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Dynamical variational approach to non-adiabatic electronic structure

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Abstract

Studying non-adiabatic effects in molecular dynamics simulations and modeling their optical signatures in linear and non-linear spectroscopies calls for electronic structure calculations in a situation when the ground state is degenerate or almost degenerate. Such degeneracy causes serious problems in invoking single Slater determinant Hartree–Fock (HF) and density functional theory (DFT) methods. To resolve this problem, we develop a generalization of time-dependent (dynamical) variational approach which accounts for the degenerate or almost degenerate ground state structure. Specifically, we propose a ground state ansatz for the subspace of generalized electronic configurations spanned on the degenerate grounds state multi-electron wavefunctions. Further employing the invariant form of Hamilton dynamics we arrive with the classical equations of motion describing the time-evolution of this subspace in the vicinity of the stationary point. The developed approach can be used for accurate calculations of molecular excited states and electronic spectra in the degenerate case.
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1. Introduction

Non-adiabatic dynamics in the vicinity of unavoided level crossings is a key mechanism in a variety of ultrafast photo-chemical and photo-physical processes among them are photo-isomerization reactions [1–6], and non-radiative energy relaxation in biological macromolecules [7–16]. Gaining an insight into these processes requires large scale non-adiabatic molecular dynamics simulations. Identification of specific dynamical features, and comparison with experiment can be done through simulations of the multiple-scale linear and non-linear optical and infrared (IR) responses [17–22]. On the other hand, optical manipulation of the photo-excited vibrational wavepackets in the vicinity of the level crossings can increase the efficiency of photo-reactions underlying a problem of coherent optical control

[23–27]. These issues motivate extensive studies of non-adiabatic dynamics which are focused on vibrational wavepackets quantum or semiclassical dynamics, which propagate through the region of the level crossings [28–30]. However, adequate parameterization of the potential energy surfaces in the level crossing region and determination of the non-adiabatic couplings require first principle techniques for calculating the electronic structure in the vicinity of the level crossing [1,9,11,14]. The optical response simulations in the same region further call for challenging dynamical, i.e. time-dependent, electronic structure calculations [5,6,30–33].

Typically, in organic molecular materials the occupied electronic orbitals are well separated by an energy gap from the virtual orbitals, and optical excitation causes transitions between these two manifolds as illustrated in Fig. 1A. In the region of the level crossing several orbitals from these manifolds approach each other producing degenerate mid-gap levels shown in Fig. 1B, and as a result the ground multi-electron state becomes degenerate. This is

A

K-N virtual orbitals

B

K-N-N_a virtual orbitals

E_g

N_a midgap orbitals

N filled orbitals
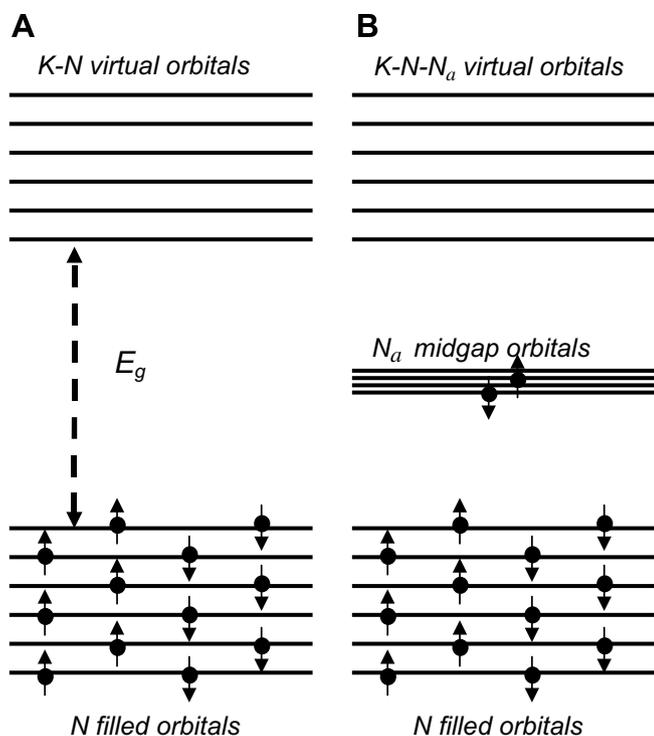
N filled orbitals

Fig. 1. Electronic orbitals structure due to: (A) Nuclei configurations away from the level crossings (non-degenerate ground state) region where the manifold of occupied (filled) orbitals is separated by an energy gap E_g from the manifold of virtual (unfilled) electronic orbitals. (B) Nuclei configurations in the vicinity of the level crossing (*n*-fold degenerate ground state) where a manifold of mid-gap (almost) degenerate orbitals appears.

a typical situation in a number of bio molecules such as rhodopsin [2,3,26], DNA base pairs [9,11], and fluorescent proteins [3,4] where different reaction dynamics occurs in the region of unavoided level crossings. The degeneracy causes a problem to apply well developed single-determinant methodologies such as Hartree–Fock (HF) and density functional theory (DFT) methods for performing stationary state variational calculations. Correlated wavefunction approaches, e.g., configuration interaction (CI) and coupled cluster (CC) techniques [34] are able to circumvent this problem. However, their implementations require tremendous increase of computational costs. To decrease the computational expense, the single-particle states are frequently partitioned into the filled orbitals (Fig. 1B) which can be described by a single Slater determinant and mid-gap active space orbitals which are subject to CI expansion. Since the dimensionality of the active space is significantly smaller than its filled orbitals counterpart, an expansion of the multi-electron wave function can be done in terms of a few single Slater determinants. Such methodologies have been extensively developed and are referred to as multi-configurational self-consistent field (MCSCF) method including popular complete active space self-consistent filed (CASSCF) technique [34–37].

Dynamical time-dependent HF (TDHF) is one of the oldest methods used to calculate electronic excitations by

following evolution of the non-degenerate ground state under the influence of an external field [38–42]. Coupled with semiempirical approaches this method has been successfully applied to describe optical response in a variety of molecular systems [43–45]. In the limit of weak fields, the TDHF and TDDFT calculations are performed in the vicinity of the stationary point using the random phase approximation (RPA) [46]. In general, the time-dependent variational approach, whose particular case is TDHF method, can be formulated in terms of classical Lagrangian equations of motion. The latter naturally give rise to the classical Hamilton dynamics. For TDHF in the RPA these equations describe dynamics of a set of harmonic oscillators which can be coupled through high order unharmonic terms [44,46,47]. TDHF methodology shares many similarities with adiabatic time-dependent DFT (TDDFT) technique, which became an effective modern tool for calculation of electronic excitations in both finite molecular systems and solids [48,49]. Formulation of TDDFT in terms of the classical Hamilton dynamics and oscillator picture of optical responses have been recently established [50–52].

In this paper, we develop a generalization of the time-dependent variational approach, specifically the TDHF method, to treat the dynamics of *degenerate ground state* in the vicinity of the stationary point. To address this challenging task we employ general formalism of classical Hamilton dynamics [53–55], and derive a set of classical equations of motion that describe the time evolution of the electronic states. To set the stage for a large variety of practical applications, we intend to develop a general formalism by considering the problem at the level of the time evolution of the electronic subspaces, spanned on the molecular orbitals that determine a variational ansatz. In Section 2, we start by introducing stationary variational principle for degenerate ground state. Although this principle has been formulated before [56–60], it sets the stage for our generalization, and we discuss it in details. Also the simplest electronic state ansatz describing the degenerate ground state is formulated in this section. Section 3 presents our central results where generalized dynamical variational principle is introduced. Based on this principle, the Hamiltonian equations for the electronic state ansatz dynamics in the vicinity of the stationary point are derived. Simplicity of the equations structure is naturally connected with the geometric properties of the adopted ansatz. Therefore in Section 4, we provide a complimentary geometric picture of the developed formalism. Concluding remarks are given in Section 5.

2. Stationary variational method

In this section, we introduce a generalization of stationary (time-independent) variational principle to describe multi-electron degenerate ground state. Development of reliable computational technique requires a set of assumptions on multi-electron wavefunction leading to a restriction of total multi-electron space where the variational

principle is formulated to a sub-space of generalized electronic configurations. This constitutes a generalized ground state ansatz also introduced in this section.

We start with the many-body electron Hamiltonian $\widehat{H}(\boldsymbol{x})$ parameterized by a set of nuclear coordinates $\boldsymbol{x}$ which participate in molecular dynamics. Adopting a quantum chemistry approach, we define a finite set of single-electron orbitals $|\chi_i\rangle$ with $i = \overline{1, K}$. After the expansion of the multi-electronic state creation and annihilation operators in the basis of single electron orbitals, the many body Hamiltonian acting in the space of all multi electron states $\mathscr{H}$ takes the following second quantization form

$$\widehat{H}(\boldsymbol{x}) = \sum_{ij} t_{ij}(\boldsymbol{x})\hat{c}_i^\dagger \hat{c}_j + \frac{1}{2}\sum_{ijkl} V_{ij,kl}(\boldsymbol{x})\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l. \quad (1)$$

Here $\hat{c}_i^\dagger$ ($\hat{c}_i$) is electron creation (annihilation) operator of the orbital state $|\chi_i\rangle$, with the spin degrees of freedom included into the index. t_{ij} is the hopping matrix element between orbitals i and j, and $V_{ij,kl}$ is the Coulomb matrix element antisymmetrized with respect to the permutations within the index pairs (i, j) and (k, l).

2.1. Exact variational method

In the simplest case of non-degenerate ground state, related multi-electron wave function $|\Psi_0\rangle$ can be chosen to be real and normalized $\langle\Psi_0|\Psi_0\rangle = 1$. Generally speaking, the stationary case can be considered in the complex spaces, however, due to time-reversal symmetry all relevant Hamiltonians are real and all solutions belong to the real parts of the relevant complex spaces. Working in real parts allows making use of this symmetry directly. Since the phase of the wave function can take arbitrary values, the latter is defined up to a factor ± 1. By minimizing the following classical Hamiltonian functional

$$H(\Psi_0) = \langle\Psi_0|\widehat{H}(\boldsymbol{x})|\Psi_0\rangle, \quad (2)$$

for fixed nuclear configuration $\boldsymbol{x}$ with the normalization condition given above, the stationary Schrödinger equation on $|\Psi_0\rangle$ can be recovered [61].

In the non-adiabatic case the ground state wavefunction is loosely defined in the neighborhood of the ground-state degeneracy. Specifically, the whole subspace of degenerate multi-electron states should be considered. Here, we focus on the situation when the nuclei configurations $\boldsymbol{x}$ lead to the formation of n (almost) degenerate mid-gap orbitals (Fig. 1B) corresponding to n-fold degeneracy of multi-electron eigenstates $|\Psi_\alpha\rangle$ with $\alpha = \overline{1, n}$. The latter are separated from the other states in $\mathscr{H}$ by a substantial energy gap. This allows us to introduce n-dimensional real subspace $\mathscr{S}$ spanned on $|\Psi_\alpha\rangle$, and a projection operator $\hat{\rho}$ onto $\mathscr{S}$ defined in $\mathscr{H}$. This operator can be represented in terms of the basis states as

$$\hat{\rho} = \frac{1}{n}\sum_{\alpha=1}^{n}|\Psi_\alpha\rangle\langle\Psi_\alpha|. \quad (3)$$

To generalize the variational principle, we define classical Hamiltonian function as projection of quantum Hamiltonian on degenerate state subspace $\mathscr{S}$

$$H(\mathscr{S}) = \text{Tr}(\hat{\rho}\widehat{H}(\boldsymbol{x})). \quad (4)$$

This Hamiltonian can be recast into the following equivalent form by using the representation of the projection operator given by Eq. (3)

$$H(\mathscr{S}) = \frac{1}{n}\sum_{\alpha=1}^{n}\langle\Psi_\alpha|\widehat{H}(\boldsymbol{x})|\Psi_\alpha\rangle. \quad (5)$$

Minimization of $H(\mathscr{S})$ with the orthonormality conditions $\langle\Psi_i|\Psi_j\rangle = \delta_{ij}$ can be achieved by introducing the Lagrange multipliers $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$, and the following function

$$h(\mathscr{S}) = \sum_{\alpha=1}^{n}\langle\Psi_\alpha|\widehat{H}(\boldsymbol{x})|\Psi_\alpha\rangle - \sum_{\alpha,\beta=1}^{n}\lambda_{\alpha\beta}\langle\Psi_\alpha|\Psi_\beta\rangle. \quad (6)$$

Standard variational procedure for $h(\mathscr{S})$ leads to a set of coupled Schrödinger equations

$$\begin{aligned}
\widehat{H}\Psi_1 &= \lambda_{11}\Psi_1 + \lambda_{12}\Psi_2 + \cdots + \lambda_{1n}\Psi_n, \\
\widehat{H}\Psi_2 &= \lambda_{21}\Psi_1 + \lambda_{22}\Psi_2 + \cdots + \lambda_{2n}\Psi_n, \\
&\vdots \\
\widehat{H}\Psi_n &= \lambda_{n1}\Psi_1 + \lambda_{n2}\Psi_2 + \cdots + \lambda_{nn}\Psi_n,
\end{aligned} \quad (7)$$

restricted to the subspace $\mathscr{S}$. Solution of these equations provides a set of eigenfunctions associated with the lowest energy state.

Note that definition of classical Hamiltonian function $H(\mathscr{S})$ given by Eq. (4) contains the trace of the operator product, and therefore, is invariant under the basis set transformations. This implies that $H(\mathscr{S})$ depends on the subspace itself (as we reflected by its argument), and the generalized variational principle has been formulated to minimize the energy of the *subspace* $\mathscr{S}$ regardless of particular choice of the basis functions. If one sets $n = 1$ in Eqs. (3)–(7) then Eq. (2) leading to non-degenerate ground state variational principle can be recovered.

2.2. Stationary electronic ansatz

To formulate an approximation for the degenerate state electronic wavefunctions, i.e. the generalized electronic state ansatz, we consider a system with even number of electrons which can occupy single-electron orbitals $|\chi_i\rangle$ where $i = \overline{1, K}$ with spin degrees of freedom included in the index. As shown in Fig. 1B, we partition these orbitals into N filled orbitals occupied by $2N$ electrons, N_a active mid-gap orbitals occupied by n_a electrons, and the virtual (unfilled) $K–N–N_a$ orbitals. Following HF approach, the multi-electron state of filled orbitals can be described by single Slater determinant $|\Omega_s\rangle$, whereas in the active space of orbitals we introduce a complete set of orthogonal n_a electron correlated states $|\zeta_\alpha\rangle$ with $\alpha = \overline{1, N_a^c}$. The latter are linear combinations of single Slater determinants

describing different occupations of active space orbitals by n_a electrons. Then among these states we select spin singlets only $|\zeta_\alpha^s\rangle$ with $\alpha = \overline{1, N_a^s}$. In general, the ansatz can be formulated in terms of all possible many body states existing in the active space. However to describe optical transitions, the restriction to the singlets is an adequate approximation. This approximation reduces the dimensionality of the active space which is a critical issue for expensive CI calculations.

Based on the introduced partitioning, we define n approximate trial wave functions as products

$$|\Psi_\alpha\rangle = |\Omega_s\rangle|\zeta_\alpha^s\rangle, \quad \alpha = \overline{1, n}. \tag{8}$$

Related subspace of generalized trial electronic configurations $\mathscr{S}_t$ embedded in $\mathscr{H}$ is spanned onto these trial wavefunctions, and the projection operator on $\mathscr{S}_t$ obtained by substituting Eq. (8) into Eq. (3) reads

$$\hat{\rho} = |\Omega_s\rangle \left(\frac{1}{n} \sum_{\alpha=1}^{n} |\zeta_\alpha^s\rangle\langle\zeta_\alpha^s| \right) \langle\Omega_s|. \tag{9}$$

According to Eqs. (1), (4) and (9), the classical Hamiltonian function projected on the space of trial configurations $\mathscr{S}_t$ (ansatz) is

$$H(\mathscr{S}_t) = \sum_{i,j} t_{ij}\rho_{ij}^s + \sum_{i,j} V_{ij,kl}\rho_{il}^s\rho_{jk}^s$$
$$+ \sum_{a,b} \left(t_{ab} + \frac{1}{2} \sum_{i,j} V_{ia,bj}\rho_{ij}^s \right) \rho_{ab}^a$$
$$+ \frac{1}{2} \sum_{a,b,c,d} V_{ab,cd}\eta_{ab,cd}^a, \tag{10}$$

where indices i, j (a, b, c, d) denote all filled and virtual (active space) orbitals. The quantity

$$\rho_{ij}^s = \langle\Omega_s|\hat{c}_i^\dagger\hat{c}_j|\Omega_s\rangle, \tag{11}$$

entering Eq. (10), is single electron density matrix acting in the space of filled and virtual orbitals. Provided the single Slater determinant is given in the basis of filled orbitals, i.e. $|\Omega_s\rangle = \hat{c}_1^\dagger \ldots \hat{c}_{2N}^\dagger|0\rangle$ with $|0\rangle$ being electron vacuum state, then ρ_{ij}^s simplifies to have non-vanishing diagonal components $\rho_{ij}^s = \delta_{ij}$ for both i and j being filled orbital indices only. Note that the Coulomb component for the filled and virtual orbitals, i.e. the second term in Eq. (10), is partitioned into the product of two single electron density matrices using Wick's theorem [55].

Eq. (10) also contains

$$\rho_{ab}^a = \frac{1}{n} \sum_{\alpha=1}^{n} \langle\zeta_\alpha^s|\hat{c}_a^\dagger\hat{c}_b|\zeta_\alpha^s\rangle, \tag{12}$$

$$\eta_{ab,cd}^a = \frac{1}{n} \sum_{\alpha=1}^{n} \langle\zeta_\alpha^s|\hat{c}_a^\dagger\hat{c}_b^\dagger\hat{c}_c\hat{c}_d|\zeta_\alpha^s\rangle, \tag{13}$$

which are respectively, single electron and correlated two-electron density matrices calculated on the active space sin-

glet states.[1] Obviously, a partitioning of the latter quantity into a product of ρ_{ab}^a according to Wick's theorem (similar to ρ_{ij}^s) cannot be done in this case. In general, the singlet states can be represented in terms of electron creation operators as

$$|\zeta_\alpha^s\rangle = \sum_{b_1,\ldots,b_{n_a}} S_{b_1,\ldots,b_{n_a}}^\alpha \hat{c}_{b_1}^\dagger \ldots \hat{c}_{b_{n_a}}^\dagger|0\rangle, \tag{14}$$

where $|0\rangle$ is electron vacuum state, and $S_{b_1,\ldots,b_{n_a}}^\alpha$ are the components of the active space many body wavefunction given in the basis of active space single electron orbitals. This expansion gives rise to a well know hierarchy of multiple point correlation functions (full CI) describing the many body states whose explicit form depends on the number of involved active space electrons.

According to the variational principle, the stationary point subspace $\overline{\mathscr{S}_t}$ can be found by minimizing the function $H(\mathscr{S}_t)$ with respect to $\mathscr{S}_t$. The first term in the expression for $H(\mathscr{S}_t)$ (Eq. (10)) contains single electron density matrix acting in the subspace of filled and virtual orbitals. This term can be minimized by standard HF procedures. Minimization of the last two terms containing correlated active space states requires exact, active space full CI calculations. Since the correlated active space states are coupled to the filled and virtual orbitals through the third term in Eq. (10), both HF and active space full CI should be done in a self-consistent way. By taking into account that electronic state ansatz (Eq. (8)) can be viewed as a linear combination of extended Slater determinants, where each term is a product of $|\Omega_s\rangle$ and a Slater determinant contributing to $|\zeta_\alpha^s\rangle$, practical implementation of the minimization procedure for the Hamiltonian $H(\mathscr{S}_t)$ can be done by using the MCSCF techniques [34–37].

3. Dynamical variational method

The stationary variational principle together with the electronic ansatz formulated in the previous section provide us with the equilibrium generalized electronic configuration subspace ($\overline{\mathscr{S}}$), constituting the stationary point of classical Hamiltonian $H(\mathscr{S})$. An external field perturbation which in our case is optical excitation corresponds to time evolution of $\mathscr{S}$ in the vicinity of $\overline{\mathscr{S}}$. This calls for a generalization of the variational principle formulated above to its dynamical version. In contrast to the stationary case where the many body wavefunction space $\mathscr{H}$, and its subspace of degenerate ground state $\mathscr{S}$ are real, the time evolution occurs in the complex spaces. It raises no problem to formulate the dynamical variational principle and dynamical ansatz, since the former real spaces are naturally embedded into their

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[1] To avoid confusion, we note that the superscripts s and a in Eqs. (11)–(13) define a subspace of the electronic states, the corresponding density matrix component belongs to, i.e., the subspace of the single-electron states or the active space. Moreover, the subscripts denote the indices of the basis set orbitals that span these subspaces. This notation will be consistently used throughout the paper.

complex counterparts forming the real part of the latter. The variational approach which we are going to implement here is based on a simple observation that, since, quantum evolution is represented by linear unitary operators it transforms any n-dimensional vector subspace of $\mathscr{H}$ that can be represented, e.g. by a set of n orthonormal vectors, to some other yet still n-dimensional vector subspace.

In this section we first, show how the evolution of the *complex* subspace $\mathscr{S}$ can be described as Hamilton classical dynamics, and further make use of this Hamiltonian picture to build dynamical variational ansatz in the vicinity of the stationary point $\overline{\mathscr{S}}$. For this purpose we introduce an extended time-dependent quantum Hamiltonian

$$\widehat{H}'(t; \boldsymbol{x}) = \widehat{H}(\boldsymbol{x}) - \mathscr{E}(t) \sum_{ij} \mu_{ij}(\boldsymbol{x}) \hat{c}_i^\dagger \hat{c}_j, \tag{15}$$

where the first term is material Hamiltonian given by Eq. (1). The second terms describes interaction between electrons and time-dependent external electric field $\mathscr{E}(t)$. The interaction is given in the dipole approximation [17], and the electronic transition dipole moment matrix elements are denoted by μ_{ij}, where, in general, the indices i, j run over all filled, virtual, and active space orbitals.

3.1. Hamiltonian formulation of variational principle

In the simplest case of non-degenerate ground state the stationary variational principle mentioned in Section 2.1 can be generalized to the dynamical variational principle. Specifically, a time dependent ground state $|\Psi_0(t)\rangle$ can be introduced, where the wavefunctions which differ by the phase factor are identical. Then a classical Lagrangian

$$\mathscr{L}(\Psi_0(t)) = i\langle \Psi_0(t)|\partial_t \Psi_0(t)\rangle - H(\Psi_0(t)), \tag{16}$$

should be considered, where $H(\Psi_0)$ is the classical Hamiltonian function defined by means of Eq. (2). Minimization of the action $S[\Psi_0] = \int_{t_i}^{t_f} dt \mathscr{L}(\Psi_0(t))$ leads to the time-dependent Schrödinger equation in the form of classical Lagrangian equations parameterized by the wavefunctions (generalized coordinates) and their time derivatives (generalized velocities). The latter can be recast to the form of classical Hamiltonian equations with the same Hamiltonian function $H(\Psi_0(t))$ and with generalized coordinates and momenta represented by linear combinations of the wave function real and imaginary parts [46]. A straightforward extension of this approach could be done to the case of n-fold degenerate multi-electron states. However, we prefer to use the language of Hamilton classical mechanics from the very beginning, since it significantly simplifies derivation of the equations of motion for the adopted degenerate electronic ground state ansatz.

Classical Hamilton dynamics is determined by two structures: classical Hamiltonian $H(\rho)$ and the Poisson bracket $\{f, g\}$ associated with two functions $f(\rho)$ and $g(\rho)$ all depending on generalized coordinates ρ_i. Specific assignment of ρ_i to parameterize the space of generalized electronic configurations $\mathscr{S}$ is given below where the time

evolution of electronic ansatz is considered. In general, the Poisson bracket can be represented using an invariant antisymmetric form $\hat{\omega}_{ij} = -\hat{\omega}_{ji}$ as

$$\{f, g\} = \sum_{ij} \hat{\omega}_{ij} \frac{\partial f}{\partial \rho_i} \frac{\partial g}{\partial \rho_j}, \tag{17}$$

and satisfies Leibniz's product rule, and the Jacobi identity [53–55]. Using this representation, the Liouville equations of motion for the generalized coordinates $d\rho_i/dt = \{H, \rho_i\}$, i.e. the Hamiltonian equations, read

$$\frac{d\rho_j}{dt} = \sum_i \hat{\omega}_{ij} \frac{\partial H(z)}{\partial \rho_i}. \tag{18}$$

Note, that in the basis set of conjugate momentum $p_i \equiv \rho_i$ and coordinate $q_j \equiv \rho_j$ where the form is diagonal, i.e. $\hat{\omega}_{ij} = -\hat{\omega}_{ji} = 1$, Eq. (18) acquires a well known form for the Hamiltonian equations [53].

Since we are interested in the dynamics in the vicinity of the stationary point $\bar{\rho}(\{H(\bar{\rho}), \bar{\rho}\} = 0)$, induced by the perturbation, the Hamiltonian $H(\rho)$ can be expanded in powers of the displacements $\delta\rho_i$

$$H(\bar{\rho} + \delta\rho) \approx H(\bar{\rho}) + \frac{1}{2} H_{kl}^{(2)}(\bar{\rho}) \delta\rho_k \delta\rho_l, \tag{19}$$

where $H_{ij}^{(2)}(\rho) = \partial^2 H(\rho)/\partial\rho_k \partial\rho_l$ and the Hamiltonian equations become

$$\frac{d\delta\rho}{dt} = -\hat{\omega} H^{(2)}(\bar{\rho}) \delta\rho, \tag{20}$$

where $\hat{\omega}$ is the Poisson bracket matrix with the elements $\hat{\omega}_{ij}$, $H^{(2)}$ is the classical Hamiltonian matrix with the components $H_{jk}^{(2)}(\rho)$, and $\delta\rho$ is a vector containing displacements $\delta\rho_k$. Eq. (20) is the final matrix form of the equations of motion which we use below to describe time-evolution of the electronic state ansatz.

3.2. Equations of motion for electronic ansatz

To derive an explicit form of Eq. (20) for the adopted electronic state ansatz Eq. (8), we should provide a representation for the invariant antisymmetric form $\hat{\omega}$, and the expansion of classical Hamiltonian $H^{(2)}$ in the vicinity of the stationary point. We address this issue below.

First, we identify the generalized coordinates entering Eqs. (17)–(20). The form of the classical Hamiltonian function given by Eq. (4) suggests that a natural choice of these coordinates is a set containing the single electron density matrix ρ^s (Eq. (11)) defined in the space of filled and virtual orbitals, the active space single electron density matrix ρ^a (Eq. (12)), and the active space two-electron density matrix η^a (Eq. (13)). These coordinates can be conveniently represented as the following block vector

$$\rho = \begin{pmatrix} \rho^s \\ \rho^a \\ \eta^a \end{pmatrix}, \tag{21}$$

where each component (matrix) is defined within different subspaces: ρ^s is a matrix defined in the space of filled and virtual orbitals, ρ^a is a single electron density matrix in the active space of correlated states. It can be diagonalized in the set of the natural orbitals. Therefore we are going to refer the subspace, where ρ^a is defined as the space of active natural orbitals. Finally, η^a is defined in the active space of all correlated singlets, and can be conveniently expanded in their basis set.

Our primary interest is the dynamics in the vicinity of the stationary point $\bar\rho$, therefore we partition Eq. (21) as $\rho = \bar\rho + \delta\rho$, where the stationary point components of $\bar\rho$ are coordinates associated with the minimum of the Hamiltonian function given by Eq. (10). To define the components of $\delta\rho$, we recall that the deviations from the stationary point are induced by the optical excitations. This suggests that we need to consider all possible optical transitions between the orbitals forming the three spaces defined by the vector ρ (Eq. (21)). Accordingly, we introduce the following (particle–hole) transition operators a in the many body state space $\mathscr{H}$

$$\widehat{U} = \sum_{a,i}(\hat{u}_{ai}u_{ai} + \hat{u}_{ia}u_{ia}), \tag{22}$$

$$\widehat{V} = \sum_{i,i'}(\hat{v}_{ii'}v_{ii'} + \hat{v}_{i'i}v_{i'i}), \tag{23}$$

$$\widehat{W} = \sum_{\alpha,\alpha'}(\hat{w}_{\alpha,\alpha'}w_{\alpha,\alpha'} + \hat{w}_{\alpha,\alpha'}w_{\alpha,\alpha'}), \tag{24}$$

where caret denotes $\mathscr{H}$ space (second quantized) operators defining the optical transitions, and related quantities v_{ij}, u_{ai}, and $w_{\alpha\alpha'}$ represent the intensities of these transitions. This is illustrated in Fig. 2. They also form matrix elements of the vector

$$\delta\rho = \begin{pmatrix} v \\ u \\ w \end{pmatrix} \tag{25}$$

entering classical equations of motion in the form of Eq. (20).

Next, we identify the operators $\hat{v}$, $\hat{u}$, and $\hat{w}$. $\hat{v}$ is defined in the space of filled and virtual orbitals, where only possible optical transitions are those between ith filled and i'th virtual orbitals. Therefore

$$\hat{v}_{ii'} = \hat{c}_i^\dagger\hat{c}_{i'},$$
$$\hat{v}_{i'i} = \hat{c}_{i'}^\dagger\hat{c}_i, \tag{26}$$

Another allowed optical transitions involve filled and active space (mid-gap) orbitals $|\chi_i\rangle$ and $|\chi_a\rangle$, respectively. These transitions perturb both ρ^s and ρ^a, and therefore, we identify

$$\hat{u}_{ai} = \hat{c}_a^\dagger\hat{c}_i,$$
$$\hat{u}_{ia} = \hat{c}_i^\dagger\hat{c}_a, \tag{27}$$

Finally, optical transition affecting η^a are transitions within the active singlet space correspond to
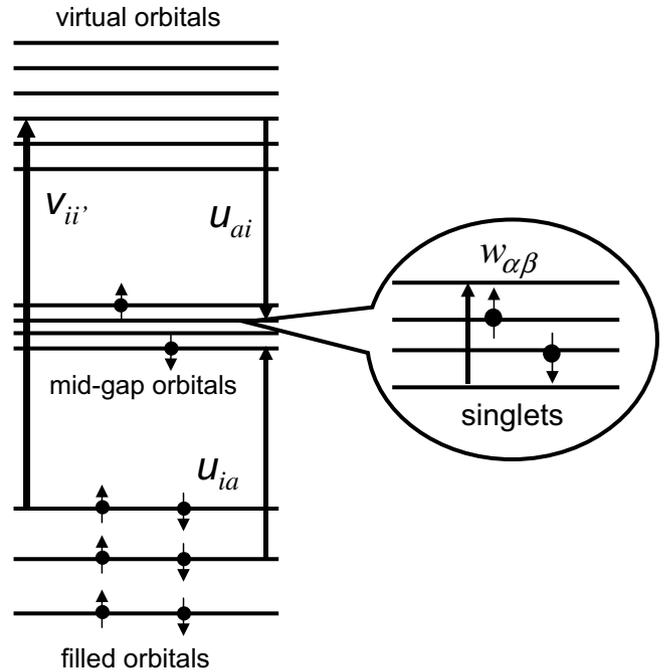

Fig. 2. Optical field induces transitions which can be associated with the components of $\delta\rho$ (Eq. (25)): v describes transitions between filled and virtual orbitals, u between active space and filled/virtual orbitals, and w between the correlated singlet states formed from the active space orbitals.

$$\hat{w}_{\alpha\alpha'} = \hat{\zeta}_\alpha^{s\dagger}\hat{\zeta}_{\alpha'}^s,$$
$$\hat{w}_{\alpha'\alpha} = \hat{\zeta}_{\alpha'}^{s\dagger}\hat{\zeta}_\alpha^s, \tag{28}$$

where $\hat{\zeta}_\alpha^{s\dagger}$ ($\hat{\zeta}_\alpha^s$) is creation (annihilation) operator of correlated singlet state in the active space which according to Eq. (14) can be represented as $\hat{\zeta}_\alpha^{s\dagger} = \sum_{b_1,...,b_{n_a}} S_{b_1,...,b_{n_a}}^\alpha \hat{c}_{b_1}^\dagger \ldots \hat{c}_{b_{n_a}}^\dagger$.

Next quantity entering the equations of motion (Eq. (20)), and which we need to calculate is the Poisson bracket (Eq. (17)). The Poisson bracket is defined by the differential 2-form whose representation is

$$\omega^{kl} = i\text{Tr}\{\hat{\rho}[\hat{t}^k,\hat{t}^l]\}. \tag{29}$$

This equation can be understood as the projection of the commutator of two operators in many body electronic space $\mathscr{H}$ on our trial subspace $\mathscr{S}_t$. Since the Poisson bracket in the quantum limit becomes a commutator, presented definition of ω^{kl} conceptually similar to the projected representation of the Hamiltonian given by Eq. (4). Operators $\hat{t}^k$ and $\hat{t}^l$ define the infinitesimal transitions leading to the Hamilton dynamics, and can be identified with the optically-induced particle–hole operators given by Eqs. (26)–(28). To calculate the 2-form we have to substitute all possible permutations of $\hat{v}$, $\hat{u}$, and $\hat{w}$ into Eq. (29).

First we calculate the block-diagonal terms, i.e. $\text{Tr}(\hat{\rho}[\hat{u},\hat{u}])$, $\text{Tr}(\hat{\rho}[\hat{v},\hat{v}])$, and $\text{Tr}(\hat{\rho}[\hat{w},\hat{w}])$ and find the following non-vanishing components

$$\omega_v^{ii',j'j} = i(\rho_{ij}^s\delta_{i'j'} - \delta_{ij}\rho_{i'j'}^s), \tag{30}$$

$$\omega_u^{ai,jb} = i(\rho_{ab}^a\delta_{ij} - \delta_{ab}\rho_{ij}^s), \tag{31}$$

$$\omega_w^{\alpha\alpha',\beta'\beta} = i\delta_{\alpha\alpha'}\delta_{\beta\beta'}. \tag{32}$$

Similar calculation of the off-diagonal blocks shows that $\text{Tr}(\hat{\rho}[\hat{u},\hat{v}]) = \text{Tr}(\hat{\rho}[\hat{u},\hat{w}]) = \text{Tr}(\hat{\rho}[\hat{v},\hat{w}]) = 0$. As a result, the 2-form is a block diagonal matrix

$$\omega = \begin{pmatrix} \omega_v & 0 & 0 \\ 0 & \omega_u & 0 \\ 0 & 0 & \omega_w \end{pmatrix} \tag{33}$$

with the matrix elements given by Eqs. (30)–(32).

To find the Poisson bracket, i.e. the antisymmetric matrix $\hat{\omega}_{ij}$, one needs to invert the 2-form ω^{ij}. The inversion is straightforward because each block of the 2-form can be diagonalized. Specifically, in the basis set of single

After expanding the exponentials in Eq. (39) into the Taylor series up to the second order (first non-vanishing) term in $H(\bar{\rho} + \delta\hat{\rho}^2)$, we find

$$\begin{aligned} \delta^2 H &= H(\bar{\rho} + \delta\hat{\rho}^2) - H(\bar{\rho}) \\ &= \frac{1}{2}\langle [\widehat{W} + \widehat{V} + \widehat{U}, [\widehat{W} + \widehat{V} + \widehat{U}, \widehat{H}]]\rangle_0 \\ &\quad + \frac{1}{2}\langle [[\widehat{W} + \widehat{V}, \widehat{U}], \widehat{H}]\rangle_0, \end{aligned} \tag{40}$$

where the short hand notation $\langle \cdot \rangle_0 \equiv \text{Tr}(\bar{\rho} \cdot)$ means averaging at stationary point. By taking the second derivative of Eq. (40) with respect to $\delta\rho$ (Eq. (25)), the classical Hamiltonian can be represented in the final block-matrix form

$$H^{(2)}(\bar{\rho}) = \begin{pmatrix} \langle[\hat{v}[\hat{v},\widehat{H}]]\rangle_0 & \langle[\hat{v}[\hat{u},\widehat{H}]]\rangle_0 + \frac{1}{2}\langle[[\hat{v},\hat{u}],\widehat{H}]\rangle_0 & \langle[\hat{v}[\hat{w},\widehat{H}]]\rangle_0 \\ \langle[\hat{u}[\hat{v},\widehat{H}]]\rangle_0 - \frac{1}{2}\langle[[\hat{u},\hat{v}],\widehat{H}]\rangle_0 & \langle[\hat{u}[\hat{u},\widehat{H}]]\rangle_0 & \langle[\hat{u}[\hat{w},\widehat{H}]]\rangle_0 - \frac{1}{2}\langle[[\hat{u},\hat{w}],\widehat{H}]\rangle_0 \\ \langle[\hat{w}[\hat{v},\widehat{H}]]\rangle_0 & \langle[\hat{w}[\hat{u},\widehat{H}]]\rangle_0 + \frac{1}{2}\langle[[\hat{w},\hat{u}],\widehat{H}]\rangle_0 & \langle[\hat{w}[\hat{w},\widehat{H}]]\rangle_0 \end{pmatrix}. \tag{41}$$

Slater determinant of filled orbitals, the single electron matrix ρ_{ij}^s becomes diagonal, with non-vanishing elements $\rho_{ij}^s = \delta_{ij}$, where both i,j describe filled orbitals. The density matrix ρ_{ab}^a is diagonal in the natural orbitals basis. We denote the diagonal matrix element (eigenvalues) by ϵ_a with $a = 1, N_a$, and note that their values confined in the interval $0 < \epsilon_a < 1$. The last ω_w block is already diagonal. Therefore, the Poisson bracket is

$$\hat{\omega} = \begin{pmatrix} \hat{\omega}^v & 0 & 0 \\ 0 & \hat{\omega}^u & 0 \\ 0 & 0 & \hat{\omega}^w \end{pmatrix} \tag{34}$$

with the matrix elements

$$\hat{\omega}_{ii',j'j}^v = -i\delta_{ij}\delta_{i'j'}, \tag{35}$$

$$\hat{\omega}_{ai,jb}^u = -i\delta_{ab}\delta_{ij}(\epsilon_a - 1)^{-1}, \tag{36}$$

$$\hat{\omega}_{\alpha\alpha',\beta'\beta}^w = -i\delta_{\alpha\alpha'}\delta_{\beta\beta'}. \tag{37}$$

The last quantity from equations of motion (Eq. (20)), left to determine is the classical Hamiltonian, expanded in the vicinity of stationary point $\overline{\mathscr{S}}$. First, we notice that operators $\widehat{U}$, $\widehat{V}$, and $\widehat{W}$ (Eqs. (22)–(24)) define infinitesimal displacements, and form Lie algebra. Therefore, a finite displacement of the projection operator $\hat{\rho}$ defining the displacement of the trial subspace $\widehat{S}_t$ is

$$\hat{\rho} = e^{\widehat{U}} e^{\widehat{W}+\widehat{V}} \bar{\rho} e^{-\widehat{W}-\widehat{V}} e^{-\widehat{U}}, \tag{38}$$

where the fact that $[\widehat{W},\widehat{V}] = 0$ is accounted for. The displacement of the projection operator induces the evolution of the classical Hamiltonian function

$$H(\hat{\rho}) = \text{Tr}(\bar{\rho} e^{-\widehat{W}-\widehat{V}} e^{-\widehat{U}} \widehat{H} e^{\widehat{U}} e^{\widehat{W}+\widehat{V}}). \tag{39}$$

In summary, the classical Hamiltonian equations in the vicinity of the stationary point are given by Eq. (20). For the adopted ansatz these equations define optically induced evolution of the density matrix $\delta\rho$ given by Eq. (25). The Poisson bracket and classical Hamiltonian function entering the equations of motion are given by Eqs. (34) and (41). By taking a product of the Poisson bracket and the Hamiltonian function classical Liouville operator can be introduced and reads

$$\mathscr{L}(\bar{\rho}) = \hat{\omega} H^{(2)}(\bar{\rho}). \tag{42}$$

The eigenvalues Ω_a and eigenvectors ξ_a of this operator satisfy the equation

$$\mathscr{L}(\bar{\rho})\xi_a = \Omega_a \xi_a, \tag{43}$$

and define observable optical transition energies and transition densities. The adopted block-matrix representation reflects that initially introduced optical transitions between the electronic orbitals (Fig. 2) are mixed and their superpositions contribute to the transitions which can be observed in experiment. The Poisson bracket $\hat{\omega}$ (Eq. (34)) is block diagonal and does not mix optical transitions, whereas the classical Hamiltonian $H^{(2)}(\bar{\rho})$ (Eq. (41)) contains off-diagonal blocks which give rise to this effect.

4. Geometrical picture of non-adiabatic variational approach

In this section, we present a geometrical picture of the formalism developed in Sections 2 and 3. The purpose of this section is to demonstrate that the simple structure of the equations introduced above originates from certain additional geometrical structures in the space M of trial generalized configurations. These geometrical structures can be associated with the physical quantities that naturally

arise in the non-adiabatic variational approaches. Although the notation we are using, which is standard in differential geometry, might appear a bit unconventional for the chemical physics audience, the material of this section is self-contained and self-explanatory. We also made an effort to introduce the basic concepts of the fiber bundles and connections (lifts) using the objects we are dealing with as primary examples. Actually the connections that are known in the physics literature as gauge fields appear in non-adiabatic dynamics theories as non-adiabatic couplings. The fiber bundles also appear in these theories, at least on the implicit level. A more detailed, still very brief summary of the basic properties of Hamilton classical dynamics, fiber bundles and connections, relevant for our applications can be found in Ref. [55]. Invariant picture of classical Hamilton dynamics is covered in detail in the famous textbook [54] by V.I. Arnold. A standard textbook [62] on differential geometry contains plenty of details on smooth fiber bundles and connections in them. The celebrated monography [63] by Yu I. Manin discusses deep connections between the gauge fields and objects that are studied in differential and complex-analytical (algebraic) geometry.

Parameterization of the quantum mechanical electronic Hamiltonian by vibrational coordinates given in Eq. (1) can be used to model the non-adiabatic molecular dynamics. Since our goal is to find an adequate description of the electronic structure in the vicinity of the level crossings where the non-adiabatic dynamics occur a definition of what we call the electronic structure for non-diabatic molecular dynamics, or simply non-adiabatic electronic structure, is requires.

We start by defining the space of all vibrational configurations X, and a subspace $X^{(n)} \subset X$ of the configurations in it so that the lowest n eigenvectors of $\widehat{H}(\boldsymbol{x})$ are detached by a gap from the rest of the spectrum. With each configuration $\boldsymbol{x} \in X^{(n)}$ we can associate a n-dimensional vector subspace $\mathscr{S}(\boldsymbol{x}) \in G(n; \mathscr{H})$ spanned onto the lowest n eigenvectors, where $G(n; \mathscr{H})$ denotes a Grassman manifold whose points are n-dimensional subspaces of the space of multi-electron configurations $\mathscr{H}$.

Stated more formally, we have a map $\mathscr{S} : X^{(n)} \rightarrow G(n; \mathscr{H})$ and an $O(n)$ bundle $\mathbb{R}^n \rightarrow E \rightarrow X^{(n)}$ induced by $\mathscr{S}$ from the universal $O(n)$ bundle over $G(n; \mathscr{H})$. We also have a connection ∇ in E identified as the non-adiabatic coupling terms induced by $\mathscr{S}$ from the canonical connection in the universal bundle. Projecting the Hamiltonian $\widehat{H}(\boldsymbol{x})$ to the fibers $E_{\boldsymbol{x}}$ we obtain a set of $n \times n$ adiabatic Hamiltonian matrices $H(\boldsymbol{x})$, or more formally a global section $H : X^{(n)} \rightarrow \mathrm{End}(E)$ of the endomorphism bundle $\mathbb{R}^{2n} \rightarrow \mathrm{End}(E) \rightarrow X^{(n)}$.

The nonadiabatic electronic structure (E, ∇, H) that consists of the bundle E describing the electronic states involved in non-adiabatic dynamics, the connection ∇ describing non-adiabatic coupling terms, and H describing the adiabatic Hamiltonian, fully determines the input needed for nonadiabatic molecular dynamics. The non-adi-

abatic structure is totally determined by the map $\mathscr{S}$, as described above, and can be obtained by applying the variational principle discussed in this section.

4.1. Stationary variational method

Exact variational principle introduced in Section 2.1 has a clear geometric interpretation if the classical Hamiltonian function $H(\mathscr{S})$ (Eq. (4)) defined as a projection on quantum Hamiltonian on $\mathscr{S}$ is considered to be a map

$$H : G(n; \mathscr{H}) \rightarrow \mathbb{R}. \tag{44}$$

Here, H depends on $\boldsymbol{x}$ parametrically, and each point on Grassman manifold $G(n; \mathscr{H})$ is an n-dimensional subspace $\mathscr{S} \subset \mathscr{H}$. For a fixed configuration $\boldsymbol{x} \in X^{(n)}$, the subspace $\mathscr{S}$ can be found by minimizing the function $H(\mathscr{S})$. Specifically, one has to find local coordinates on $G(n; \mathscr{H})$ which parameterize $\mathscr{S}$, and can be represented by the wavefunctions satisfying the Schrödinger equation (7).

A variational approximation (ansatz) is generated by choosing a submanifold of *generalized trial configurations* $M \subset G(n; \mathscr{H})$ whose points are subspaces $\mathscr{S}_t \in \mathscr{H}$ spanned by n trial wavefunctions. In the case of non-degenerate ground state, the trial manifold $M \subset G(1; \mathscr{H})$ is simply formed from single multi-electron wavefunctions each representing an element of projective space $\mathbb{P}(\mathscr{H}) \cong G(1; \mathscr{H})$, where the normalized wavefunctions that differ by a phase prefactor are considered to be identical. We emphasize, that in contrast to non-degenerate case, the trial manifold for n-fold degenerate case is spanned by n multi-electron wavefunctions which are elements of $G(n; \mathscr{H})$ rather than $\mathbb{P}^1(\mathscr{H})$. After restricting the classical Hamiltonian function to this manifold

$$H : M \rightarrow \mathbb{R}, \tag{45}$$

its minimization with respect to $\mathscr{S}_t \in M$ leads to an approximation for the stationary point $\overline{\mathscr{S}}$. Once the stationary point is found related components of the non-adiabatic electronic structure (E, ∇, H) could be determined in a standard way [50,64].

We are now in a position to define the structure of the manifold of generalized trial configurations M associated with the adopted in Section 2.2 electronic state ansatz (Eq. (8)). Any trial generalized configuration for our ansatz, represented by a point in M can be described in the following way. Denoting the space of single molecular electron orbitals by V_0, with $\dim(V_0) = K$, we partition it into two orthogonal components $V_0 = V_{el} \oplus V_u$, the space V_{el} of orbitals that can be occupies, and the space V_u of (always) unoccupied orbitals. Among that which can be possibly occupied, we select N_a active mid-gap orbitals and denote the space spanned on them by $V_a \subset V_{el}$. The rest N orbitals in V_{el}, which are completely occupied, span the space $V_f \subset V_{el}$ of filled orbitals. Note that V_a and V_f are mutually orthogonal and $V_{el} = V_a \oplus V_f$.

The structure defined above can be fully described by a set $V_a \subset V_{el} \subset V_0$ of nested vector subspaces with

$\dim V_a = N_a$ and $\dim V_{el} = N_a + N$. The space of such configurations represented by nested vector subspaces $V_a \subset V_{el} \subset V_0$ is known as the flag space $F(N_a, N_a + N; V_0)$, it has a standard structure of a compact complex-analytical manifold. The flag space can be viewed as a fiber bundle (or, more generally a fibration) over a Grassman manifold in the following sense. Consider a pair of maps

$$G(N; V_a^\perp) \xrightarrow{e} F(N_a, N_a + N; V_0) \xrightarrow{p} G(N_a; V_0), \qquad (46)$$

where the flag space is referred to as the total space, $G(N_a; V_0)$ as the base, whereas the projection map p maps (projects) the total space to the base. For any point $V_a \in G(N_a; V_0)$ represented for this particular case by some active space we refer to $p^{-1}(V_a)$ as the fiber over the point V_a in our particular case the fiber $p^{-1}(V_a)$ is given by all $(N_a + N)$-dimensional vector spaces $V_{el} \supset V_a$ that contain V_a. Each of such spaces is totally determined by the component $V_f \subset V_a^\perp$, defined earlier, and therefore represents a point in $G(N; V_a^\perp)$, which means $p^{-1}(V_a) \cong G(N; V_a^\perp)$. It is easy to understand that fibers over different points V_a are actually different, yet equivalent spaces. This is a standard feature of fibrations (bundles). The left space in Eq. (46) represents its fiber. More formally if one chooses some point $V_a \in G(N_a; V_0)$ (usually referred to as the base point), then the map e represents the natural embedding of the fiber over the base point into the total space. The term fibration is due to the fact that set-theory-wise the total space

$$F(N_a, N_a + N; V_0) = \bigcup_{V_a \in G(N_a; V_0)} p^{-1}(V_0) \qquad (47)$$

is a union of all fibers, parametrized by the base. Although Eq. (47) is written for our particular example, it actually holds for a generic fibration. Strictly speaking, a fibration is something more than just a union of fibers, since the total space has a structure of a smooth manifold that is preserved by the projection map. We will not further discuss these standard issues, all necessary information can be found in standard textbooks on differential geometry.

Another fibration that together with the one given by Eq. (46) plays an important role for a convenient representation of M can be easily defined as follows. We start with introducing the (tautological) bundle

$$V_a \rightarrow E(N_a; V_0) \rightarrow G(N_a; V_0), \qquad (48)$$

whose fiber over a point $V_a \in G(N_a; V_0)$ is V_a, considered as a vector space (which rationalizes the term "tautological"). We further consecutively apply fiber-wise the operations $\wedge^{n_a}$, $\{\cdot\}^s$, and $G(n; \cdot)$ to arrive at the bundle

$$\{\wedge^{n_a} V_a\}^s \rightarrow G(n; \{\wedge^{n_a} V_a\}^s) \rightarrow G(N_a; V_0). \qquad (49)$$

We are now in a position to provide a convenient description of the trial manifold M for our ansatz. Consider a trial configuration $\mathscr{S} \in M$. According to our earlier description it is fully described by the following set of data: an N_a-dimensional active space $V_a \subset V_0$, an N-dimensional space $V_f \subset V_0$ of completely filled orbitals, with $V_f \perp V_a$, and an

n-dimensional space $V_c \subset \{\wedge^{n_a} V_a\}^s$, spanned on n generic (correlated) n_a-electron singlet states based on active orbitals. Here $\{\wedge^{n_a} V_a\}^s \subset \wedge^{n_a} V_a$ denotes the subspace of singlet states. Stated differently the trial configurations $\mathscr{S} \in M$ are represented by triples (V_a, V_f, V_c) with the aforementioned conditions. Associating with such a configuration $\mathscr{S} = (V_a, V_f, V_c)$ its first component, the latter being a point $V_a \in G(N_a; V_0)$, results in a representation of the configuration space as a bundle

$$G(N; V_a^\perp) \times G(n; \{\wedge^{n_a} V_a\}^s) \rightarrow M \rightarrow G(N_a; V_0). \qquad (50)$$

The bundle structure given by Eq. (50) should be interpreted as follows. A simple inspection shows that a fiber in Eq. (50) is represented by a cartesian product of the fibers of the fibrations given by Eqs. (46) and (49). A more careful treatment shows that this property is preserved on the global level, i.e. the fibration on Eq. (50) is the fiberwise cartesian product of $G(n, \{\wedge^{n_a} E(N_a; V_0)\}^s) \rightarrow G(N_a; V_0)$ and $F(N_a, N_a + N; V_0) \rightarrow G(N_a; V_0)$ over $G(N_a; V_0)$. This can be represented by the following standard diagram

$$
\begin{array}{ccc}
M & \longrightarrow & G\left(n, \{\wedge^{n_a} E(N_a; V_0)\}^s\right) \\
\downarrow & & \downarrow \\
F(N_a, N_a + N; V_0) & \longrightarrow & G(N_a; V_0)
\end{array}
\qquad (51)
$$

It is instructive to note that the other two maps in the diagram of Eq. (51) naturally represent bundles with the total space M:

$$G(n; \{\wedge^{n_a} V_a\}^s) \rightarrow M \rightarrow F(N_a, N_a + N; V_0) \qquad (52)$$

$$F(N_a, N_a + N; V_0) \rightarrow M \rightarrow G(n; \{\wedge^{n_a} E(N_a; V_0)\}^s) \qquad (53)$$

The representation of the trial manifold M as a fiberwise product of two standard bundles, supported by the diagram of Eq. (51) plays an important role in the generalization of the stationary ansatz to its dynamical counterpart.

A natural embedding $M \subset G(n; \mathscr{H})$ that is needed to define the variational Hamiltonian dynamics in M can be achieved by noticing that the space of multi-electron states $\mathscr{H}$ can be represented as anti-symmetrized product of spaces of single electron orbitals V_0, specifically $\mathscr{H} \cong \wedge^{N+n_a} V_0$. This allows us to associate a point $(V_a, V_f, V_c) \in M$ with a point in the Grassman manifold $G(n; \mathscr{H})$ which is a direct product $\widehat{\Omega}_s \otimes \hat{\zeta}_c^s$ of $2N$-electron state obtained by fully occupying the single-electron orbitals $\widehat{\Omega}_s$ (single Slater determinant) and space of singlets $\hat{\zeta}_c^s$ in the space of correlated n_a-electron states. Since, the second quantization is a natural way to represent operators mapping $G(n; \mathscr{H})$ on itself, and since we have established a map $M \rightarrow G(n; \mathscr{H})$ by embedding $M \subset G(n; \mathscr{H})$, we can now discuss how the restriction of the classical Hamiltonian on M given by Eq. (45) can be calculated. Specifically, the Hamiltonian $\widehat{H}$ and the ansatz states $\widehat{\Omega}_s \otimes \hat{\zeta}_c^s$ can be represented in terms of the second quantization operators given in the basis of single electron orbitals due to the fact that $\mathscr{H} \cong \wedge^{N+n_a} V_0$. Then the projection of the quantum Hamiltonian on these states can be calculated explicitly
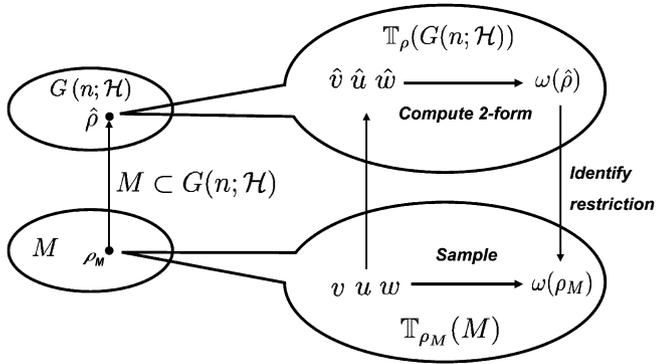
Fig. 3. Illustration of differential form and classical Hamiltonian pull-back. Mapping $\rho^M \to \hat{\rho}$ is due to the natural embedding $M \subset G(n; \mathcal{H})$. Accordingly, in the associated tangent spaces the operator mapping $(v, u, w) \to (\hat{v}, \hat{u}, \hat{w})$ exists. All possible pairs from the set (v, u, w) in $\mathbb{T}_{\rho^M}(M)$ should to be sampled, and their images $(\hat{v}, \hat{u}, \hat{w})$ in $\mathbb{T}_{\hat{\rho}}(G(n; \mathcal{H}))$ should be substituted to $\omega(\hat{\rho})$. The result of the calculations is identified as the form restriction $\omega(\rho^M)$. Similar procedure is used to perform the Hamiltonian pull-back.

using the algebra of second quantization. This procedure is illustrated in Fig. 3, and called pull-back. Its technical implementations was presented in Section 2.2, resulting in the explicit form of classical Hamiltonian (Eq. (10)) restricted to M.

4.2. Dynamical variational method

The most general, invariant, representation of classical Hamiltonian equations for $\rho \in G(n; \mathcal{H})$ is [54,55]

$$\frac{d\rho}{dt} = (dH \otimes \mathrm{id}_{\mathbb{T}_\rho(G(n;\mathcal{H}))})\hat{\omega}(\rho), \tag{54}$$

where $\hat{\omega}(\rho) \in \mathbb{T}_\rho(G(n; \mathcal{H})) \otimes \mathbb{T}_\rho(G(n; \mathcal{H}))$ is an asymmetric bivector that determines the canonical Poisson bracket acting in the Grassmanian $G(n; \mathcal{H})$. We denote points of the Grassmanian with ρ, since a vector space V that represents a point can be uniquely associated with a matrix $\rho \in \mathrm{End}(\mathcal{H})$ with the properties $\rho^2 = \rho$ and $\mathrm{rank}\rho = n$ that projects $\mathcal{H}$ into V. The equations of motion in the form of Eq. (54) can be interpreted as the action of differential 1-form

$$dH = \sum_k \frac{\partial H}{\partial \rho^k} d\rho_k, \tag{55}$$

represented by external differential of the classical Hamiltonian on $G(n; \mathcal{H})$, on the left component of the bivector $\hat{\omega}$. The result of this action is a number multiplied by the right component of the bivector. Substitution of Eq. (55) together with the Poisson bracket

$$\hat{\omega} = \sum_{ij} \hat{\omega}_{ij}(\rho) \frac{\partial}{\partial \rho_i} \otimes \frac{\partial}{\partial \rho_j}, \tag{56}$$

given in the local coordinate representation, with $\hat{\omega}_{ij} = -\hat{\omega}_{ji}$, into Eq. (54) yields coordinate representation of the Hamiltonian in Eq. (18) introduced in Section 3.1.

The Poisson bracket is uniquely determined by the closed differential form $\omega \in A^{1,1}(G(n; \mathcal{H}))$ that induces the canonical symplectic structure on the Grassman manifold, and in some local coordinates can be represented in a form

$$\omega = \sum_{ij} \omega^{ij}(\rho) d\rho_i \wedge d\rho_j, \tag{57}$$

The Jacobi identity for the Poisson bracket being reformulated for the symplectic form reads $d\omega = 0$, which means that the form is closed [54]. Once we know the representation for the symplectic form, the Poisson bracket can be immediately obtained by inverting ω^{ij}, specifically, $\hat{\omega}_{ij} = (\omega^{-1})^{ij}$, or equvalently $\sum_{ij} \hat{\omega}_{ik} \omega^{kj} = \delta_i^j$.

According to Eqs. (54)–(57) the classical Hamilton dynamics on Grassman manifold $G(n; \mathcal{H})$ is fully determined by the symplectic form ω and the classical Hamiltonian function H. A representation for the latter quantity can be obtained by projecting the quantum Hamiltonian (Eq. (1)) on the Grassman manifold $G(n; \mathcal{H})$ as given by Eq. (4). The canonical symplectic form for a Grassmanian can also be constructed if we interpret $\hat{\rho}$ as a map $\hat{\rho} : G(n; \mathcal{H}) \to \mathrm{End}(\mathcal{H})$ that associates the point of the Grassmanian with the corresponding projection operator (as described above), specifically

$$\omega(\hat{\rho}) = i\mathrm{Tr}\{\hat{\rho}[d\hat{\rho} \wedge d\hat{\rho}]\}. \tag{58}$$

Note that the caret is used to distinguish the projection operators acting in many body electron space $\mathcal{H}$ from points on Grassman manifold. The invariant representation in Eq. (58) can easily be recast to the local coordinate representation

$$\omega(\rho) = i \sum_{ij} \mathrm{Tr}\{\hat{\rho}[\hat{t}^i, \hat{t}^j]\} d\rho_i \wedge d\rho_j, \tag{59}$$

where $\hat{t}^i = \partial\hat{\rho}/\partial\rho^i$ are operators in $\mathcal{H}$ whose action induces tangent vectors within $\mathbb{T}_\rho(G(n; \mathcal{H}))$. According to Eq. (59), components ω^{ij} of the symplectic form can be calculated using Eq. (29) used in Section 3.2.

Application of the exact dynamical variational principle given by Eqs. (54)–(59) to describe an approximate evolution of the electronic state ansatz (Eq. (8)) requires the calculations of the symplectic form and classical Hamiltonian restrictions to the manifold of the generalized trail configurations defined by Eq. (51). These calculations can be performed by implementing the form and the Hamiltonian pull-back from $G(n; \mathcal{H})$ to M which is based on the embedding $M \subset G(n; \mathcal{H})$ (Fig. 3). The Hamiltonian pull-back was already introduced above and according to Eq. (59) can be done to the symplectic form in the same way.

As shown in Fig. 3, pull-back of the form requires sampling all tangent vectors from $\mathbb{T}_\rho(M)$ and substitution of their preimages from $\mathcal{H}$ into Eqs. (29) and (59), first, we consider the properties of $\mathbb{T}_\rho(M)$ induced by the fiber bundle structure which was introduced in the previous subsection. This is achieved by using the notion of a connection in a bundle; in the physics literature connections are called

gauge fields. Connections in bundles can be defined in several equivalent ways. For our purposes the most convenient approach is based on interpreting connections as lift operators. For our bundle a connection can be defined as a set of lift operators

$$\nabla_\rho : \mathbb{T}_{\rho^a}(G(N_a; V_0)) \to \mathbb{T}_\rho(M); \quad \rho^a = p(\rho) \tag{60}$$

parametrized by points $\rho \in M$ of the total space. The term lift reflects the fact that a lift operator "lifts" the tangent vectors in the base to the tangent vectors in the total space as illustrated in Fig. 4. Extensive discussion of this issue can be found in Ref. [62,63], and brief introduction in Ref. [55]. The lift induces the splitting of $\mathbb{T}_\rho(M)$ into the tangent space of the base and the tangent space of the fibers all defined in Eq. (51)

$$\mathbb{T}_{\rho^M}(M) \cong \mathbb{T}_{\rho^a}(G(N_a; V_0)) \oplus \mathbb{T}_\rho\big(G(N; V_a^\perp) \times G(n; \{\wedge^{n_a} V_0\}^s)\big). \tag{61}$$

To define a connection (lift) described in Eq. (60), we make use of the fact that the bundle represented by Eq. (50) constitutes a cartesian fiberwise product of the bundles given by Eqs. (46) and (49). Stated differently this means that

Fig. 4. Illustration of the lift operation. Consider a fiber to the base at point ρ^a, and associated tangent spaces touching at points ρ and ρ^a, respectively. Then an arbitrary vector ζ in the total space can be decomposed into two components denoted by $\zeta_\parallel$ and $\nabla_\rho \xi$. The former component belongs to the tangent space of the fiber. The latter component $\nabla_\rho \xi$ is the lift of some vector ξ from the tangent space to the base at point ρ^a. In other words, ζ is fully defined by $\zeta_\parallel$ and ξ.

the cartesian product structure of the fibers is preserved on the global level. The first Grassmanian in the cartesian product of the second component in the direct sum in Eq. (61) represents the fibers of the flag-space bundle [Eq. (46)] which has a well-defined canonical connection. The second Grassmanian represents the fibers of the bundle given by Eq. (49). To introduce a canonical connection in the latter, we note that the tautological bundle [Eq. (48)] is also equipped with the canonical connection. Fiberwise application of a sequence of operations $\wedge^{n_a}$, $\{\cdot\}^s$, and $G(n; \cdot)$ to the tautological bundle can be also extended to the connections. Stated differently, this induces a connection in the bundle described by Eq. (49), hereafter also referred to as the canonical connection. According to Eq. (50) showing that the fibers of M are cartesian products, and that this bundle structure is globally preserved (the aforementioned statement about the fiberwise product structure of our main bundle), the lift ∇_ρ can be simply defined as a direct sum of the canonical connections defined for the components of the fiberwise cartesian product.

The cartesian product of the fibers in Eq. (50) allows to perform further decomposition of the tangent space

$$\mathbb{T}_{\rho^M}(M) \cong \mathbb{T}_{\rho^a}(G(N_a; V_0)) \oplus \mathbb{T}_{\rho^s}(G(N; V_a^\perp)) \oplus \mathbb{T}_{\eta^a}(G(n; \{\wedge^{n_a} V_0\}^s)), \tag{62}$$

and the introduced connection allows to decompose the Poisson bracket in $\mathbb{T}_{\rho^M}(M)$ into the sum

$$\hat{\omega}(\rho^M) = \hat{\omega}_{\rho^a} \oplus \hat{\omega}_{\rho^s} \oplus \hat{\omega}_{\eta^a}. \tag{63}$$

whose components $\hat{\omega}_{\rho^a} \in \mathbb{T}_{\rho^a}(G(N_a; V_0)) \otimes \mathbb{T}_{\rho^a}(G(N_a; V_0))$, $\hat{\omega}_{\rho^s} \in \mathbb{T}_{\rho^s}(G(N; V_a^\perp)) \otimes \mathbb{T}_{\rho^s}(G(N; V_a^\perp))$, and $\hat{\omega}_{\eta^a} \in \mathbb{T}_{\eta^a}(G(n; \{\wedge^{n_a} V_0\}^s)) \otimes \mathbb{T}_{\eta^a}(G(n; \{\wedge^{n_a} V_0\}^s))$ are represented by the canonical Poisson brackets in the corresponding Grassmanians. Also, the off-diagonal elements of the bivector associated with $\mathbb{T}_{\rho^a}(G(N_a; V_0))$, $\mathbb{T}_{\rho^s}(G(N; V_a^\perp))$, and $\mathbb{T}_{\eta^a}(G(n; \{\wedge^{n_a} V_0\}^s))$ vanish, once the decomposition of Eq. (62) is provided by the canonical connection (lift), defined above.

Calculations in Section 3.2 where the displacement (particle–hole) operators v, u, and w can be identified as the elements of the tangent spaces in Eq. (62), respectively, confirm Eq. (63) by providing in Eq. (34) the block diagonal matrix representation of the Poisson bracket. These calculations also represent the implementation of the Poisson bracket pull-back (Fig. 3), since, they use the algebra of second quantization (Eqs. (26)–(28)) defined in $\mathscr{H}$. Note that the pull-back of the Hamiltonian function does not correspond to the block diagonal form (Eq. (41)), and that the off-diagonal blocks mix the tangent spaces from Eq. (62).

We conclude this section with a summary of reasons for involving some basic machinery of differential geometry for our applications. The Poisson bracket involved in our approximate variational dynamics is conceptually very simple: it is obtained as a pull-back (Fig. 3) of the Poisson bracket involved in the exact (complete) variational dynamics. However, for practical applications of the
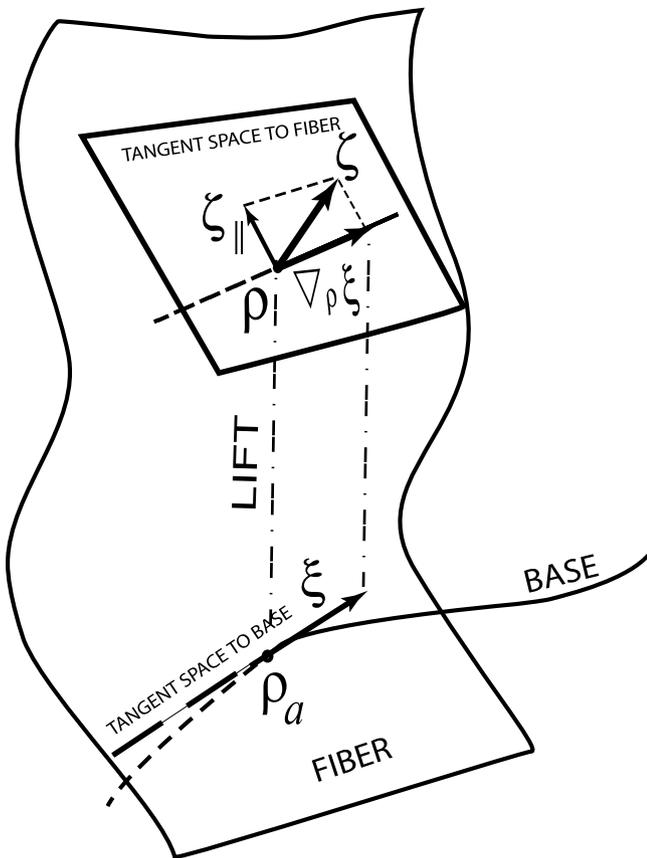
proposed ansatz it should be computed explicitly. The Poisson bracket described as a simple decomposition by Eq. (63) and the comments immediately following the equation actually constitutes a result of an explicit calculation; the details will be published elsewhere. The decomposition is possible due to the decomposition of the tangent space [Eq. (62)]. The latter results from the fact that our trial space M has a structure of a bundle over the Grassmanian $G(N_a; V_0)$, and more than that constitutes a fiberwise cartesian product over the same base. The decomposition of the tangent space and, therefore, the decomposition of the Poisson bracket depends on the connection choice. In particular, the decomposition does not have necessarily a block-diagonal form of Eq. (63). We have used the bundle product structure of M to define a canonical connection based on canonical connections in standard bundles, involved in the construction. We have demonstrated that once the described canonical connection is used for the tangent space decomposition the relevant (i.e. obtained via the pull-back procedure) Poisson bracket has a block-diagonal form and the components are represented by the well-known canonical Poisson brackets [Eq. (58)] in the relevant Grassmanians. Stated differently, not only we computed the relevant Poisson bracket explicitly, but also applied a geometrical picture to express it in a very universal way in terms of canonical Poisson brackets and standard fiber bundles over Grassmanians.

5. Concluding remarks

Classical equations of motion presented by Eqs. (20), (25), (34) and (41) constitute our central result, which can be used to study the non-adiabatic electronic-state dynamics in a variety of (bio)molecular systems. [2–4,9,11,26] We have explicitly derived these dynamical equations and presented them in the most general 3×3 block-matrix form. The latter representation is useful for understanding their internal structure. Impending numerical implementation of the developed approach and further analysis of the physical properties associated with the equations structure, requires specification of the active space dimensionality, which obviously varies from one system to another. The aforementioned dimensionality determines the truncation level for the chain of coupled equations that contain the correlated multi-electron density matrices defined in the active space. Further development of the self-consistent method for the non-adiabatic molecular dynamics, that involves the quantum mechanical or semi-classical nuclei wavepacket propagation, requires the knowledge on the non-adiabatic couplings between the potential energy surfaces. This can be done on the fly by using the time-dependent electronic density matrix, parameterized by the nuclei coordinates, which can be calculated using the proposed set of classical equations of motion.

Based on the approach discussed above we propose a self-consistent method to model two-color pump–probe spectroscopic response associated with the wavepackets dynamics in the vicinity of unavoided level crossing. This scheme is illustrated in Fig. 5 The photo-excitation of a vibrational wavepacket takes place far from the level crossing region as shown in Fig. 5A. For this nuclei configuration the ground electronic state is non-degenerate, and therefore optically allowed transitions occur between filled and virtual orbitals only. Within the proposed approach these transitions can be determined by the TDHF calculations. Further propagation of the excited wavepacket shown in Fig. 5B is due to the quantum mechanical or
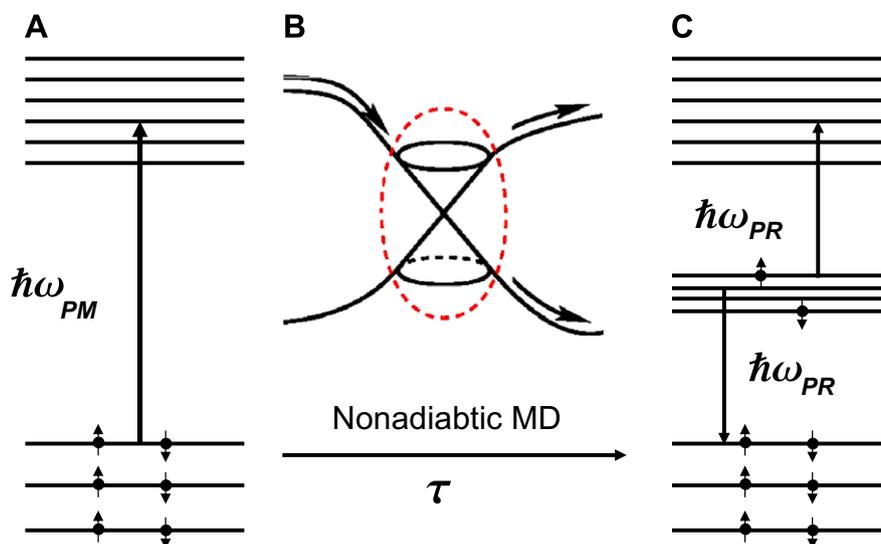

Fig. 5. Proposed scheme of two-color pump–probe spectroscopy. (A) Photo-excitation of vibrational wave-packet at the energy $\hbar\omega_{PM}$ in the region away from the level crossing. In this region only transitions between occupied and virtual orbitals exist. (B) Quantum mechanical/semiclasscial propagation of photo-excited wavepacket to the region of level crossing. (C) In the level crossing region the mid-gap states appear, and associated response can be monitored by the probe pulse delayed by time τ whose energy $\hbar\omega_{PR}$ matches the mid-gap transitions.

semiclassical molecular dynamics. Once the wavepacket reaches the level crossing as shown in Fig. 5 (C), the mid-gap states appear corresponding to the degenerate ground electronic state. Wavepacket dynamics in this region are non-adiabatic and the optical transitions which carry information about it are mixed transitions to the mid-gap states. Accordingly, they can be probed with the laser pulse tuned to the mid-gap transition energy. The time evolution of the signal should reflect specific features, e.g., changes in the transition selection rules associated with the non-adiabatic wavepacket dynamics. Specific determination of these features can be done after the implementation of the proposed technique into computational code and performing detailed simulations for specific molecular systems. Proposed scheme can be further extended to model coherent four-wave-mixing experiment.

Further development of the technique includes extension to TDDFT framework. Both TDHF and the TDDFT follow the dynamics of a similar quantity: a single Slater determinant that can be uniquely described by an idempotent single-electron density matrix ρ (with $\rho^2 = \rho$) [47,50,65,66]. However, they yield different equations of motion for $\rho(t)$, stemming from the different interpretation of $\rho(t)$. In the TDHF, $\rho(t)$ is viewed as an approximation for the actual single-electron density matrix [47] whereas in TDDFT $\rho(t)$ is an auxiliary quantity constrained to merely reproduce the correct electronic charge distribution at all times [67,68]. TDDFT is formally exact. However, in practice it yields approximate results since exact expressions for the exchange-correlation energy $E_{xc}[n(\mathbf{r})]$ and the corresponding potential $v_{xc}(\mathbf{r}, [n])$ in the KS scheme are not available and are introduced semiempirically. A close resemblance between TDHF and TDDFT (especially its adiabatic version) may be established by formulating KS density functional theory (DFT) in terms of the density matrix ρ rather than on the KS orbitals [50]. This formal similarity makes it possible to apply the same algorithms for solving the equations of motion for density matrix.

In conclusion, we have proposed a dynamical variational ansatz to describe the time evolution of the degenerate electronic state which occur in the vicinity of unavoided level crossing. The approach is based on Hamiltonian equations of motion and determine the evolution of the whole subspace spanned on the ground state wavefunctions. Adopted geometric picture of the developed formalism provides a complimentary point of view on the dynamics which can be associated with the Hamilton dynamics in the tangent spaces of the fibers. Geometric consideration sheds light onto the internal simplicity of the derived equations of motion, and in particular the simple block-diagonal representation of the Poisson bracket. The derived equations can be used to calculate the spectroscopic observables such as transition energies and densities, and provide with a self-consistent simulation scheme for investigation of the non-adiabatic dynamics features in the time-resolved optical response. Further development of the technique includes extensions to non-adiabatic TDDFT methods.

Acknowledgements

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