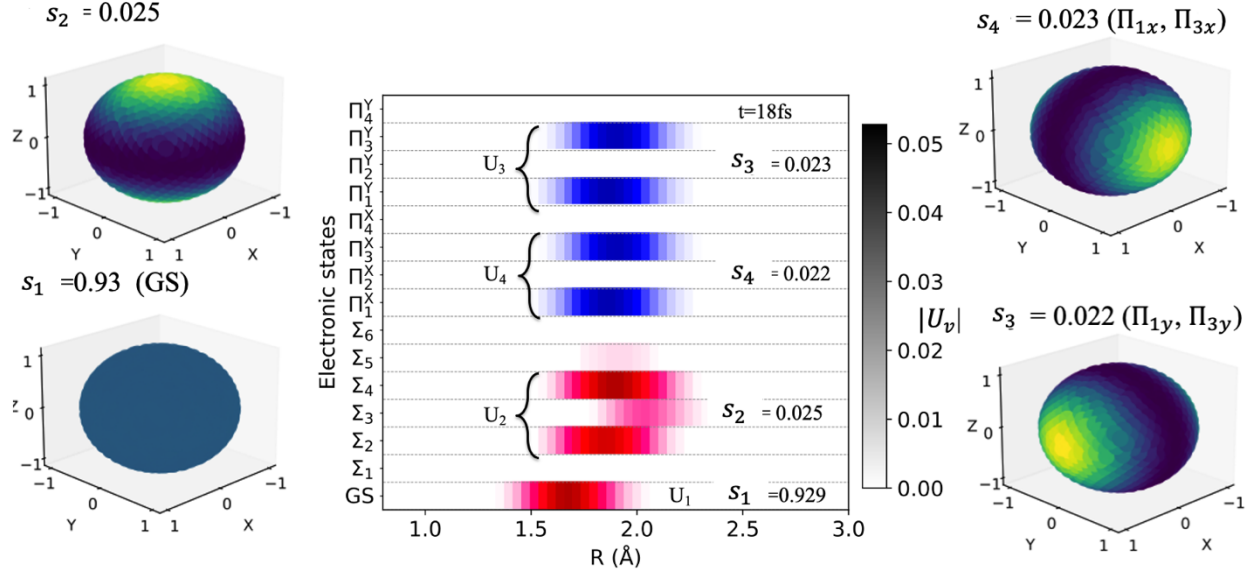


Figure 13. Localization of the four principal orientations on the electronic states on the grid (the U_v vectors) as heatmaps as a function of the internuclear distance R (middle) as well the localization of the corresponding four molecular orientations, V_v on the unit sphere, on the left and on the right.

From Figure 13, one can see that the largest principal orientation V_1 is uniform on the unit sphere with a molecular vector U_1 localized on the GS. The second largest principal molecular vector U_2 is localized on the excited Σ states with a principal orientation vector V_2 oriented along the z axis. The next two principal orientations are numerically degenerate: U_3 and U_4 are localized on the Π_y and Π_x components of the Π states. The fact that several electronic states contribute to the same principal orientations implies that electronic coherences, $\rho_v^{el} = \text{Tr}_{nuc}[\rho_v^{mol}(t)]$, and the entanglement between nuclear and electronic degrees of freedom built at the excitation step is robust with respect to averaging over molecular orientations, Figure 14 a and b. The difference with the pure state cases discussed on sections 3 and 4 is that there is no electronic coherences between the ground state and the excited Σ and Π states at the level of the ensemble. There are also no coherences between excited Σ and Π states. This affects molecular properties that are dependent on the electronic coherences, as the molecular polarization, $\langle \mu(t) \rangle = \sum_{v=1}^{N_{min}} s_v \text{Tr}[\mu \rho_v^{mol}(t)]$, see Figure 14c. The SVD analysis of the principal orientations of the ensemble shows that electronic coherences survive averaging over random initial molecular

orientations. It provides insights on the stereodynamics of the ensemble. Each principal orientation is correlated with a specific set of electronic states.

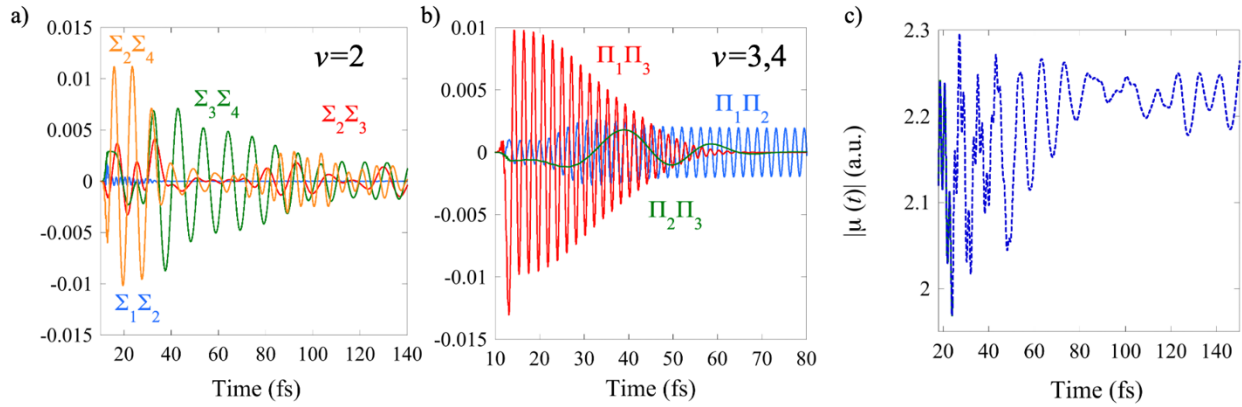


Figure 14. Electronic coherences in an ensemble of initially random molecular orientations. a) among excited Σ states (second principal orientation), b) among Π states (third and fourth principal orientations). c) the time dependence of the molecular polarization of the ensemble.

6. On algebraic structure and quantum computing

The form of the wave function that we use on a grid, Eq. (7) and the use of a finite difference scheme for the kinetic energy, the simplest, three point case used in Eq. (8), implies an unexpected symmetry. The Hamiltonian that can give rise to equation (8) has a near neighbor coupling that is well familiar for the electronic tight binding or Hückel approximation or for the Ising model of magnetism. It can also be used in the so-called Pariser-Parr-Pople Hamiltonian or the simpler version known in solid state physics as the Mott model.^{92,93} It is a symmetry that in quantum chemistry is behind the Unitary group approach.⁹⁴

To cast the symmetry in a general form we assume a grid as in section 2 with i being an index of an interval. Then consider N^2 operators, E_{ij} that in terms of the orthonormal gate functions Θ_j have the form $E_{ij} = \Theta_i \Theta_j$. It follows that these operators are closed under commutation:

$$[E_{ij}, E_{kl}] = E_{il} \delta_{jk} - E_{kj} \delta_{li}$$

In technical terms these operators close a Lie algebra known as $SU(N)$.⁹⁵ This is the same algebra that describes a set of linearly coupled qubits as in a quantum hardware.

At this point our discussion bifurcates. In one direction it means that we have an approach to mimic the operation of a quantum computer.⁹⁶ On a direction that is directly in line with the aims of this chapter, this shows how a quantum computer can be optimally useful to simulate ultrafast

multi-electronic-states dynamics.

7. Final remarks

Our quantum dynamical simulations clearly show that the electronic coherences and the entanglement between the electronic and nuclear motion resulting from the excitation of a molecule by a short in time – broad in energy atto or few fs pulse controls the force on the nuclei and can be controlled by the pulse parameters. One can further show that entanglement and electronic coherences are robust when averaging over initial random molecular orientations with respect to the polarization direction of the electric field, which shows that control is possible in more realistic experimental conditions.⁹¹ It is to be expected that further work will provide extensions to several nuclear degrees of freedom.

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References

- (1) Corkum, P. B.; Krausz, F. Attosecond science. *Nat. Phys.* **2007**, *3* (6), 381-387. DOI: [10.1038/nphys620](https://doi.org/10.1038/nphys620).
- (2) Kling, M. F.; Vrakking, M. J. J. Attosecond Electron Dynamics. *Ann. Rev. Phys. Chem.* **2008**, *59*, 463-492.
- (3) Krausz, F.; Ivanov, M. Attosecond physics. *Rev. Mod. Phys.* **2009**, *81* (1), 163-234.
- (4) Lepine, F.; Ivanov, M. Y.; Vrakking, M. J. J. Attosecond molecular dynamics: fact or fiction? *Nat Photon* **2014**, *8* (3), 195-204, Review. DOI: [10.1038/nphoton.2014.25](https://doi.org/10.1038/nphoton.2014.25).
- (5) Ranitovic, P.; Hogle, C. W.; Rivière, P.; Palacios, A.; Tong, X. M.; Toshima, N.; González-Castrillo, A.; Martin, L.; Martín, F.; Murnane, M. M.; et al. Attosecond vacuum UV coherent control of

- molecular dynamics. *Proc. Natl. Acad. Sci. USA* **2014**, *111* (3), 912-917. DOI: 10.1073/pnas.1321999111 Scopus.
- (6) Chang, Z.; Corkum, P. B.; Leone, S. R. Attosecond optics and technology: progress to date and future prospects [Invited]. *J. Opt. Soc. Am. B* **2016**, *33* (6), 1081-1097. DOI: 10.1364/JOSAB.33.001081.
- (7) Ramasesha, K.; Leone, S. R.; Neumark, D. M. Real-Time Probing of Electron Dynamics Using Attosecond Time-Resolved Spectroscopy. *Ann. Rev. Phys. Chem.* **2016**, *67* (1), 41-63. DOI: 10.1146/annurev-physchem-040215-112025 (accessed 2016/09/20).
- (8) Nisoli, M.; Decleva, P.; Calegari, F.; Palacios, A.; Martín, F. Attosecond Electron Dynamics in Molecules. *Chem. Rev.* **2017**, *117*, 10760–10825. DOI: 10.1021/acs.chemrev.6b00453.
- (9) Remacle, F.; Levine, R. D. An electronic time scale for chemistry. *Proc. Natl. Acad. Sci. USA* **2006**, *103* (May 2), 6793-6798.
- (10) Jasper, A. W.; Nangia, S.; Zhu, C.; Truhlar, D. G. Non-Born–Oppenheimer Molecular Dynamics. *Acc. Chem. Res.* **2006**, *39* (2), 101-108. DOI: 10.1021/ar040206v.
- (11) Nest, M. The multi-configuration electron–nuclear dynamics method. *Chem. Phys. Lett.* **2009**, *472* (4), 171-174. DOI: <https://doi.org/10.1016/j.cplett.2009.03.013>.
- (12) Haxton, D. J.; Lawler, K. V.; McCurdy, C. W. Multiconfiguration time-dependent Hartree-Fock treatment of electronic and nuclear dynamics in diatomic molecules. *Phys. Rev. A* **2011**, *83* (6), 063416. DOI: 10.1103/PhysRevA.83.063416.
- (13) Ide, Y.; Kato, T.; Yamanouchi, K. Non-Born–Oppenheimer molecular wave functions of H₂ by extended multi-configuration time-dependent Hartree–Fock method. *Chem. Phys. Lett.* **2014**, *595–596*, 180-184. DOI: <http://dx.doi.org/10.1016/j.cplett.2014.01.055>.
- (14) Hammes-Schiffer, S. Theory of Proton-Coupled Electron Transfer in Energy Conversion Processes. *Acc. Chem. Res.* **2009**, *42* (12), 1881-1889. DOI: 10.1021/ar9001284.
- (15) Gerber, R. B.; Ratner, M. A. Self-Consistent-Field Methods for Vibrational Excitations in Polyatomic Systems. In *Advances in Chemical Physics*, Advances in Chemical Physics, 1988; pp 97-132.
- (16) Manthe, U.; Meyer, H. D.; Cederbaum, L. S. Wave-packet dynamics within the multiconfiguration Hartree framework: General aspects and application to NOCl. *J. Chem. Phys.* **1992**, *97* (5), 3199-3213. DOI: 10.1063/1.463007 (accessed 2/22/2025).
- (17) Beck, M. H.; Jäckle, A.; Worth, G. A.; Meyer, H. D. The multiconfiguration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets. *Physics Reports* **2000**, *324* (1), 1-105. DOI: [https://doi.org/10.1016/S0370-1573\(99\)00047-2](https://doi.org/10.1016/S0370-1573(99)00047-2).
- (18) Abedi, A.; Maitra, N. T.; Gross, E. K. U. Correlated electron-nuclear dynamics: Exact factorization of the molecular wavefunction. *J. Chem. Phys.* **2012**, *137* (22), 22A530. DOI: 10.1063/1.4745836 (accessed 2022/04/18).
- (19) Abedi, A.; Agostini, F.; Gross, E. K. U. Mixed quantum-classical dynamics from the exact decomposition of electron-nuclear motion. *Europhys. Lett.* **2014**, *106* (3), 33001. DOI: 10.1209/0295-5075/106/33001.
- (20) Born, M.; K.Huang. *Dynamical Theory of Crystal Lattices*; Oxford; Oxford University Press, 1954.
- (21) Epstein, S. T. Ground-State Energy of a Molecule in the Adiabatic Approximation. *J. Chem. Phys.* **1966**, *44* (2), 836-837. DOI: 10.1063/1.1726771 (accessed 2/22/2025).

- (22) Levine, R. D. The chemical shape of molecules: an introduction to dynamic stereochemistry. *J. Phys. Chem.* **1990**, *94* (26), 8872-8880. DOI: 10.1021/j100389a006.
- (23) Domcke, W.; Yarkony, D. R.; Köppel, H. Conical Intersections: Theory, Computations, Experiments. World Scientific: Singapore, 2011.
- (24) Matsika, S. Electronic Structure Methods for the Description of Nonadiabatic Effects and Conical Intersections. *Chem. Rev.* **2021**, *121* (15), 9407-9449. DOI: 10.1021/acs.chemrev.1c00074.
- (25) Smith, F. T. Diabatic and Adiabatic Representations for Atomic Collision Problems. *Phys. Rev.* **1969**, *179* (1), 111-123.
- (26) Baer, M. *Beyond Born-Oppenheimer: Electronic Nonadiabatic Coupling Terms and Conical Intersections*; Hoboken (NJ); Wiley, 2006.
- (27) Herek, J. L.; Materny, A.; Zewail, A. H. Femtosecond control of an elementary unimolecular reaction from the transition-state region. *Chem. Phys. Lett.* **1994**, *228* (1), 15-25. DOI: [https://doi.org/10.1016/0009-2614\(94\)00910-4](https://doi.org/10.1016/0009-2614(94)00910-4).
- (28) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge; Cambridge University Press, 2005.
- (29) Nakamura, H. *Introduction to non adiabatic dynamics*; Singapore; World Scientific, 2019.
- (30) Tully, J. C. Molecular dynamics with electronic transitions. *J. Chem. Phys.* **1990**, *93* (2), 1061-1071. DOI: doi:<http://dx.doi.org/10.1063/1.459170>.
- (31) Heller, E. J. Time-dependent approach to semiclassical dynamics. *J. Chem. Phys.* **1975**, *62* (4), 1544-1555. DOI: 10.1063/1.430620.
- (32) Heller, E. J. Frozen Gaussians: A very simple semiclassical approximation. *J. Chem. Phys.* **1981**, *75* (6), 2923-2931. DOI: 10.1063/1.442382 (accessed 4/6/2025).
- (33) Ben-Nun, M.; Levine, R. D.; Fleming, G. R. Solvent-induced nonadiabatic transitions in iodine: An ultrafast pump-probe computational study. *J. Chem. Phys.* **1996**, *105* (8), 3035-3056. DOI: 10.1063/1.472175 (accessed 4/6/2025).
- (34) Ajay, J. S.; Komarova, K. G.; Remacle, F.; Levine, R. D. Time-dependent view of an isotope effect in electron-nuclear nonequilibrium dynamics with applications to N₂. *Proc. Natl. Acad. Sci. U.S.A* **2018**, *115*, 5890-5895, 10.1073/pnas.1804455115.
- (35) Ben-Nun, M.; Martínez, T. J.; Levine, R. D. Multiple traversals of a conical intersection: electronic quenching in Na* + H₂. *Chem. Phys. Lett.* **1997**, *270* (3), 319-326. DOI: [https://doi.org/10.1016/S0009-2614\(97\)00369-2](https://doi.org/10.1016/S0009-2614(97)00369-2).
- (36) Curchod, B. F. E.; Martínez, T. J. Ab Initio Nonadiabatic Quantum Molecular Dynamics. *Chem. Rev.* **2018**, *118* (7), 3305-3336. DOI: 10.1021/acs.chemrev.7b00423.
- (37) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; et al. Advances in methods and algorithms in a modern quantum chemistry program package. *Phys. Chem. Chem. Phys.* **2006**, *8* (27), 3172-3191, 10.1039/B517914A. DOI: 10.1039/B517914A.
- (38) Gelfand, N.; Komarova, K.; Remacle, F.; Levine, R. D. Nonadiabatic dynamics in a forest of coupled states: Electronic state branching in the VUV photodissociation of N₂. *J. Chem. Phys.* **2023**, *158* (16), 164302. DOI: 10.1063/5.0148798 (accessed 5/11/2023).
- (39) Spelsberg, D.; Meyer, W. Dipole-allowed excited states of N[_{sub} 2]: Potential energy curves, vibrational analysis, and absorption intensities. *J. Chem. Phys.* **2001**, *115* (14), 6438-6449.

- (40) Ayari, T.; M., D.-L.; R., L.; A., G. G.; L., N.; A., B. H.; H., G.; R., B. S.; and Hochlaf, M. State-to-state dissociative photoionization of molecular nitrogen: the full story. *Advances in Physics: X* **2020**, 5 (1), 1831955. DOI: 10.1080/23746149.2020.1831955.
- (41) Colbert, D. T.; Miller, W. H. A novel discrete variable representation for quantum mechanical reactive scattering via the S-matrix Kohn method. *J. Chem. Phys.* **1992**, 96 (3), 1982-1991. DOI: 10.1063/1.462100 (accessed 4/6/2025).
- (42) Lill, J. V.; Parker, G. A.; Light, J. C. The discrete variable–finite basis approach to quantum scattering. *J. Chem. Phys.* **1986**, 85 (2), 900-910. DOI: 10.1063/1.451245 (accessed 4/6/2025).
- (43) Tannor, D. J. *Introduction to quantum mechanics. A time-dependent perspective*; Sausalito; University Science Book, 2007.
- (44) Kosloff, R. Time-dependent quantum-mechanical methods for molecular dynamics. *J. Phys. Chem.* **1988**, 92 (8), 2087-2100. DOI: 10.1021/j100319a003.
- (45) Kosloff, R. Propagation Methods for Quantum Molecular Dynamics. *Ann. Rev. Phys. Chem.* **1994**, 45, 145-178.
- (46) Song, Y.; Gao, H.; Chang, Y. C.; Hammoutene, D.; Ndome, H.; Hochlaf, M.; Jackson, W. M.; Ng, C. Y. Quantum-state dependence of product branching ratios in vacuum ultraviolet photodissociation of N₂. *Astrophys. J.* **2016**, 819 (1), 13. DOI: 10.3847/0004-637x/819/1/23.
- (47) Liu, M.; Jiang, P.; Lu, L.; Yin, T.; Ma, L.; Cheng, M.; Yin, Q.-Z.; Gao, H. Strong Isotope-dependent Photodissociation Branching Ratios of N₂ and Their Potential Implications for the 14N/15N Isotope Fractionation in Titan's Atmosphere. *Astrophys. J.* **2021**, 923 (2), 196. DOI: 10.3847/1538-4357/ac2f97.
- (48) Riss, U. V.; Meyer, H. D. Reflection-free complex absorbing potentials. *J. Phys. B* **1995**, 28 (8), 1475. DOI: 10.1088/0953-4075/28/8/012.
- (49) Kosloff, R.; Kosloff, D. Absorbing boundaries for wave propagation problems. *J. Comput. Phys.* **1986**, 63 (2), 363-376. DOI: [https://doi.org/10.1016/0021-9991\(86\)90199-3](https://doi.org/10.1016/0021-9991(86)90199-3).
- (50) Jasper, A. W.; Kendrick, B. K.; Mead, C. A.; Trulhar, D. G. Non-Born-Oppenheimer Chemistry : Potential surfaces, couplings and dynamics. In *Modern Trends in Chemical Reactions Dynamics: Experiment and Theory*, Yang, X., Liu, K. Eds.; Singapore; World Scientific, 2004; pp 329-391.
- (51) Pacher, T.; Cederbaum, L. S.; Köppel, H. Adiabatic and Quasidiabatic States in a Gauge Theoretical Framework. In *Advances in Chemical Physics*, Vol. 84; Wiley, 1993; pp 293-391.
- (52) Nielsen, M. A.; L., C. I. *Quantum Computation and Quantum Information*; Cambridge; Cambridge University Press, 2010.
- (53) Ekert, A.; Knight, P. L. Entangled quantum systems and the Schmidt decomposition. *Am. J. Phys.* **1995**, 63 (5), 415-423. DOI: 10.1119/1.17904 (accessed 2022/03/24).
- (54) Horodecki, R.; Horodecki, P.; Horodecki, M.; Horodecki, K. Quantum entanglement. *Rev. Mod. Phys.* **2009**, 81 (2), 865-942. DOI: 10.1103/RevModPhys.81.865.
- (55) Aspect, A.; Dalibard, J.; Roger, G. Experimental Test of Bell's Inequalities Using Time-Varying Analyzers. *Phys. Rev. Lett.* **1982**, 49 (25), 1804-1807. DOI: 10.1103/PhysRevLett.49.1804.
- (56) Aspect, A.; Grangier, P.; Roger, G. Experimental Realization of Einstein-Podolsky-Rosen-Bohm Gedankenexperiment: A New Violation of Bell's Inequalities. *Phys. Rev. Lett.* **1982**, 49 (2), 91-94. DOI: 10.1103/PhysRevLett.49.91.
- (57) Hou, X.-W.; Chen, J.-H.; Ma, Z.-Q. Dynamical entanglement of vibrations in an algebraic model. *Phys. Rev. A* **2006**, 74 (6), 062513. DOI: 10.1103/PhysRevA.74.062513.

- (58) Li, J.; Kais, S. Entanglement classifier in chemical reactions. *Sci. Adv.* **2019**, *5* (8), eaax5283. DOI: 10.1126/sciadv.aax5283 (accessed 2022/03/27).
- (59) Li, J.; Sajjan, M.; Kale, S. S.; Kais, S. Statistical Correlation Between Quantum Entanglement and Spin–Orbit Coupling in Crossed Beam Molecular Dynamics. *Adv. Quantum Technol.* **2021**, 2100098. DOI: 10.1002/qute.202100098.
- (60) Sanz-Vicario, J. L.; Pérez-Torres, J. F.; Moreno-Polo, G. Electronic-nuclear entanglement in $\{\mathrm{H}\}_2^+$: Schmidt decomposition of non-Born-Oppenheimer wave functions expanded in nonorthogonal basis sets. *Phys. Rev. A* **2017**, *96* (2), 022503. DOI: 10.1103/PhysRevA.96.022503.
- (61) McKemmish, L. K.; McKenzie, R. H.; Hush, N. S.; Reimers, J. R. Quantum entanglement between electronic and vibrational degrees of freedom in molecules. *J. Chem. Phys.* **2011**, *135* (24), 244110. DOI: 10.1063/1.3671386 (accessed 2022/03/24).
- (62) Haxton, D. J.; Lawler, K. V.; McCurdy, C. W. Qualitative failure of a multiconfiguration method in prolate spheroidal coordinates in calculating dissociative photoionization of $\{\mathrm{H}\}_2^+$. *Phys. Rev. A* **2015**, *91* (6), 062502. DOI: 10.1103/PhysRevA.91.062502.
- (63) Vatasescu, M. Entanglement between electronic and vibrational degrees of freedom in a laser-driven molecular system. *Phys. Rev. A* **2013**, *88* (6), 063415. DOI: 10.1103/PhysRevA.88.063415.
- (64) Izmaylov, A. F.; Franco, I. Entanglement in the Born–Oppenheimer Approximation. *J. Chem. Theory Comput.* **2017**, *13* (1), 20–28. DOI: 10.1021/acs.jctc.6b00959.
- (65) Blavier, M.; Gelfand, N.; Levine, R. D.; Remacle, F. Entanglement of electrons and nuclei: A most compact representation of the molecular wave function. *Chem. Phys. Lett.* **2022**, *804*, 139885. DOI: <https://doi.org/10.1016/j.cplett.2022.139885>.
- (66) Blavier, M.; Gelfand, N.; Levine, R. D.; Remacle, F. Controlling the Time Evolution of Electron–Nuclei Entanglement for Steering Vibronic Coherences Dynamics Induced by Short 1–2 fs Optical Pulses. In *Proceedings of the 8th International Conference on Attosecond Science and Technology*, Cham, 2024//, 2024; Argenti, L., Chini, M., Fang, L., Eds.; Springer International Publishing: pp 83–100. DOI: https://doi.org/10.1007/978-3-031-47938-0_9.
- (67) Golub, G. H.; Loan, C. F. V. *Matrix Computations* Baltimore; John Hopkins University Press, 2013.
- (68) Golub, G. H.; Reinsch, C. Singular Value Decomposition and Least Squares Solutions. In *Linear Algebra*, Wilkinson, J. H., Reinsch, C., Bauer, F. L. Eds.; Berlin, Heidelberg; Springer Berlin Heidelberg, 1971; pp 134–151.
- (69) van den Wildenberg, S.; Mignolet, B.; Levine, R. D.; Remacle, F. Temporal and spatially resolved imaging of the correlated nuclear-electronic dynamics and of the ionized photoelectron in a coherently electronically highly excited vibrating LiH molecule. *J. Chem. Phys.* **2019**, *151* (13), 134310. DOI: 10.1063/1.5116250 (accessed 2019/10/27).
- (70) Zhang, T.; Golub, G. H. Rank-one approximation to high order tensors. *Siam J. Matrix Anal. Appl.* **2001**, *23* (2), 534–550.
- (71) Blavier, M.; Komarova, K.; Gonçalves, C. E. M.; Levine, R. D.; Remacle, F. Electronic Coherences Steer the Strong Isotope Effect in the Ultrafast Jahn–Teller Structural Rearrangement of Methane Cation upon Tunnel Ionization. *J. Phys. Chem. A* **2021**, *125* (43), 9495–9507. DOI: 10.1021/acs.jpca.1c06431.

- (72) Gonçalves, C. E. M.; Levine, R. D.; Remacle, F. Ultrafast geometrical reorganization of a methane cation upon sudden ionization: an isotope effect on electronic non-equilibrium quantum dynamics. *Phys. Chem. Chem. Phys.* **2021**, *23* (21), 12051-12059, 10.1039/D1CP01029H. DOI: 10.1039/D1CP01029H.
- (73) Cardosa-Gutierrez, M.; Levine, R. D.; Remacle, F. Electronic coherences built by an attopulse control the forces on the nuclei. *J. Phys. B At. Mol. Opt. Phys.* **2024**, *57* (13), 133501. DOI: 10.1088/1361-6455/ad4fd3.
- (74) Nijjar, P.; Jankowska, J.; Prezhdo, O. V. Ehrenfest and classical path dynamics with decoherence and detailed balance. *J. Chem. Phys.* **2019**, *150* (20), 204124. DOI: 10.1063/1.5095810 (accessed 6/25/2023).
- (75) Doltsinis, N. L. Molecular dynamics beyond the Born-Oppenheimer approximation: Mixed quantum-classical approaches. In *Computational nanoscience: Do it yourself!*, Grotendorst, J., Blügel, S., Marx, D. Eds.; Jülich; John von Neuman Institute for computing, 2006.
- (76) Subotnik, J. E. Augmented Ehrenfest dynamics yields a rate for surface hopping. *J. Chem. Phys.* **2010**, *132* (13), 134112. DOI: 10.1063/1.3314248 (accessed 7/15/2023).
- (77) Valentini, A.; van den Wildenberg, S.; Remacle, F. Selective bond formation triggered by short optical pulses: quantum dynamics of a four-center ring closure. *Phys. Chem. Chem. Phys.* **2020**, *22* (39), 22302-22313, 10.1039/D0CP03435E. DOI: 10.1039/D0CP03435E.
- (78) Stapelfeldt, H.; Seideman, T. Colloquium: Aligning molecules with strong laser pulses. *Rev. Mod. Phys.* **2003**, *75* (2), 543-557. DOI: 10.1103/RevModPhys.75.543.
- (79) Gordon, R. J.; Zhu, L.; Seideman, T. Coherent Control of Chemical Reactions. *Acc. Chem. Res.* **1999**, *32* (12), 1007-1016. DOI: 10.1021/ar970119l.
- (80) Ghafur, O.; Rouzee, A.; Gijsbertsen, A.; Siu, W. K.; Stolte, S.; Vrakking, M. J. J. Impulsive orientation and alignment of quantum-state-selected NO molecules. *Nature Physics* **2009**, *5* (4), 289-293. DOI: 10.1038/Nphys1225.
- (81) Kraus, P. M.; Baykusheva, D.; Wörner, H. J. Two-Pulse Field-Free Orientation Reveals Anisotropy of Molecular Shape Resonance. *Phys. Rev. Lett.* **2014**, *113* (2), 023001. DOI: 10.1103/PhysRevLett.113.023001.
- (82) Fleischer, S.; Zhou, Y.; Field, R. W.; Nelson, K. A. Molecular Orientation and Alignment by Intense Single-Cycle THz Pulses. *Phys. Rev. Lett.* **2011**, *107* (16), 163603. DOI: 10.1103/PhysRevLett.107.163603.
- (83) Zare, R. N. *Angular Momentum, Understanding Spatial Aspects in Chemistry and Physics*; New York; Wiley, 1991.
- (84) Bernstein, R. B. *Chemical Dynamics via Molecular Beam and Laser Techniques*; Oxford; Oxford University Press, 1992.
- (85) Bernstein, R. B.; Herschbach, D. R.; Levine, R. D. Dynamical aspects of stereochemistry. *J. Phys. Chem.* **1987**, *91* (21), 5365-5377. DOI: 10.1021/j100305a001.
- (86) Calegari, F.; Ayuso, D.; Trabattoni, A.; Belshaw, L.; De Camillis, S.; Anumula, S.; Frassetto, F.; Poletto, L.; Palacios, A.; Decleva, P.; et al. Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses. *Science* **2014**, *346* (6207), 336-339, 10.1126/science.1254061.
- (87) Kraus, P. M.; Mignolet, B.; Baykusheva, D.; Rupenyan, A.; Horný, L.; Penka, E. F.; Grassi, G.; Tolstikhin, O. I.; Schneider, J.; Jensen, F.; et al. Measurement and laser control of attosecond charge migration in ionized iodoacetylene. *Science* **2015**, *350* (6262), 790-795. DOI: 10.1126/science.aab2160.

- (88) Nisoli, M.; Decleva, P.; Calegari, F.; Palacios, A.; Martín, F. Attosecond Electron Dynamics in Molecules. *Chem. Rev.* **2017**, *117* (16), 10760-10825. DOI: 10.1021/acs.chemrev.6b00453.
- (89) Månsson, E. P.; Latini, S.; Covito, F.; Wanie, V.; Galli, M.; Perfetto, E.; Stefanucci, G.; Hübener, H.; De Giovannini, U.; Castrovilli, M. C.; et al. Real-time observation of a correlation-driven sub 3 fs charge migration in ionised adenine. *Commun. Chem.* **2021**, *4* (1), 73. DOI: 10.1038/s42004-021-00510-5.
- (90) Schwickert, D.; Ruberti, M.; Kolorenč, P.; Usenko, S.; Przystawik, A.; Baev, K.; Baev, I.; Braune, M.; Bocklage, L.; Czwalińska, M. K.; et al. Electronic quantum coherence in glycine molecules probed with ultrashort x-ray pulses in real time. *Sci. Adv.* **2022**, *8* (22), eabn6848. DOI: 10.1126/sciadv.abn6848 (accessed 2023/07/01).
- (91) Cardoso-Gutierrez, M.; Levine, R. D.; Remacle, F. Electronic Coherences Excited by an Ultra Short Pulse Are Robust with Respect to Averaging over Randomly Oriented Molecules as Shown by Singular Value Decomposition. *The Journal of Physical Chemistry A* **2024**, *128* (15), 2937-2947. DOI: 10.1021/acs.jpca.3c07856.
- (92) Remacle, F.; Levine, R. D.; Schlag, E. W.; Weinkauf, R. Electronic Control of Site Selective Reactivity: A Model Combining Charge Migration and Dissociation. *J. Phys. Chem. A* **1999**, *103*, 10149-10158.
- (93) Remacle, F.; Levine, R. D. Electronic Response of Assemblies of Designer Atoms : The Metal - Insulator Transition and the Role of Disorder. *J. Am. Chem. Soc.* **2000**, *122*, 4084-4091.
- (94) Paldus, J. Group theoretical approach to the configuration interaction and perturbation theory calculations for atomic and molecular systems. *J. Chem. Phys.* **1974**, *61* (12), 5321-5330. DOI: 10.1063/1.1681883 (accessed 4/30/2025).
- (95) Gilmore, R. *Lie groups, Lie algebras and some of their applications*; Mineola; Dover, 2012.
- (96) Hamilton, J. R.; Levine, R. D.; Remacle, F. Constructing Dynamical Symmetries for Quantum Computing: Applications to Coherent Dynamics in Coupled Quantum Dots. *Nanomaterials* **2024**, *14* (24), 2056.