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Coherent dynamics in solar energy transduction

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Citation

Eisenmayer, T. J. (2014, December 15). *Coherent dynamics in solar energy transduction*. Retrieved from <https://hdl.handle.net/1887/30117>

Version: Corrected Publisher's Version

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Title: Coherent dynamics in solar energy transduction

Issue Date: 2014-12-15

Chapter 2

Theoretical Methods

In section 2.1 the fast (electrons) and slow (nuclei) variables are separated using the adiabatic (Born-Oppenheimer) approximation. Density Functional Theory is introduced and excited state methods are discussed. Section 2.2 contains the methods used in this thesis to evolve the nuclei within and beyond the adiabatic approximation.

2.1 Methods I: The Electronic Problem

The total unperturbed Hamiltonian:

$$\begin{aligned}\hat{\mathcal{H}}(\mathbf{r}, \mathbf{R}(t)) = & - \sum_J \frac{1}{2M_J} \nabla_J^2 - \sum_j \frac{1}{2} \nabla_j^2 + \sum_{J < K} \frac{Z_J Z_K}{|\mathbf{R}_J - \mathbf{R}_K|} \\ & + \sum_{j < k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} - \sum_{Jj} \frac{Z_J}{|\mathbf{R}_J - \mathbf{r}_j|}\end{aligned}\quad (2.1)$$

can be condensed to a nuclear kinetic energy $\hat{T}_n$ and an electronic Hamiltonian $\hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}(t))$:

$$\hat{\mathcal{H}}(\mathbf{r}, \mathbf{R}(t)) = \hat{T}_n + \hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}(t)), \quad (2.2)$$

such that:

$$[\hat{T}_n + \hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}(t))] \Psi_I(\mathbf{r}, \mathbf{R}(t)) = E_I(\mathbf{R}(t)) \Psi_I(\mathbf{r}, \mathbf{R}(t)), \quad (2.3)$$

where the electron-nuclear wavefunctions $\Psi_I(\mathbf{r}, \mathbf{R}(t))$ can be further decomposed into electronic $\psi_I(\mathbf{r}; \mathbf{R}(t))$ and nuclear $\chi_I(\mathbf{R}(t))$ wavefunctions using the adiabatic (Born-Oppenheimer) approximation based on the large difference in mass between nuclei and electrons:

$$\Psi_I(\mathbf{r}, \mathbf{R}(t)) = \psi_I(\mathbf{r}; \mathbf{R}(t)) \chi_I(\mathbf{R}(t)), \quad (2.4)$$

leaving the electronic problem:

$$\hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}(t))\psi_0(\mathbf{r}; \mathbf{R}(t)) = E_0(\mathbf{R}(t))\psi_0(\mathbf{r}; \mathbf{R}(t)), \quad (2.5)$$

where $\psi_0(\mathbf{r}; \mathbf{R}(t))$ is the electronic ground state with energy E_0 subject to a static external potential generated by the (positive) nuclei. The equation for the nuclei then becomes:

$$(\hat{T}_n + E_0(\mathbf{R}(t)))\chi(\mathbf{R}(t)) = E(\mathbf{R}(t))\chi(\mathbf{R}(t)). \quad (2.6)$$

2.1.1 The Ground State

The Electron Density

The scheme of Kohn, Hohenberg and Sham [1,2] for approximating the ground state of equation 2.5, commonly referred to as Density Functional Theory (DFT), has become a widespread tool to predict, model and interpret a large variety of scientific and applied problems. The central quantity in DFT is the ground state electron density:

$$\rho_0(\mathbf{r}) = N \int_{-\infty}^{+\infty} d\mathbf{r}_2^3 \cdots \int_{-\infty}^{+\infty} d\mathbf{r}_N^3 \psi_0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi_0^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (2.7)$$

where N is the number of electrons and the integrals run over $N - 1$ electronic coordinates. It has been proven that the ground state electronic wavefunction is a unique functional of the ground state electron density: $\psi_0 = \psi[\rho_0]$. It follows that the ground state expectation value of any observable O is a functional of the electron density:

$$O_0[\rho_0] = \langle \psi_0[\rho_0] | \hat{O} | \psi_0[\rho_0] \rangle, \quad (2.8)$$

including the ground state energy E_0 :

$$E_0[\rho_0] = \langle \psi_0[\rho_0] | \hat{\mathcal{H}}_e | \psi_0[\rho_0] \rangle. \quad (2.9)$$

The second Hohenberg-Kohn theorem introduces the variational principle into DFT [1], stating that every guess of the density ρ_0 and hence the wavefunction ψ_0 will yield an energy that is higher than the true ground state energy E_0 . This allows for a practical numerical scheme to minimize the ground state energy through progressive iterative 'guessing' of the density.

The Kohn-Sham Energy Functional

The main difficulty in DFT lies in finding the Kohn-Sham energy functional $E_{KS}[\rho_0]$. As the electronic problem is considered for a fixed nuclear configuration the nuclear-nuclear term is trivial and can be added as a constant. The electron-nuclear energy functional can be conveniently decomposed into a sum of single-particle potentials $v_{ext}(\mathbf{r})$:

$$E_{n-el}[\rho_0] = \langle \psi_0[\rho_0] | V_{n-el} | \psi_0[\rho_0] \rangle = \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_0(\mathbf{r}). \quad (2.10)$$

that may be seen as an external potential generated by the (positive) nuclei in which the electrons move. The complicated energy term is the electron-electron energy functional $E_{el-el}[\rho_0]$. It can be approximated classically through a Coulomb term involving the electron density $\rho(\mathbf{r})$ with the remainder being an unknown QM energy functional $E_{qm}[\rho_0]$:

$$E_{el-el}[\rho_0] = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left[\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \right] + E_{qm}[\rho_0]. \quad (2.11)$$

Finally, the kinetic energy $T_{el}[\rho_0]$ is also non-trivial and can be approximated by summing all the kinetic energies of the Kohn-Sham orbitals $\phi_i(\mathbf{r})$ with the remainder being some unknown kinetic correlation energy $T_c[\rho_0]$:

$$T_{el}[\rho] = \sum_i^N \langle \phi_i(\mathbf{r}) | -\frac{1}{2} \nabla^2 | \phi_i(\mathbf{r}) \rangle + T_c[\rho]. \quad (2.12)$$

Exchange-Correlation Functionals

The unknown functional $E_{qm}[\rho]$ and the kinetic correlation energy $T_c[\rho]$ are together termed the exchange-correlation energy $E_{XC}[\rho]$. This functional requires approximations that are crucial to the accuracy of DFT and that are becoming ever more sophisticated. The Local Density Approximation (LDA) was one of the first to be developed and its energy functional reads:

$$E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{XC}(\rho(\mathbf{r})) d\mathbf{r}, \quad (2.13)$$

where ϵ_{XC} is the exchange-correlation energy of a homogeneous electron gas. An improvement to this approximation came with the development of the Generalized Gradient Approximation (GGA) [3] that includes a functional dependence on the gradient of the density $\nabla\rho$:

$$E_{XC}^{GGA}[\rho, \nabla\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r}. \quad (2.14)$$

The recent accurate class of hybrid approximations combine exact Hartree Fock exchange E_X^{HF} :

$$E_X^{HF} = -\frac{1}{2} \sum_{i,j}^{occ} \int d\mathbf{r}' d\mathbf{r} \frac{\phi_i^*(\mathbf{r}')\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.15)$$

through fitted or calculated parameters (i.e. α) with any number of other exchange-correlation functionals:

$$E_{XC}^{hybrid} = \alpha E_X^{HF} + (1 - \alpha) E_{XC}^{GGA}. \quad (2.16)$$

The Kohn-Sham Equations

The conceptual step in the Kohn-Sham formalism [2] is to define an effective single-particle potential $v_{eff}(\mathbf{r})$ of a non-interacting system of electrons such that it reproduces the electron density of the true interacting system. The effective potential contains the functional derivatives of the known external and Coulomb energy terms ($v_{ext}(\mathbf{r})$ and $v_{Coul}(\mathbf{r})$) plus the unknown $v_{XC}(\mathbf{r})$ that can be approximated through the exchange-correlation functionals discussed above. The density is then constructed through the set of orbitals $\phi_i(\mathbf{r})$ that minimizes the energy functional. This leads to the Kohn-Sham equations:

$$[-1/2\nabla^2 + v_{eff}(\mathbf{r})] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.17a)$$

$$\sum_i^N |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r}). \quad (2.17b)$$

In practice 2.17a is solved self-consistently by generating an initial guess for the density, using the guess to calculate an effective potential $v_{eff}(\mathbf{r})$, solving 2.17a to obtain a set of orbitals ϕ_i and calculate a density from these orbitals with 2.17b that is used to start a new iteration until a predefined convergence criterion is met.

Basis sets

The molecular orbitals are constructed through linear combinations of pre-defined functions ξ_i called basis sets:

$$\phi_i(\mathbf{r}) = \sum_1^k c_{i\iota} \xi_{\iota}. \quad (2.18)$$

with coefficient $c_{i\iota}$ and where k is the number of basisfunctions. In the ADF quantum chemical suite [4] used in this thesis the basis functions are of the Slater type:

$$\xi(\mathbf{r}) = \Upsilon_{lm} r^n e^{-\zeta r}, \quad (2.19)$$

where Υ are the spherical harmonics, l, m, n the quantum numbers and ζ determines the long-range decay of the function. The Gaussian program [5] is named after its basis functions of the contracted form:

$$\xi(\mathbf{r}) = \Upsilon_{lm} r^n \sum_1^p c_p e^{\alpha_p r^2}, \quad (2.20)$$

where c_p is the contraction coefficient corresponding to the exponent α_p . The CPMD implementation of DFT [6] uses pseudopotentials to describe the core electrons and plane waves for the valence electrons:

$$\xi(\mathbf{r}) = e^{i\mathbf{G}\mathbf{r}}, \quad (2.21)$$

where $\mathbf{G}$ is the wave vector. Finally, in OCTOPUS [7], a numerical grid is used where the functions are represented by values on a set of points in real-space.

2.1.2 Excited States

Linear Response Time-Dependent DFT

The most general and most rigorous formalism to approximate excited states within DFT is time-dependent DFT (TDDFT). The theoretical justification follows from the theorem of Runge and Gross [8]. Similarly to ground state DFT the Runge-Gross theorem establishes that the time-dependent single particle potential $v_{eff}(\mathbf{r}, t)$ and kinetic term $-1/2\nabla^2$ acting on the non-interacting time-dependent orbitals $\varphi_i(\mathbf{r}, t)$ uniquely define the time-dependent density $\rho(\mathbf{r}, t)$ through the time-dependent Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}, t)\right] \varphi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) \quad (2.22a)$$

$$\sum_i^N |\varphi_i(\mathbf{r}, t)|^2 = \rho(\mathbf{r}, t). \quad (2.22b)$$

The interaction with a photon is a small perturbation to the time-dependent density. Therefore, to first order, the linear response of the density will depend only on the ground state density, which can conveniently be found from the DFT framework considered so far. The poles of the response function will consequently give the excitation energies and the pole strengths can be considered the DFT equivalents of QM oscillator strengths.

Special Cases

Several methods are also available for targeting specific excited states, such as approximating the lowest singlet excited state and charge transfer excited states.

In restricted open-shell Kohn-Sham (ROKS) the lowest excited singlet state is approximated by considering separately the closed-shell doubly occupied orbitals and the open-shell singly occupied orbitals [9,10]. This method is particularly relevant if one is interested in computationally efficient excited state dynamics of the lowest excited singlet state [11].

In constrained DFT (CDFT) [12] charge transfer energies and geometries can be assessed by constraining charges on predefined regions of the molecule. Therefore, if one has some a priori knowledge of where the photoinduced electron and hole could be localized, this method can approximate the energy of charge transfer excited states.

2.2 Methods II: Propagating the Nuclei

As a first approximation for propagating the nuclei one can neglect the quantum mechanical effects and solve Newton's second law of motion for the nuclei $\mathbf{R}_I$ in a classical molecular dynamics framework:

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = -\nabla V_C(\mathbf{R}_I) = F(\mathbf{R}_I), \quad (2.23)$$

where $F(\mathbf{R}_I)$ is the force acting on the nuclei due to the potential $V_C(\mathbf{R}_I)$ generated by the electrons. Usually this potential is approximated by a simple parametrized force field [e.g. 13].

2.2.1 Adiabatic Molecular Dynamics

A more sophisticated approach is called first-principles molecular dynamics (AIMD) and was pioneered by Car and Parrinello, who were the first to unify electronic structure theory in the form of DFT and molecular dynamics [14]. The basic scheme in AIMD [15,16] is to calculate the adiabatic ground state energy as the expectation value of the electronic Hamiltonian:

$$E_0 = \langle \psi_0(\mathbf{r}; \mathbf{R}(t)) | \hat{\mathcal{H}}_e | \psi_0(\mathbf{r}; \mathbf{R}(t)) \rangle. \quad (2.24)$$

Using the Hellman-Feynman theorem the force

$$F(\mathbf{R}_I) = -\nabla_I \langle \psi_0(\mathbf{r}; \mathbf{R}(t)) | \hat{\mathcal{H}}_e | \psi_0(\mathbf{r}; \mathbf{R}(t)) \rangle \quad (2.25)$$

acting on the nuclei can be calculated from the expectation value of the derivative of the electronic Hamiltonian with respect to the nuclear coordinates:

$$F(\mathbf{R}_I) = -\frac{\partial E_0}{\partial \mathbf{R}_I} = \left\langle \psi_0(\mathbf{r}; \mathbf{R}(t)) \left| -\frac{\partial \hat{\mathcal{H}}_e}{\partial \mathbf{R}_I} \right| \psi_0(\mathbf{r}; \mathbf{R}(t)) \right\rangle. \quad (2.26)$$

However, in practical numerical applications the employed basis set is incomplete and additional terms need to be calculated, the so called 'incomplete basis set correction' calculated from the gradients of the basis functions and the 'non-self consistency correction'. The equation of motion for the nuclei is:

$$\begin{aligned} M_I \frac{d^2 \mathbf{R}_I}{dt^2} &= -\nabla_I \langle \psi_0(\mathbf{r}; \mathbf{R}(t)) | \hat{\mathcal{H}}_e | \psi_0(\mathbf{r}; \mathbf{R}(t)) \rangle \\ &= -\nabla_I V_E^0(\mathbf{R}_I), \end{aligned} \quad (2.27)$$

where $V_E^0(\mathbf{R}_I)$ is the ground state multidimensional potential energy surface (PES) that maps the potential as a function of the nuclear coordinates. So far the electronic structure method was not specified. To incorporate DFT the expectation value of the electronic Hamiltonian is equated to the Kohn-Sham energy:

$$\langle \psi_0(\mathbf{r}; \mathbf{R}(t)) | \hat{\mathcal{H}}_e | \psi_0(\mathbf{r}; \mathbf{R}(t)) \rangle = E_{KS}[\{\phi_i\}], \quad (2.28)$$

where the Kohn-Sham energy functional is:

$$\begin{aligned} E_{KS}[\{\phi_i\}] = & T_{el}[\{\phi_i\}] + \int d\mathbf{r} V_{ext}(\mathbf{r}) \rho(\mathbf{r}) \\ & + \frac{1}{2} \int d\mathbf{r} V_H(\mathbf{r}) \rho(\mathbf{r}) + E_{XC}[\rho]. \end{aligned} \quad (2.29)$$

The usual algorithm for propagating the nuclei in AIMD is the velocity Verlet:

$$\begin{aligned} \mathbf{x}(t + \Delta t) &= \mathbf{x}(t) + \mathbf{v}(t) \Delta t + \frac{1}{2} \mathbf{a}(t) \Delta t^2 \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \frac{\mathbf{a}(t) + \mathbf{a}(t + \Delta t)}{2} \Delta t, \end{aligned} \quad (2.30)$$

where $\mathbf{x}(t)$ represents a position vector, $\mathbf{v}(t)$ the velocity and $\mathbf{a}(t)$ acceleration. The typical timestep Δt used in this thesis is 0.1 fs and most simulations are performed with a thermostat in a canonical NVT ensemble.

2.2.2 Nonadiabatic Molecular Dynamics

In first-principles molecular dynamics the nuclear motion takes place on a single adiabatic potential energy surface, the ground state. Nonadiabatic dynamics is a generalization of this principle for multiple adiabatic states, including the transitions between states. A general strategy for this in the Schrödinger picture of QM is to construct the total time-dependent *electronic* wavefunction $\psi(\mathbf{r}, t)$ from a basis of adiabatic functions [17]:

$$\psi(\mathbf{r}, t) = \sum_i c_i(t) \psi_i(\mathbf{r}; \mathbf{R}(t)), \quad (2.31)$$

where $c_i(t)$ are the time-dependent coefficients. Substituting this expansion into the time-dependent Schrödinger equation for the electrons:

$$i \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \hat{\mathcal{H}}_e \psi(\mathbf{r}, t) \quad (2.32)$$

and by projecting both sides of the resulting expression onto the set $\Psi_j(\mathbf{r}, \mathbf{R}(t))$, the following equation for the time-dependent coefficients $c_j(t)$ is obtained [17]:

$$i \frac{\partial c_j(t)}{\partial t} = \left[\hat{\mathcal{H}}_{ji}(\mathbf{r}, \mathbf{R}(t)) - i \left\langle \psi_j(\mathbf{r}; \mathbf{R}(t)) \left| \frac{\partial \psi_i(\mathbf{r}; \mathbf{R}(t))}{\partial t} \right\rangle \right] c_i(t), \quad (2.33)$$

where the electronic Hamiltonian matrix elements between state j and i are:

$$\hat{\mathcal{H}}_{ji}(\mathbf{r}, \mathbf{R}(t)) = \langle \Psi_j(\mathbf{r}; \mathbf{R}(t)) | \hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}(t)) | \Psi_i(\mathbf{r}, \mathbf{R}(t)) \rangle. \quad (2.34)$$

The nonadiabatic coupling between adiabatic state functions is contained in the second term between brackets in 2.33, which can easily be seen by using the chain rule:

$$\mathbf{d}_{ji}(\mathbf{r}, \mathbf{R}(t)) = \langle \psi_j(\mathbf{r}; \mathbf{R}(t)) | \nabla_{\mathbf{R}} \psi_i(\mathbf{r}; \mathbf{R}(t)) \rangle \cdot \frac{d\mathbf{R}}{dt}, \quad (2.35)$$

Thus, in this framework there are essentially two terms that promote transitions, the off-diagonal Hamiltonian matrix elements $\hat{\mathcal{H}}_{ji}(\mathbf{r}, \mathbf{R}(t))$ and the nonadiabatic coupling $\mathbf{d}_{ji}(\mathbf{r}, \mathbf{R}(t))$. As discussed in the introduction the process of interest in this thesis is the evolution of a pure exciton state ($c_{ex}(0) = 1$) into a charge transfer state ($c_{ct}(\tau) = 1$). To achieve this some nuclear motion is required, as $\hat{\mathcal{H}}_{ji}(\mathbf{r}, \mathbf{R}(t))$ and $\mathbf{d}_{ji}(\mathbf{r}, \mathbf{R}(t))$ will only change in time through their dependence on $\mathbf{R}(t)$.

Tully's Surface Hopping

A commonly used algorithm to approximate this time-dependent problem was developed by Tully [18]. In Tully's nonadiabatic dynamics the nuclear motion takes place on a single potential energy surface, while evolving multiple adiabatic states simultaneously. The nonadiabatic coupling between all states is evaluated along the trajectories to calculate transition probabilities. If the probability reaches above a certain threshold generated by a random number, the algorithm will invoke an instantaneous nonadiabatic transition between states. Although this method is accurate in describing equilibrium behaviour on long timescales [19], the description of gradual coherent charge transfer from an excitonic state to a charge transfer state is

limited by the instantaneous nature of the transitions in this framework. Recent experimental and theoretical work indicates that the oscillatory charge transfer process has an associated nonzero timescale and involves a mixing of adiabatic states.

Ehrenfest TDDFT

In Ehrenfest dynamics, the electronic motion originates directly from solving the time-dependent electronic Schrödinger equation for the time-dependent electronic wavefunction $\psi(\mathbf{r}, t)$.

$$i\frac{\partial\psi(\mathbf{r}, t)}{\partial t} = \hat{\mathcal{H}}_e\psi(\mathbf{r}, t). \quad (2.36)$$

Consequently, for every newly obtained electronic wavefunction $\psi(\mathbf{r}, t+\Delta t)$, where Δt is very small ($\sim 10^{-18}s$) forces can be calculated to evolve the nuclei according to:

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = -\nabla_I \langle \psi(\mathbf{r}, t) | \hat{\mathcal{H}}_e | \psi(\mathbf{r}, t) \rangle, \quad (2.37)$$

which includes nonadiabatic transitions and the possibility of mixing between (adiabatic) states. In this way coherent evolution of an exciton into a charge transfer state can be simulated in real-time.

The implementation of the Ehrenfest formalism within TDDFT is through the time-dependent Kohn-Sham equations that give the time evolution of the time-dependent Kohn-Sham orbitals $\phi_i(\mathbf{r}, t)$ and the time dependent density $\rho(\mathbf{r}, t)$:

$$i\frac{\partial}{\partial t}\varphi_i(\mathbf{r}, t) = [-1/2\nabla^2 + v_{eff}(\mathbf{r}, t)]\varphi_i(\mathbf{r}, t)$$

$$\sum_i^N |\varphi_i(\mathbf{r}, t)|^2 = \rho(\mathbf{r}, t). \quad (2.38)$$

The time-dependent Kohn-Sham orbitals $\varphi_i(\mathbf{r}, t)$ can subsequently be expanded in terms of adiabatic Kohn-Sham orbitals $\phi_i(\mathbf{r}; \mathbf{R}(t))$:

$$\varphi(\mathbf{r}, t) = \sum_i c_i(t)\phi_i(\mathbf{r}; \mathbf{R}(t)), \quad (2.39)$$

that are obtained through a regular time-independent DFT optimization (section 2.1). The time evolution of the coefficients then becomes [20]:

$$i \frac{\partial c_i(t)}{\partial t} = \sum_j c_j(t) (\epsilon_j \delta_{ij} - \mathbf{d}_{ij}), \quad (2.40)$$

where ϵ_j is the energy of adiabatic orbital j and $\mathbf{d}_{ij}$ the nonadiabatic coupling $\langle \phi_i(\mathbf{r}; \mathbf{R}(t)) | \nabla_{\mathbf{R}} | \phi_j(\mathbf{r}; \mathbf{R}(t)) \rangle \cdot d\mathbf{R}/dt$ between orbital i and j .

As in adiabatic dynamics, the classical equation of motion for the nuclei follows from the time derivative of the Kohn-Sham energy functional:

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = - \frac{\partial E_{KS}[\rho(\mathbf{r}, t)]}{\partial \mathbf{R}_I}. \quad (2.41)$$

Now, by modifying the nonadiabatic coupling $\mathbf{d}_{ij}$ between adiabatic orbitals the nuclear motion can invoke nonadiabatic transitions. Thus, a framework is in place to approximate in real-time the photoinduced charge transfer in molecules.

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