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Quantum dynamics beyond the Born-Oppenheimer approximation in molecular systems

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Abstract

Representing the wavefunction of quantum systems scales exponentially with the number of particles, which makes quantum simulations of molecules intractable. The Born-Oppenheimer approximation utilizes the difference in timescales of dynamics of electrons and nuclei to split the problem into two simpler problems associated with each type of particle by using the Born-Oppenheimer representation. While this approximation is a cornerstone of quantum chemistry, it neglects important effects when a molecule undergoes an ultrafast process where both electrons and nuclei evolve on a similar timescale. In this case, one must go beyond this approximation. Unfortunately, the Born-Oppenheimer representation exhibits two major drawbacks that make exact simulations impossible: i) a geometric phase in the electronic wavefunctions, and ii) a non-integrable term in the Hamiltonian. After exposing these problems, I will present an alternative employing time-dependent electronic wavefunctions: the moving crude adiabatic states.

Keywords: Quantum molecular dynamics, Moving Crude Adiabatic

Introduction

Simulation of matter at the molecular scale requires applying quantum mechanical concepts to describe electrons and nuclei. Quantum mechanics describes matter as a wavefunction, which can be understood as a superposition of a large number of possible configurations that span a Hilbert space. Numerical approaches to simulating quantum systems scale exponentially with the number of particles, which makes the simulations intractable. The time evolution of the system is described by the Schrödinger equation

$$|\partial\Psi/\partial t(t)\rangle = -i\hat{H}|\Psi(t)\rangle, \quad (1)$$

where t is the time parameter, $|\Psi(t)\rangle$ is the molecular wavefunction, and \hat{H} is the molecular Hamil-

tonian where the potential energy is given by the Coulomb interactions between the particles.

Thanks to the mass ratio of the electrons and nuclei, the electronic timescale is much shorter than the nuclear timescale. Then, electrons instantaneously adapt to the motion of the nuclei, while the nuclei experience the average field of the electrons. This separation is achieved by: i) splitting the Hamiltonian into nuclear kinetic energy and the electronic Hamiltonian, $\hat{H}_e(R)$, which contains the remaining terms and depends on the nuclear positions R , and ii) imposing that electrons are represented by stationary states, also named adiabatic states, of \hat{H}_e and associated with the electronic eigenenergies $\varepsilon_n(R)$:

$$\hat{H}_e(R)|\varphi_n(R)\rangle = \varepsilon_n(R)|\varphi_n(R)\rangle. \quad (2)$$

These electronic states form a basis on which one can expand the molecular wavefunction

$$|\Psi(R, t)\rangle = \sum_{n=1}^{\infty} |\varphi_n(R)\rangle \chi_n(R, t). \quad (3)$$

The Born-Oppenheimer approximation imposes that the electronic part of the total wavefunction is confined in a given electronic state and the total wavefunction reads $|\Psi(R, t)\rangle \approx |\varphi_n(R)\rangle |\chi_n(R, t)\rangle$. This approximation is a cornerstone of chemistry and is often valid for molecular systems close to equilibrium at ambient temperature, where only the ground electronic state is populated. However, this approximation can fail dramatically when the system is excited to a higher electronic state, and strong couplings allow for transitions between electronic states such that more terms in Eq. 3 are required. An interesting case occurs in the presence of geometries named conical intersections, where the electronic states energies are degenerate $\varepsilon_n = \varepsilon_{n+1}$ and the interstate coupling becomes infinite [1]. Conical intersections are ubiquitous in dynamics involving excited states. Extra dif-

difficulties arise at these geometries: i) the electronic states acquire a geometric phase (also named Berry phase) upon encircling the conical intersections [2], and ii) a non-integrable intrastate (diagonal) term appear [3].

In this talk, I will first give numerical examples of failure in the Born-Oppenheimer representation. Then, I will present an alternative representation that handles the mentioned difficulties.

1 Limitations of the Born-Oppenheimer representation

Since electronic states are parameterized by the nuclear positions, the nuclear kinetic energy action on the electronic states gives rise to the so-called non-adiabatic couplings. These non-adiabatic couplings can be intra- or interstate couplings.

A first difficulty comes from the fact that inter and intrastate couplings diverge at conical intersections, which can lead to numerical instabilities. In particular, the intrastate terms are not integrable [3]. These must necessarily be excluded from the equation to obtain a finite solution. The second difficulty comes from the appearance of a geometric phase attached to electronic states when they are transported on a closed loop around the conical intersection in the nuclear coordinate space [2]. Thus, electronic states are double-valued functions of the nuclear coordinates and so must be the nuclear components $\chi_n(R, t)$. Imposing double-valued boundary conditions on the latter is impossible without prior knowledge of the conical intersections positions. Therefore, not accounting for this double-valuedness is another common necessary approximation. These arbitrary approximations can lead to significant changes in the dynamics of molecular systems. I will expose these issues on numerical examples employing simple vibronic models [4].

2 A new representation for direct molecular quantum dynamics

Choosing the adiabatic representation greatly reduces the many-electron Hilbert space to only N_s number of important electronic states in Eq. (3). Regarding the nuclear components, one can also avoid exponential scaling by employing a time-dependent basis that adapts along the dynamics. Gaussian functions $g(R, q_k[t])$ with time

evolving centers $q[t]$ are commonly chosen in order to employ local approximate models and simplify space integrations. Then, the nuclear components read

$$\chi_n(R, t) = \sum_{k=1}^{N_g} C_{kn}(t)g(R, q_k[t]), \quad (4)$$

where $\{C_{kn}(t)\}$ are time-dependent complex coefficients. Nevertheless, Gaussian functions are not double-valued functions and have no specific cusp behavior that can avoid non-integrability of the intrastate terms.

To resolve this difficulty, we adopt a new type of electronic wavefunctions that are solutions of Eq. (2) only at the Gaussians' centers:

$$\hat{H}_e(q_k[t])|\varphi_n(q_k[t])\rangle = \varepsilon_n(q_k[t])|\varphi_n(q_k[t])\rangle. \quad (5)$$

This small change removes the parametric dependence of the electronic states on the nuclear coordinates, such that the resulting states are not double-valued and do not give rise to any non-integrable term. I will present numerical simulations to support these findings [5].

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