Impulsive Iterative Inversion.

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Abstract

An inversion procedure which can obtain molecular potentials from impulsive experiments is presented. It is based on the time reversal symmetry of the mechanical equations of motion which allow propagation backwards to the original state. Because the experimental data does not supply the full picture necessary for backward propagation and is therefore inconclusive, an iterative procedure has been developed which is a combination of a forward and backward propagation. This allows the inclusion of data distributed in time from the beginning to the end of the experiment. The full power of time dependent quantum mechanical propagation methods is employed. The inversion procedure is applied to the coloumb explosion experiment. The collinear coloumb explosion of DHD^+ is used to demonstrate the procedure step by step form the experimental velocity distribution to the molecular potential. A full quantum mechanical inversion procedure for impulsive ultra short laser pulse experiments is developed. A demonstration for the ICN molecule is supplied.

I. Introduction

Inverting experimental data can be looked upon as similar to the task of the historian who views a complex situation and tries to infer its reasons and causes. This process is complicated because usually the current picture is blurred which means that the inference is based only on a partial knowledge of the situation. Moreover the inference is not unique, meaning that it may not be the only explanation. The physical chemist who faces these problems has the advantage he can use time reversal symmetry. If formally the sign of time is reversed in the equations of motion, the current picture should return to its original form. It is this tool of time reversal combined with high quality time dependent quantum propagation techniques, that allow an effective inversion procedure. The present work focusses on inferring the molecular potential from experiments which have an impulsive character i.e. in which large changes happen in very short time.

The general problem of inversion has been addressed by many authors [1-4]. Mathematically the inversion problem is ill posed since more than one solution can exist for a set of experimental data. A typical example is the inversion of spectra by the one dimensional RKR semiclassical method. Already in this example, the inversion is not unique; a transformation of the potential that will preserve the action between two turning points will produce the same spectra. Most successful inversion methods are one dimensional, the reason being the large degree of over-determination in higher dimensional problems. Mathematical approaches based on formal scattering theory have been proposed [1], but it is rare that the experiment can supply the required data. An exception is a multiple dimensional approach based on an iterative self consistent field reduction to coupled one dimensional problems. It has been applied successfully to the inversion of spectral data [2].

In physical chemistry The usual situation of insufficient experimental data has lead to heuristic approach in which the experiment is modeled by first assuming a known potential. The computed results from the model are compared to the experiment. At this point the potential is modified for another try. The lack in this procedure is that there is no guaranty of convergence. Moreover good simulation of multidimensional problems are numerically expensive. The advantage, on the other hand, of the heuristic approach is that there are no restrictions on the quality or completeness of the experimental data.

The development of new experimental tools, in particular, impulsive methods and new theoretical techniques have supplied the motivation for reconsidering the inversion problem. The best known example of an impulsive experiment is the coloumb explosion experiment [5]. A molecule is accelerated and then passed through a very thin film which on a timescale of 10^{-17} seconds is ionized. In this process the nuclei exhibit a sudden change from the bound molecular potential to a repulsive coloumb potential. Experimentally the time of flight of all nuclei is monitored. From this data the asymptotic relative momentum distribution of all participating nuclei is obtained. Another example of an impulsive experiment is photodissociation of a molecule using light pulses in the femtosecond regime. For a very short light pulse the nuclei are moved instantaneously from the ground potential surface to an excited one. Experimental data can be obtained either by time of flight spectra or by monitoring the dynamics using a second short pulse.

Inversion schemes for impulsive experiments exclusively based on classical mechanics have been applied to these problems [6]. A critical evaluation of this procedure becomes concerned with the applicability of classical mechanics to these dynamical molecular processes. Another concern is the validity of the impulsive assumption. At least for existing femtosecond experiments the pulses are not short enough in relation to molecular motion to be considered impulsive.

In this presentation, a full quantum scheme for inversion of incomplete experimental data is presented. The insight for this study has come from the development of laser selective chemistry and in particular the use of optimal control theory [7][8]. Similar conceptual problems arise in trying to infer the optimal light pulse which induces a particular chemical outcome. The rest of this paper is devoted to illustrate these ideas.

II. Coloumb explosion inversion

The coloumb explosion technique serves as an ideal example for an impulsive experiment [5]. The process can be described by the following steps: First, the molecule is prepared in a well defined initial state. This is usually done by a jet cooled source and a lazer preparation method. For the analysis it is assumed that the molecule is either in the ground state or in a well defined eigenstate. The second step is to accelerate the molecule. It is assumed during this step that the state of the molecule does not change. The third step is the stripping stage where the molecule is passed through a thin foil in which the field is strong enough to ionize the molecule in a very short time so that the nuclei do not have time to change their positions. Once the molecule is ionized, it moves under the influence of a repulsive coloumb potential. The final stage is a time of flight measurement of all nuclei constituting the molecule. The experiment is then repeated many times to obtain a velocity distribution. The relative momentum distribution of the nuclei can be constructed by subtracting the center of mass velocity. Two points should be emphasized: 1) the impulsive nature of the change from the unknown potential to the known coloumb potential. 2) The complete momentum distribution measurement of all participating particles.

The main purpose of the experiment is to invert the experimental data and obtain the molecular potential. The inversion proceeds as follows: First, from the asymptotic momentum distribution the initial wavefunction $\psi(R,t=0)$ is inferred. Once the initial wavefunction is known, the molecular potential can be obtained. Examining the first stage with the aid of microscopic reversibility, it would be expected that the asymptotic data could be propagated backward, but a typical problem of inversion emerges. The experimental data which is supplied as the asymptotic relative momentum distribution, is insufficient to invert the data. In quantum mechanics the momentum observable is equivalent to the absolute value squared of the asymptotic wavefunction in momentum space at $t = \infty$: $P(k) = |\psi(k,t=\infty)|^2$. The crucial part that is missing in order to reconstruct the wavefunction is the phase factor $e^{i\phi(k)}$. On the other hand if the wavefunction at $t=0$ is an eigenstate, the initial phase is known to be constant but the absolute value of the wavefunction is not known and is the object of inversion. At this point one is faced with the problem that the known facts about the system are split between the times $t=0$ and $t=\infty$. The iterative inversion procedure is designed to let the ends meet to obtain a wavefunction consistent with all known data.

The inversion procedure is as follows:

A. Construct the best possible guess for the molecular potential. One can use previous potential fits from spectroscopic data or ab-initio potential calculations.
B. Use the relaxation procedure [9] to obtain the ground state wavefunction of the trial potential of step A. This wavefunction is the input for the iterative procedure and therefore becomes $\psi_0(R,t=0)$.
C. Propagate the initial wavefunction of the n th iteration $\psi_n(R,t=0)$ from $t=0$ to $t=\infty$ using the coloumb potential obtaining $\psi_n(R,t=\infty)$.
D. Transfer the wavefunction into momentum space: $\psi_n(k,t=\infty)$.
E. Combine the phase of the wavefunction of D and the amplitude in momentum space obtained from the experimental data, to produce a new final wavefunction:

$$\psi_n^f(K,t=\infty) \; = \; |\psi_E(k)| \frac{\psi_n(k,t=\infty)}{|\psi_n(k,t=\infty)|} \tag{2.1}$$

where: $|\psi_E(k)|$ is the square root of the experimental momentum distribution. Transform the wavefunction back to configuration space: $\psi_n^f(R,t=\infty)$.
F. Propagate backwards from $t=\infty$ to $t=0$, the wavefunction of E, to obtain: $\psi_n^f(R,t=0)$
G. Adjust the phase of the wavefunction of F to be constant $\psi_{n+1}(R,t=0) \; = \; |\psi_n^f(R,t=0)|$. This wavefunction is the input for the $n+1$ iteration.
H. Repeat steps C to G until convergence is obtained.

I. From the iterative final wavefunction $\psi_l^f(R,t{=}0)$ of the l th iteration obtain the potential by rewriting the stationary Schrödinger equation:

$$V(R) = \left[\frac{1}{2m} \nabla^2 \psi_l^f(R,t{=}0) \right] \frac{1}{\psi_l^f(R,t{=}0)} + E \qquad (2.2)$$

Comments: 1) Although the algorithm described is general, there is a computational advantage for using the Fourier method representation [10]. This is because of the ease of transformation from coordinate to momentum space. 2) The final time $t{=}\infty$ can be chosen to be finite, provided the asymptotic momentum distribution has been reached. It can be tested by calculating the residual coloumb potential energy expectation: $<\psi|V_{col}|\psi>$. 3) High quality time propagation methods in which the phase error is minimal, have to be used [11]. In particular the last inversion step (step I) is sensitive to the absolute accuracy of the propagation method. 4) The use of interaction representation [12] can be advantageous because momentum is constantly shifted to higher values.

A two dimensional study of the coloumb explosion of collinear DHD$^+$ will be used to illustrate the procedure. Other one and two dimensional studies have been carried out with the conclusion that the following illustration is typical. Figure 1 displays the final relative momentum distribution function.
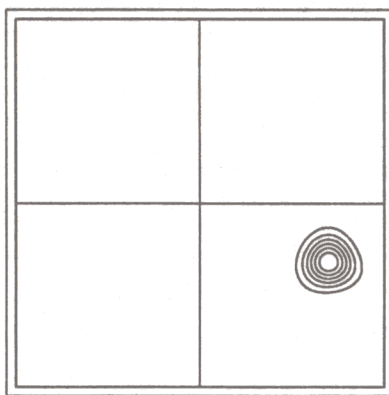

Figure 1 : countour plot of the final momentum distribution, the cross hairs point to the origin (0,0) .

This distribution represents the coloumb explosion experimental data. A grid of 128x128 points was used in coordinate R space or in momentum k space. Jackobi coordinates were used and a Fourier representation scheme. The time propagation was carried out using the Chebychev method [10]. (all units used are atomic units).

The algorithm is now followed step by step.

Step A: To emphasize the fast convergence, a very poor initial guess of the molecular potential was chosen. Figure 2 displays this potential. In comparison to the real molecular potential the potential minimum is shifted by 0.4 a.u. and the vibrational frequencies are only half the value of the original potential.

Step B: The initial wavefunction $\psi_0(R, t=0)$ is produced on the potential of A by the relaxation method. It is shown in figure 2 superimposed on the potential of step A. To further emphasize the convergence the kinetic energy operator in the Hamiltonian was calculated with a 1/3 of the reduced mass. Figure 3 shows the wavefunction superimposed on the true molecular potential. The energy of this wavefunction in comparison to the real ground state, is shifted by 0.15 a.u. (4. ev).
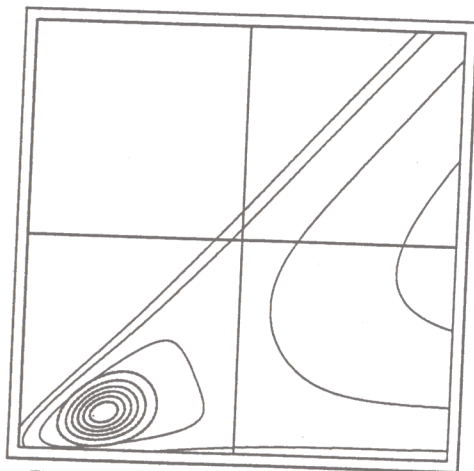

Figure 2: contour plot of trial potential (solid line) and the ground state of this potential (dashed line)
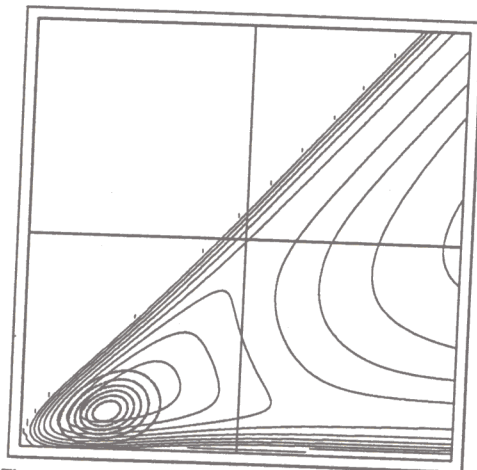
Figure 3: contour plot of the true potential (solid line) and the ground state of trial potential (dashed line)

Step C: The wavefunction is propagated to the final asymptotic time chosen to be 120 a.u. . The wavefunction $\psi_0(R, t=120)$ is displayed in figure 4.
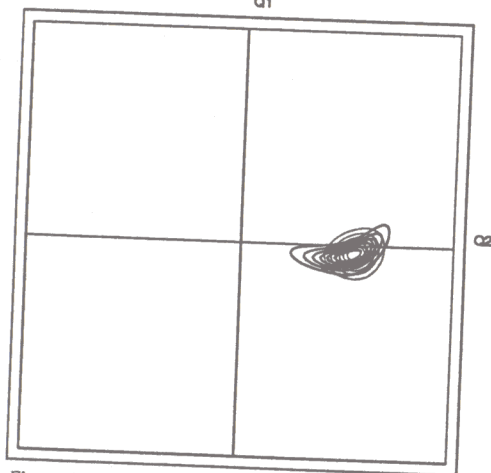

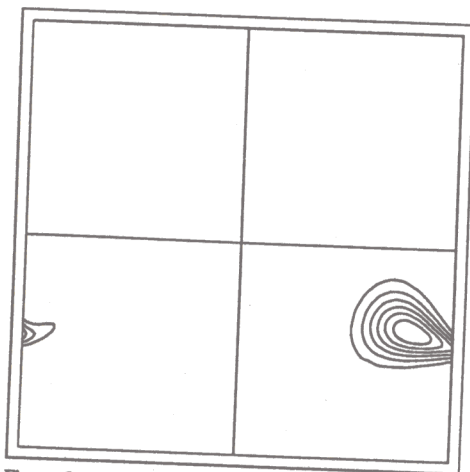Figure 4: asymptotic wavefunction in coordinate space.

Figure 5: asymptotic wavefunction in momentum space.

Step D: Figure 5 shows the wavefunction in momentum space $\psi_0(k, t=120)$. The momentum distribution is clearly broader in comparison to the experimental data of figure 1.

Step E: The combined wavefunction using the phase of D and the amplitude of figure 1 is produced: $\psi_0^f(k, t=120)$. This is the focal point of the inversion in which the forward propagated wavefunction which carries the phase is matched with the asymptotic data which carries the amplitude. This wavefunction in coordinate space is displayed in figure 6.
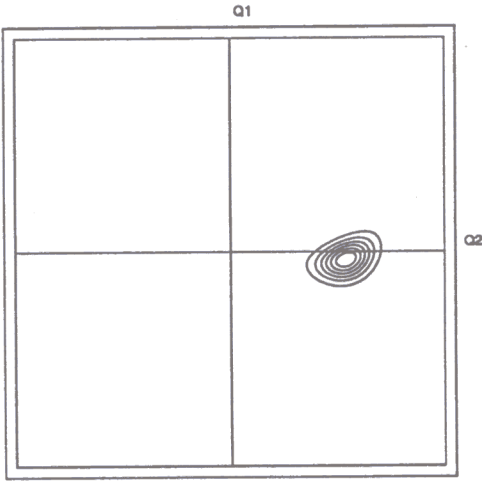
Q1

Q2

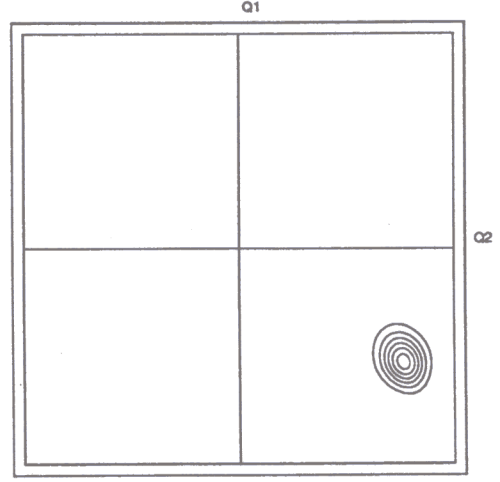Figure 6: initial sate for backward propagation.

Q1

Q2

Figure 7: backward propagated wavefunction first iteration

Step F: Propagation backward in time to obtain $\psi_0^f(R, t=0)$ shown in figure 7.
Step G: Adjustment of phase to obtain the input of the next iteration.
Step H: Figure 8 shows the convergence of $\psi_n(k, t=120)$ while figure 9 shows $\psi_n^f(R, t=0)$.
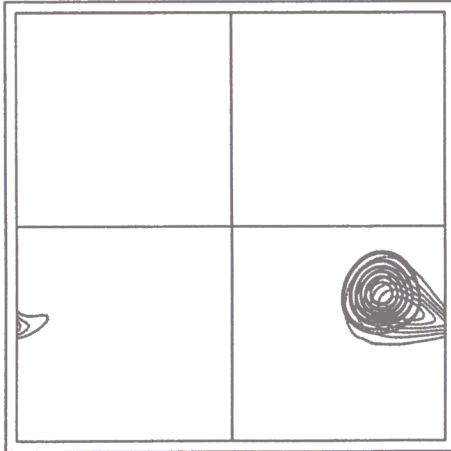

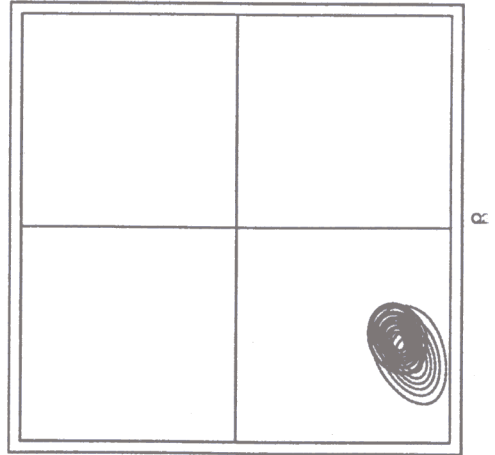Figure 8: iterated wavefunction in momentume space

α

Figure 8: iterated wavefunction in coordinate space

Five iterations were enough to converge the results.

Step I: Figure 10 compares the potential obtained by the inversion to the true potential used to produce the "experimental" data of figure 1.
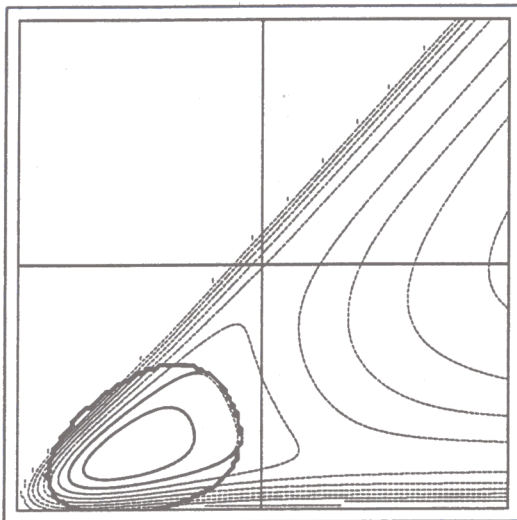

Figure 10: The inverted potential (solid) superimposed on the tru molecular potential (dashed).

The figure displays clearly the window in coordinate space where the wavefunction has significant amplitude in which meaningful results can be obtained. In order to shift this window, an excited initial state should be employed.

On examining the evolution of the wavepacket both in coordinate and momentum space (figures 2-10), it is evident that the wavefunction is compact. This fact makes it possible to use dynamical grid approaches in which the grid follows the wavefunction in coordinate as well as momentum space. This shift can be carried out either at every time step such as in the work of Feldman [12], or continuously by the use of the interaction representation.

The amazing fact about the inversion procedure is its robustness and fast convergence. Four iterations were enough to obtain converged results of the wavefunction and of the potential in regions of space of up to 10% of the maximum wavefunction. After ten iterations, the potential could be obtained in regions which are up to 2% of the maximum wavefunction. The frequent transformations from coordinate to momentum space creates an effective filter able to eliminate experimental noise.

At this point the procedure should be compared to the classical inversion procedure. The main difference is that the classical inversion procedure trajectories are sent backwards one by one. The difficulty is to identify the position in which to stop the integration of each trajectory. In multidimensional systems such a stopping point is not unique. The global quantum iterative procedure avoids the difficulty. Another problem arizes from the omission of the zero point motion in the classical procedure. This in turn leads to wavefunction in coordinate space which is too broad and which manifests itself with a molecule which appears to be floppy. This effect is particularly important in molecules containing hydrogen.

Inversion of short pulse experimental data.

The impulsive experimental process can be carried out by using light as the driving force. Based on the Frank Condon principle, the nuclei do not move during the absorption of light. The introduction of ultra fast pulsed light sources enables the use of light in an impulsive inversion procedure. A classical procedure based on these ideas has been suggested by Bernstien and Zewail [6]. The ICN molecule is used to illustrate the procedure. The experiment starts with the molecule in the ground electronic surface assumed to be known (surface g). Then impulsively, the molecule is transferred to the first excited surface which is repulsive (surface v). The forces on this potential photodissociate the molecule to I + CN. After a preset time delay another impulsive pulse transfers the system to the second excited potential which is assumed to be known (surface u). The reason is that this excited state is associated with the CN chromophore and therefore is almost independent of the I-CN distance. The purpose of the inversion procedure is to obtain the shape of the first excited potential surface using a series of two pulse experiments where the time delay between pulses and central frequency of the second pulse is varied.

At this point, one should summarize the known facts about the experiment. As the ground potential surface is known, the initial wave function of the experiment $\psi_g(t=0)$ can be calculated. The final measurement supplies the final probability on the second excited surface:

$$|<\psi_{u_l}(t=\infty)|\psi_{u_l}(t=\infty)>|^2$$

(3.1)

for each pulse sequence l. The dynamics is governed by the time dependent Schrödinger equation for three surfaces:

$$i\hbar \frac{\partial}{\partial t}\begin{bmatrix}\psi_u \\ \psi_v \\ \psi_g\end{bmatrix} = \begin{bmatrix}\hat{H}_u & \hat{V}_{vu} & \hat{V}_{gu} \\ \hat{V}_{uv} & \hat{H}_v & \hat{V}_{gv} \\ \hat{V}_{ug} & \hat{V}_{vg} & \hat{H}_g\end{bmatrix} \cdot \begin{bmatrix}\psi_u \\ \psi_v \\ \psi_g\end{bmatrix}$$

(3.2)

where $\hat{H}_i = \frac{\hat{P}^2}{2m} + V_i$ is the diagonal part of the Hamiltonian, $V_{ij} = \mu^{ij}\varepsilon(t)$ where μ^{ij} is the dipole moment between surface i and j and $\varepsilon(t)$ represents the amplitude of the electromagnetic field. The pulse envelope is assumed to be Gaussian:

$$\varepsilon(t) = Ae^{-\frac{(t-t_l)^2}{2\sigma}}\cos(\omega_l t)$$

(3.3)

where the maximum amplitude is obtained at $t = t_l$, and the central frequency of the pulse is ω_l. The first excitation pulse has the same form but a constant frequency.

The inversion procedure seeks the potential of $\hat{H}$, ie : $\hat{V}_v$, the first excited state potential. Once again the known facts about the system are distributed through time. At $t = 0$ the system is known to be in the ground state $\psi_g(t=0)$ which can be calculated knowing the ground state potential $\hat{V}_g$ and the relaxation method [9]. At $t=0$ the amplitude of the other states is zero. For each experiment the time and central frequency of the two pulses is known. At the final time $t = \infty$ the probability to be on the second excited state is measured. From this data obtained from a set of L independent experiments, the excited state potential is inferred. Since the amount of experimental data is limited, a potential is sought which has minimum deviation from a known potential form. Mathematically this is equivalent to seeking the minimum of the functional J_1:

$$J_1 = \int_0^\infty \left[\hat{V}_v^o(R) - \hat{V}_v^n(R)\right]^2 dR$$

(3.4)

Where $\hat{V}_{v_n}^o$ is the reference potential which can be obtained from ab-initio calculations or some other method. $\hat{V}_v^n$ is the inferred new potential. Once a potential is set the dynamics can be solved for all sequences of pulses. The results are compared to the experiment. The objective is then to minimize the difference between the experimental and calculated data:

$$J_2 = \sum_{l=1}^{L} \left[<\psi_{u_l} | \psi_{u_l}>_l - A_l \right]^2 \qquad (3.5)$$

where the sum is on all experiments performed and the wavefunction ψ_{u_l} is the result of the calculation of the lth experiment and A_l is the measured data of the l th experiment. The two functionals J_1 and J_2 which are to be minimized are subject to the constraint that the dynamics is governed by the Schrödinger equation. This in turn leads to the minimalization of the functional J_3:

$$J_3 = \alpha J_1 + J_2 + \sum_{l=1}^{L} \int_0^{\infty} \left[<\chi_l | (i\frac{\partial}{\partial t} - \hat{H}) | \psi_l> + c.c \right] dt \qquad (3.6)$$

Where χ_l is the Lagrange multiplier arising because the motion is constrained by the Schrödinger equation. α is a weight which emphasizes the minimization of J_1 or J_2. To minimize equation (3.6) both the wavefunction ψ_l and the potential $\hat{V}_v$ are varied independently. The result which is obtained by integrating by parts and taking the variations $\delta\psi_l$ and $\delta\hat{V}_v$ to zero is a set of Euler Lagrange equations. From the variation of ψ one obtains:

$$i\frac{\partial\psi_l}{\partial t} = \hat{H}_l\psi_l \qquad (3.7)$$

where $\hat{H}_l$ is the hamiltonian of the lth pulse sequence. Equation (3.7) is subject to the initial conditions:

$$\psi_l(0) = \begin{bmatrix} 0 \\ 0 \\ \psi_g(0) \end{bmatrix} \qquad (3.8)$$

and the backward equation of motion for χ:

$$-i\frac{\partial\chi_l}{\partial t} = \hat{H}_l\chi_l \qquad (3.9)$$

subject to the final conditions:

$$\chi_l(t=\infty) = \begin{bmatrix} A_l \dfrac{\psi_{u_l}(t=\infty)}{<\psi_{u_l} | \psi_{u_l}>} \\ 0 \\ 0 \end{bmatrix} \qquad (3.10)$$

From the variation of the potential one obtains:

$$\Delta \hat{V}_\nu(R) = \frac{1}{L} \sum_{l=1}^{L} \int_{t=0}^{\infty} \left[\psi_{\nu_l}(R,t) \chi_{\nu_l}^*(R,t) + c.c. \right] dt \qquad (3.11)$$

where ΔV_ν is the difference between the reference potential and the new potential.

Examining equation (3.11) the final potential difference is obtained by the overlap of the forward moving wavefunction ψ which originated on the ground state and the backward moving wavefunction χ which originated on the second excited state u. The meeting ground is the first excited state potential which is determined by this process. An iterative procedure to solve these equation for the ICN molecule is under way [14].

The inversion procedure just described can be complicated if one adds the lack of knowledge of the dipole functions $\mu^{ij}(R)$. Also the molecule has two more degrees of freedom which have not been considered. Nevertheless this procedure can be the first step in a more elaborate assault on the full complexity of the molecular potentials and dipole functions.

Conclusions

Time reversal symmetry which allows propagation backwards in time has enabled a new inversion procedure. Because the experimental data is inconclusive a full picture which can be used as an initial state for backward propagation cannot be constructed. The problem is overcome by a combination of forward and backward propagation which enables additions to the experimental data from sources of knowledge about the molecule. The two examples presented both rely on the same principle. The coloumb explosion data is more complete than the ICN impulsive pulse experiment. The result is faster convergence and less input from guessed potentials. The illustration shows that multidimensional inversion converges rapidly. The iterative process serves both as a filter for noisy experimental data and as a way to incorporate knowledge distributed through the sequence of events. The extension of these ideas to more degrees of freedom is closely related to the development of multidimensional time dependent propagation technique. A method using bound coordinates for triatomic molecules is under development [12]. Other methods such as the use of hyperspherical coordinates are also under investigation.

The main obstacle in the development of inversion procedures has been the inconclusiveness of experimental data. The mathematical inversion procedures use strong analytic properties to fill in the gap. This in turn leads to very strong demands on the quality of the experimental data. The iterative procedure developed here succeeds because the inversion goal is more modest. Instead of relying completely on the experimental findings the method incorporates intelligent guesses on the potential. Convergence of the iterative procedure, unlike the mathematical inversion, only means that a local minimum has been reached. This weaker result on the other hand has the advantage that the requirements on the experimental data are relaxed guaranteeing that a molecular potential is obtained. A similar approach has been proposed by Shi and Rabitz [15] for inversion of scattering data. The method is based on the stationary solution of the scattering problem and therefore does not utilise directly the time reversal symmetry.

To conclude, the work presented here only begins to reveal the wealth of phenomena which be tackeled. With the appearence of new experimental possibilities and the development of new three-dimensional time dependent propagation methods many molecules can be investigated. These methods will lead eventually to new insight on the structure of many moleculs.

Acknowledgements

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