Extracting molecular Hamiltonian structure from time-dependent fluorescence intensity data

Constantin Brif and Herschel Rabitz
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Abstract
We propose a formalism for extracting molecular Hamiltonian structure from inversion of time-dependent fluorescence intensity data. The proposed method requires a minimum of a priori knowledge about the system and allows for extracting a complete set of information about the Hamiltonian for a pair of molecular electronic surfaces.

1 Introduction
A long standing objective is the extraction of molecular Hamiltonian information from laboratory data. The traditional approaches to this problem attempt to make use of time-independent (spectroscopic and scattering) data [1, 2, 3]. Another approach aims to use ultrafast temporal data, with information on molecular potentials and dipole moments obtained for spatial regions sampled by evolving wave packets. Research in this direction has been especially intense during the last few years [4, 5, 6, 7, 8, 9]. This activity is inspired by recent progress in the technology of ultrafast laser pulses [10, 11], which makes possible observations of molecular dynamics with increasingly higher spatial and temporal resolution.

Due to the difficulty of the Hamiltonian inversion problem, it is common to assume that some a priori knowledge of the system is available. For example, one technique [6] proposes to extract time-evolving wave functions and excited-state potentials using time-resolved and frequency-resolved fluorescence data and knowledge of the ground-state potential, the transition frequencies, and the transition dipole moment. The inverse tracking method [7], proposed for recovering the potential energy and dipole moment of a molecular electronic surface by monitoring the temporal evolution of wave packets, explicitly assumes knowledge of the initial excited wave functions. Clearly, such assumptions impair self-consistency and at least partially undermine the inversion objectives. Although the desire to simplify the inversion algorithm by making a priori assumptions about what is known and unknown is understandable, it has remained an open question about whether these assumptions are actually necessary.

This letter addresses the latter point by proposing an inversion formalism that makes use of minimal a priori knowledge about the system. The formalism is designed to operate between two electronic surfaces, with electronic and vibrational transitions driven by two fast laser pulses, which allows for extracting the potential energies and dipole moments for both surfaces as well as the electronic transition dipole moment. The extraction is based on the inversion of the time-dependent fluorescence intensity data obtained from the detection of spontaneous emission in transitions between the electronic surfaces. The proposed formalism lays the ground work for extracting a complete set of information about a pair of electronic surfaces in a closed way, with a minimum of a priori assumptions about the molecular Hamiltonian. This letter presents
the conceptual foundation of this novel approach, and a detailed numerical algorithm with simulations will be presented elsewhere.

2 The physical picture

Consider the ground and excited electronic molecular surfaces with potential energies $V_g(x)$ and $V_e(x)$ and dipole moments $\mu_g(x)$ and $\mu_e(x)$, respectively. The dipole moment for the electronic transition between the two surfaces is $M(x)$. For the sake of conceptual clarity, we consider a one-dimensional problem; the generalization for the multidimensional case is straightforward.

The setup includes two time-dependent locked laser fields: $\epsilon_0(t)$ drives transitions between the two electronic surfaces (the carrier frequency of this laser will be typically in the visible or ultraviolet part of the spectrum), and $\epsilon_1(t)$ drives transitions between vibrational levels within each of the two surfaces (the carrier frequency of this laser will be typically in the infrared). The role of the driving fields is to excite the molecular wave packet and guide its motion on the surfaces. It is physically reasonable that the potentials and dipole moments may be reliably extracted only in the region sampled by the evolving wave packet. We assume that interactions with other electronic surfaces and incoherent processes (e.g., thermal excitation and collisional relaxation) are negligible. Ultrafast laser technology has made great advances recently, but preparation of the infrared pulse of a desired shape is still a challenging technical problem. We will consider the general situation, with two locked driving fields and five unknown functions (two potentials and three dipole moments), but taking $\epsilon_1 = 0$ the problem is easily reduced to a simpler one, with only one driving field $\epsilon_0$ and three unknown functions ($V_g$, $V_e$ and $M$).

The Hamiltonian of the system in the Born-Oppenheimer, electric-dipole and rotating-wave approximations takes the form:

$$H = H_g(x, p, t)\sigma_{gg} + H_e(x, p, t)\sigma_{ee} - M(x)\epsilon_0(t)(\sigma_{eg} + \sigma_{ge}),$$

where $\sigma_{ij} = |i\rangle\langle j|$ (with $i, j = g, e$) are transition-projection operators for the electronic states $|g\rangle$ and $|e\rangle$. Here, $x$ and $p$ are the canonical position and momentum for the vibrational degree of freedom, $H_g$ and $H_e$ are the vibrational Hamiltonians in the ground and excited electronic states,

$$H_i(x, p, t) = T + V_i(x) - \mu_i(x)\epsilon_1(t), \quad i = e, g,$$

and $T = p^2/2m$ is the kinetic energy of the vibrational motion.

We assume that the initial state of the system is $|\Psi(0)\rangle = |u_0\rangle|g\rangle$, where $u_0(x)$ is the vibrational ground state localized in the known harmonic part of the potential $V_g(x)$. The state of the system at any time $t$ will be of the form

$$|\Psi(t)\rangle = |u(t)\rangle|g\rangle + |v(t)\rangle|e\rangle,$$

with the normalization condition $\int dx \ (|u(x, t)|^2 + |v(x, t)|^2) = 1$. The Schrödinger equation, $i\hbar \partial_t |\Psi(t)\rangle = H |\Psi(t)\rangle$, then takes the form

$$i\hbar \partial_t u(x, t) = -\frac{\hbar^2}{2m} \partial_x^2 u(x, t) + [V_g(x) - \mu_g(x)\epsilon_1(t)]u(x, t) - M(x)\epsilon_0(t)v(x, t),$$

$$i\hbar \partial_t v(x, t) = -\frac{\hbar^2}{2m} \partial_x^2 v(x, t) + [V_e(x) - \mu_e(x)\epsilon_1(t)]v(x, t) - M(x)\epsilon_0(t)u(x, t),$$

with the initial conditions $u(x, 0) = u_0(x)$, $v(x, 0) = 0$. 

2
The radiation emitted spontaneously by the molecule via transitions between the excited and ground electronic surfaces contains information about the wave packet. This fact has been used to reconstruct unknown vibrational wave packets in the method of emission tomography \[13\]. Our aim is different: we assume that the initial state of the system is known and want to extract the unknown potentials \(V_g\) and \(V_e\) and dipole moments \(\mu_g, \mu_e,\) and \(M\) from information contained in the time-dependent fluorescence. We choose the time-dependent intensity of the emitted radiation, \(I(t)\), as the observable. This intensity is \(I(t) = E^+(t)E^-(t)\), where \(E^+(t)\) is the negative-frequency part of the electric field operator of the emitted radiation. \(E^+\) is proportional to \(M\sigma\), so the measured quantity is
\[
\langle I(t) \rangle = \kappa \langle \Psi(t) | M^2 \sigma_{ee} | \Psi(t) \rangle.
\] (6)
where \(\kappa\) is a proportionality constant.

3 Extraction of the Hamiltonian structure

The physical picture above leads to the following mathematical problem: extract the potentials and dipole moments from the measured intensity \(\langle I(t) \rangle\), assuming that the initial state and the two driving fields are known (note that a number of advanced experimental techniques have been recently developed for characterization of ultrashort optical pulses \[13\] \[14\] \[15\] \[16\]).

We start from the Heisenberg equation of motion, \(ih\frac{dI}{dt} = [I, H]\), to obtain
\[
\frac{i\hbar}{\kappa} \frac{d\langle I \rangle}{dt} = \langle \Psi(t) | [M^2, T] \sigma_{ee} - \epsilon_0(t) M^3 (\sigma_{eg} - \sigma_{ge}) | \Psi(t) \rangle.
\] (7)

Using form (3) of the wave function, we rewrite (7) as an integral equation for \(M(x)\):
\[
\int dx [M^2(x) F(x, t) + M^3(x) G(x, t)] = \frac{\hbar}{2\kappa} \frac{d\langle I \rangle}{dt},
\] (8)

where
\[
F(x, t) = \frac{\hbar^2}{2m} \text{Im} \{v(x, t) \partial^2_x v^*(x, t)\}, \quad G(x, t) = \epsilon_0(t) \text{Im} \{u^*(x, t) v(x, t)\}.
\] (9)

In order to obtain equations for the other unknown functions (two potentials and two dipole moments), we consider the second time derivative of \(\langle I(t) \rangle\). Then, using (3), we derive the following integral equation:
\[
\frac{\hbar^2}{\kappa} \frac{d^2\langle I \rangle}{dt^2} + T_M(t) = \int dx [V_e(x) - V_g(x) - \epsilon_1(t) \mu_e(x) + \epsilon_1(t) \mu_g(x)] S_M(x, t)
+ \int dx [V_e(x) - \epsilon_1(t) \mu_e(x)] R_M(x, t),
\] (10)

where
\[
R_M(x, t) = \frac{\hbar^2}{m} \text{Re} \left\{ v^*(x, t) [\partial^2_x, M^2(x)] v(x, t) \right\},
\] (11)
\[
S_M(x, t) = -2\epsilon_0(t) M^3(x) \text{Re} \left\{ u^*(x, t) v^*(x, t) \right\}.
\] (12)
where equation (10) takes the form

\[ \frac{\hbar^4}{4m^2} \int dx v^*(x,t) [M^2(x) \partial_x^4 - 2\partial_x^2 M^2(x) \partial_x^2 + \partial_x^4 M^2(x)]v(x,t) \]

\[ + \frac{\hbar^2}{m} \epsilon_0(t) \text{Re}\left\{ \int dx v^*(x,t) [M^3(x) \partial_x^2 + M^2(x) \partial_x^2 M(x) - 2 \partial_x^2 M^3(x)]u(x,t) \right\} \]

\[ + 2\epsilon_0(t) \int dx M^4(x) (|v(x,t)|^2 - |u(x,t)|^2). \]  

(13)

It is convenient to formally enumerate the unknown functions,

\[ f_1(x) = V_g(x), \quad f_2(x) = V_e(x), \quad f_3(x) = d_0 \mu_g(x), \quad f_4(x) = d_0 \mu_e(x), \]  

(14)

where \( d_0 = 1 \text{ V/m} \), so all the functions \( f_r(x) \) have the dimension of energy. Then the integral equation (10) takes the form

\[ \int dx \sum_{r=1}^{4} K_r(x,t) f_r(x) = g(t), \]  

(15)

where

\[ K_1(x,t) = -S_M(x,t), \quad K_2(x,t) = R_M(x,t) + S_M(x,t), \]  

(16)

\[ K_3(x,t) = -\tilde{\epsilon}_1(t) K_1(x,t), \quad K_4(x,t) = -\tilde{\epsilon}_1(t) K_2(x,t), \]  

(17)

\[ g(t) = \frac{\hbar^2}{\kappa} \frac{d^2}{dt^2} + T_M(t), \]  

(18)

and \( \tilde{\epsilon}_1 = d_0^{-1} \epsilon_1 \) is the scaled (dimensionless) field.

It is important to emphasize that in fact equations (8) and (15) represent an infinite number (or, in practice, a large number) of equations corresponding to different times. We will use this fact in the regularization procedure below. Of course, equation (13) is nonlinear because the wave function depends on the potentials and dipole moments. Similarly, a solution \( M \) of (8) depends on the wave function and thereby depends on other unknown functions. Consequently, the problem at hand, including the integral equations and the Schrödinger equation, is highly nonlinear. More importantly, the solution for such a system of integral equations is generally not unique and the problem is ill-posed (i.e., the solution is not stable against small changes of the data). These characteristics are common to virtually all inverse problems and arise because the data used for the inversion are inevitably incomplete. Consequently, we need to regularize the problem by imposing physically motivated constraints on the unknown functions. For example, we may use the fact that physically acceptable potentials and dipoles should be smooth functions and tend to zero asymptotically as \( x \rightarrow \infty \) (in the case of the dipole, the atoms are assumed to separate as neutrals). By taking into account this information, some constraints are imposed on the solutions, singling out the functions with desirable physical properties. This regularization procedure will stabilize the solution.

The regularized solution of equation (15) is achieved by minimizing the functional

\[ \mathcal{J} = \int_0^t dt' \left[ \int dx \sum_{r=1}^{4} K_r(x,t') f_r(x) - g(t') \right]^2 + \sum_{r=1}^{4} \alpha_r \int dx f_r^2(x). \]  

(19)

Here, \( \alpha_r \) are standard regularization parameters which denote the tradeoff between reproducing the laboratory data and obtaining the solution with smooth and regular functions. The time
integration in (19) has a simple physical meaning: the measured intensity brings in information about the potentials and dipoles at each instance of time and we want to use all the laboratory information which has been accumulated during the period from time zero until \( t \). The choice of the functional (19) is not unique, and other forms of regularization may be considered as well.

Taking the variation of the functional \( J \) with respect to the unknown functions \( f_r(x) \) involves a subtlety related to the nonlinearity of the problem: the kernels \( K_r \) and the free term \( g \) depend on the wave function and on \( M(x) \) and thereby depend on \( f_r(x) \). The practical (numerical) solution of any nonlinear problem includes some kind of linearization. Here, the point at which we make the linearization is determined in the regularization procedure. We choose to take the variation of the functional \( J \) in equation (19) only with respect to the explicit dependence on \( f_r(x) \). Then we obtain the set of regularized equations:

\[
\int dx' \sum_{r=1}^{4} \mathcal{R}_{pr}(x, x', t)f_r(x') + \alpha_p f_p(x) = g_p(x, t),
\]

where

\[
\mathcal{R}_{pr}(x, x', t) = \int_0^t dt' K_p(x, t')K_r(x', t'),
\]

\[
g_p(x, t) = \int_0^t dt' K_p(x, t')g(t').
\]

With \( p, r = 1, 2, 3, 4 \), we have the system of four integral equations with four unknown functions (two potentials and two moments).

Now we want to regularize equation (8) for the electronic transition dipole \( M \). This equation is highly nonlinear: in addition to the dependence on \( M \) in the wave function, it also involves second and third powers of \( M \). Once again, we may choose at which point to make the linearization. We prefer to linearize at an early stage, in order to obtain an equation of a simple form. Thus we define

\[
F_M(x, t) = M^2(x)F(x, t), \quad G_M(x, t) = M^2(x)G(x, t),
\]

and write the functional

\[
\mathcal{J}_M = \int_0^t dt' \left[ \int dx M(x)G_M(x, t') + \int dx F_M(x, t') - g_M(t') \right]^2 + \alpha_M \int dx M^2(x).
\]

Here, \( g_M(t) \) is the right-hand side of equation (8). The regularized solution of equation (8) is achieved by minimizing this functional. And we choose the linearization procedure by taking the variation of \( \mathcal{J}_M \) in equation (24) only with respect to the explicit dependence on \( M \) (that is, we treat \( F_M \) and \( G_M \) as independent of \( M \)). Then we obtain

\[
\int dx' \mathcal{R}_M(x, x', t)M(x') + \alpha_M M(x) = g_M(x, t),
\]

where

\[
\mathcal{R}_M(x, x', t) = \int_0^t dt' G_M(x, t')G_M(x', t'),
\]

\[
g_M(x, t) = \int_0^t dt' G_M(x, t') \left[ g_M(t') - \int dx' F_M(x', t') \right].
\]
Finally, the integral equations (20) and (25) for the potentials and dipole moments and the
Schrödinger equations (4) and (5) for the components of the wave function form the full set of
coupled equations for the unknown functions, with \langle I(t) \rangle, \epsilon_0(t), and \epsilon_1(t) as input data.

We conclude the presentation of the formalism with a schematic outline of the inversion
algorithm which will be numerically implemented in a forthcoming work. First, the algorithm
will start with trial functions for the potentials and dipoles to propagate the wave function from
t = 0 to t = \Delta t. Using trial functions at the first step is not an excessive demand for two
reasons: (i) For a sufficiently small time increment \Delta t, the evolution of the wave function is
mainly affected by the values of the potentials and dipoles in the region where \textit{u}_0(x) is localized,
i.e., in the harmonic region of the ground potential surface; such information is usually known
with reasonable accuracy. (ii) As more data becomes available, the initial trial functions will
be replaced by those which match the measured fluorescence intensity. The second step will
use the measured fluorescence intensity, the wave function components \textit{u}(\Delta t) and \textit{v}(\Delta t), and
the initial trial functions for solving equations (25) and (24) to obtain the next evaluation of
the potentials and dipoles. These functions will be once again substituted into the Schrödinger
equation to propagate the wave packet from \textit{t} = \Delta t to \textit{t} = 2\Delta t. The procedure will be repeated
many times with new laboratory data incorporated at each time step. The recorded fluorescence
intensity, \langle I(t) \rangle, contains information about the potentials and dipoles in the region where the
wave packet is localized at moment \textit{t} as well as where it was prior to that time. The sequential
marching forward in time over the data track acts to refine the potentials and dipoles at each
time step.

4 Discussion

This letter sets forth the formalism of a novel comprehensive approach to the inversion of
molecular dynamics from time-dependent laboratory data. One of the main features of the
proposed inversion method is initiation in the well-known ground state and use of external
driving fields to excite the wave packet and guide its motion on the ground and excited potential
surfaces. Different driving fields will induce different dynamics and may be more or less helpful
for the inversion procedure. Consequently, we are left with the attractive prospect of choosing
the driving fields to be optimally suited for assisting the extraction of unknown potentials and
dipoles from laboratory data. This choice may be facilitated by a closed learning loop [17] in the
laboratory, starting with a number of different trial fields. According to the inversion objectives,
a learning algorithm will determine the best candidates and direct the fields to shapes which
are best suited to produce these objectives. Natural objectives are to maximize the spatial
region where the potentials and dipoles are reliably extracted. Physical intuition suggests that
one may learn more about the Hamiltonian at a specific spatial point if the wave packet is not
spread over the whole potential surface but is essentially localized in a narrow region around this
point. Consequently, the driving fields best suited for the inversion will control the dispersion of
the wave packet and guide its motion in a desired large spatial region. A numerical simulation
of the algorithm, including its closed-loop learning features, will be the next step towards its
laboratory implementation.
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