Princeton University

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"EXTRACTION OF HIGH QUALITY POTENTIAL SURFACES FROM LABORATORY DATA"

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A new direct inversion algorithm is being developed, capable of taking high quality laboratory pump-probe data and directly inverting it to potential surface and optical coupling coefficient information. The algorithm is based on employing the laboratory data in a two-stage noniterative inversion. Inversion with simulated data shows that the developing algorithm is capable of being highly efficient and superior to any other available techniques.

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Annual Technical Report

"EXTRACTION OF HIGH QUALITY POTENTIAL SURFACES FROM LABORATORY DATA"

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Background.

The purpose of this research is to establish the feasibility of developing an algorithm with unique capabilities for taking high quality laboratory data and directly inverting it to valuable Hamiltonian information, including potential surfaces and optical coupling coefficients. The only existing means for treating such problems has consisted of tedious iterative algorithms to fit intuitively chosen functional forms to the sought-after Hamiltonian quantities. Such an approach is an art at best, and constraining the form of the sought-after information can give highly misleading results. An ideal algorithm would impose no functional forms for the sough-after information, nor would it call for iteration of the dynamical equation to fit the data. An additional motivation for developing a new algorithm is the emerging capability of performing ultrafast optical pump-probe experiments in a routine fashion. Newly available optical pulse shaping tools should greatly facilitate such experiments, and they are also directly connected with the rapidly developing field of molecular control.

With the above background and motivations, we have been pursuing the development of an algorithm with special capabilities. The logic leading to the development of this algorithm is based on the allied subject of *tracking* of molecular dynamics events. We have introduced this latter topic into the control of molecular dynamics under a separate AFOSR grant, and that research led us to the present work on inversion. The basic rudiments of the inversion algorithm are now in hand, and all indications point to it being highly successful, for the stated purposes. An outline of the algorithm and an indication of its capabilities is given below.

Direct Inversion Algorithm.

A. Time-Dependent Pump-Probe Data.

Ultrafast sub-picosecond temporal data is becoming increasingly available in the laboratory. Presently, optical sources are being used both for the pump and probe processes, and efforts are under way to use ultrafast X-ray or electron diffraction as a direct probe of the evolving molecular structure, following the pump event. Regardless of the probe, experiments are feasible for both ground state dynamics and motion on excited electronic surfaces. An especially appealing physical picture envisions a sequence of experiments, each corresponding to ever-increasing excitation within the molecule. During this process, the evolving molecular dynamics (i.e., wavepacket) would explore an ever-larger region of the potential surface in a systematic fashion. It is this picture, and its associated observational data, which we have developed into a rigorously founded inversion algorithm.

The basic elements of the algorithm are quite straightforward, and are summarized here. First, we denote as O the operator associated with the observations. The observations could be of many types, including temporal correlation measurements, ultrafast imaging of the dynamics, etc. Regardless of the circumstances, the operator O may always be taken as known. The expectation value of this operator $\langle O(t)\rangle$ is the available laboratory data. This latter expectation value rigorously satisfies the Heisenberg equation of motion

$$it\frac{d}{dt}\langle O\rangle = \langle[K,O]\rangle + \langle[V,O]\rangle + \varepsilon(t)\langle[\mu,O]\rangle \qquad (1)$$

where K is the kinetic energy operator, V is the sought-after potential energy, and μ is the possibly also sought-after electric dipole function. The pump electric field is $\varepsilon(t)$, and in general, this latter field may be present even during the probe process. Equation (1) is ideal as a starting point for an inversion algorithm as it contains the data $\langle O(t)\rangle$ and the sought-after unknown V and/or μ. For illustration, we will first set $\varepsilon(t) = 0$, assuming that a prior pump pulse has prepared a dynamical

non-stationary state and laboratory data has been taken to prescribe the left-hand side of Eq. (1). This equation may be rewritten as

$$\langle [V,O] \rangle = i\hbar \frac{d}{dt} \langle O \rangle - \langle [K,O] \rangle \tag{2}$$

which, in turn, may be *formally* solved for the potential, as it appears explicitly only in a linear fashion in Eq. (2).

$$V(x) = \langle [\bullet,O] \rangle^{-1} [i\hbar \frac{d}{dt} \langle O \rangle - \langle [K,O] \rangle] \tag{3}$$

The inverse $\langle [\bullet,O] \rangle^{-1}$ can be generated by recognizing that Eq. (2) is a Fredholm integral equation for V(x). Equation (3) is only a formal solution, as it still contains the unknown wavefunction in the expectation values. However, we rigorously know that these wavefunctions satisfy Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = [K + V]\Psi \tag{4}$$

with a specified initial condition. Thus, we may numerically integrate Eq. (4) by substitution of Eq. (3) for the potential. This integration will yield the time-dependent wavefunction $\Psi(t)$, which may, in turn, be substituted back onto the right-hand side of Eq. (3) to close this process and explicitly yield the potential function. There are two particular points to note here: (a) the data $\langle O(t) \rangle$ enters explicitly into the inversion process of solving Eq. (4), through its presence in Eq. (3), and (b) although we normally think of Schrödinger's equation as linear in the wavefunction, when posed in the inverse sense, it becomes highly nonlinear, which is evident by substitution of Eq. (3) into Eq. (4). The inevitable nonlinearity of the inversion algorithm arises since the sought-after potential does not have any simple linear relation to the laboratory data. As the evolving

molecular motion explores increasingly larger regions of the potential surface, the potential V(x) correspondingly will be explored and determined.

Once the potential V(x) is determined, a second set of experiments could be performed to extract the optical dipole function $\mu(x)$ by including the pump field $\varepsilon(t)$ during the observation process. The logic of this second-stage inversion is exactly similar to that of the potential above, with now the last term in Eq. (1) retained. We have recently undertaken a simulation of this two-stage process for diatomic molecules, with typical results shown in Figure (1). The regions of the functions V(x) and $\mu(x)$ that are determined corresponds to that sampled by the evolving dynamical wavepacket. The results are of high accuracy and are extremely encouraging, regarding the ultimate viability of the algorithm.

B Inversion with High Resolution CW Spectral Data.

The algorithm above is based on the physical picture of the molecular dynamical wavepacket sampling distinct regions of the potential surface as it evolves, and the potential being mapped out in a one-for-one match of this evolutionary process. In the weak optical field regime, where such experiments would likely be carried out, a relation exists between the temporal data and some sequence or combination of more traditional spectroscopic measurements. The advantage of using cw spectral techniques is their high precision, but until now, such data has largely defied utility for inversion (except for diatomics), due to the lack of an algorithm that can explicitly handle the data in a logical fashion. The above new algorithm may be adapted to utilize high resolution spectral data as input. In this sense, the temporal nature of the algorithm may be viewed as an artifice, to create synthetic time-dependent tracks from the cw data. Thus, the algorithm above becomes a logical means for organizing the cw data into a format that makes it amenable for stable and reliable inversion. A number of issues need to be explored, to fully take advantage of this connection to cw data for inversion, and the motivation is quite high since the latter data is readily available and typically of excellent quality. This prospect will be explored in later stages of the research.

Summary and Projected Next Stage of the Research.

The research has past a critical developmental step, through the prescription of an overall noniterative direct inversion algorithm for pump-probe laboratory data. The algorithm is based on rigorous quantum mechanical relationships, and does not rely on perturbation theory or artificial functional forms for the potential. The preliminary illustrations with simulated data are quite encouraging, and a host of issues need further exploration. In particular, we plan to study the stability of the algorithm to laboratory noise, and develop the mathematical and numerical tools to simultaneously determine the variance of the inverted potential and optical coupling coefficients. We also plan to explore an extension of this algorithm to treat high quality spectral intensities line intensities and positions as input. As these topics are developed, available laboratory data will be inserted into the algorithm, for explicit illustration of its capabilities. Finally, at an advanced stage, we plan to draw together the inversion algorithm and optimal design techniques, with the latter tools being developed under an independent AFOSR grant ("Optimal Control of Molecular Motion"). The aim here will be to provide the means to optimally design a sequence of experiments whose explicit purpose is for inversion, to determine valuable Hamiltonian information. The combination of optimal molecular control and a stable inversion algorithm could lead to an unprecedented capability for learning about molecules and the forces within them.

Figure 1

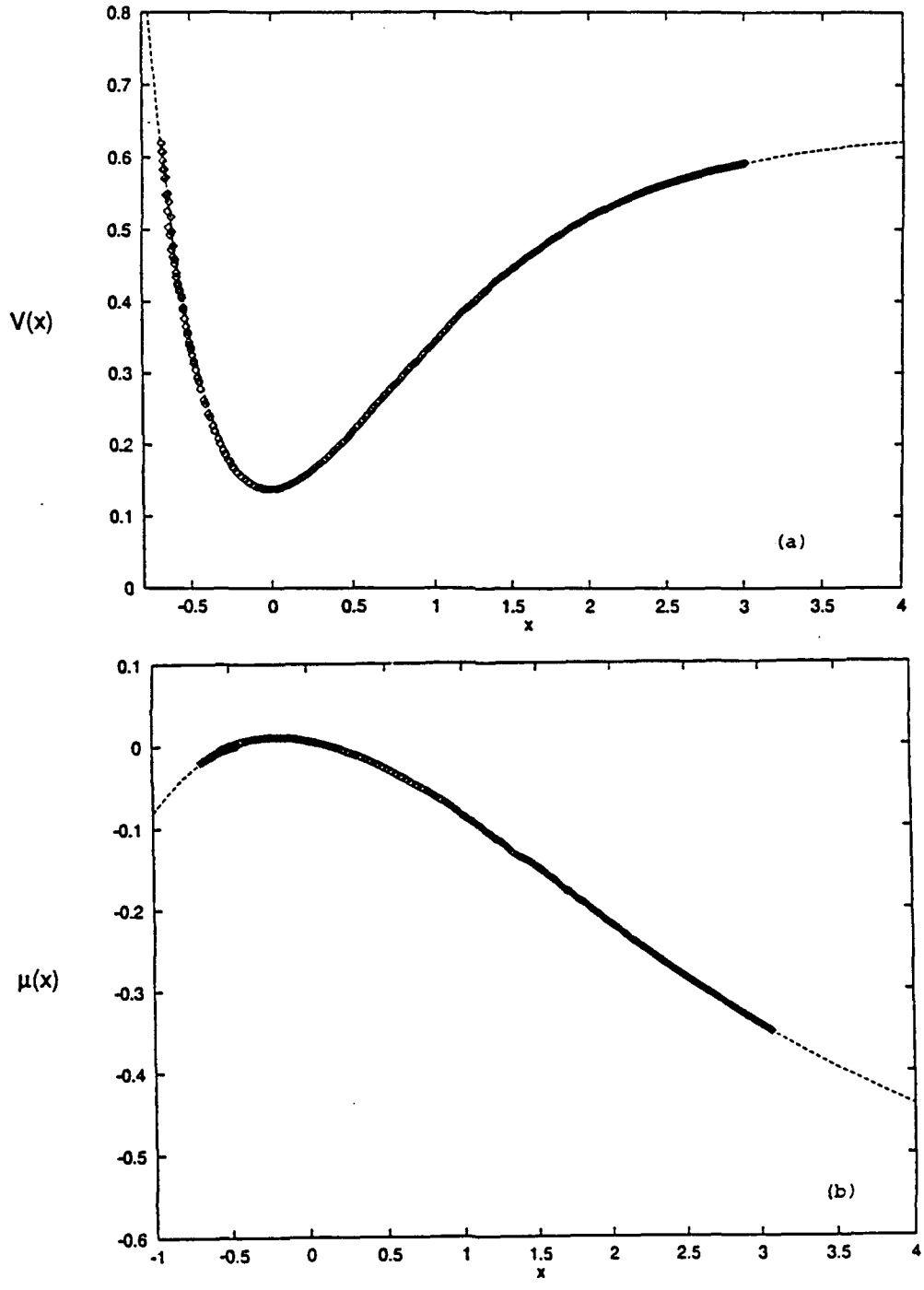

Figure 1: The extracted potential (a) and the dipole function (b) from a simulated ultrafast pump-probe experiment. The points ✧ are the recovered values over the regions sampled by the evolving wavepacket dynamics.