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$\pi/2$ Pulse Shaping *via* Inverse Scattering of Central Potentials

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It is shown that the inversion of the undamped Bloch equation for an amplitude-modulated broadband $\pi/2$ pulse can be precisely treated as an inverse scattering problem for a Schrödinger equation on the positive semiaxis. The pulse envelope is closely related to the central potential and asymptotically the wave function takes the form of a regular solution of the radial Schrödinger equation for *s*-wave scattering. An integral equation, which allows the calculation of the pulse amplitude (the potential) from the phase shift of the asymptotic solution, is derived. An exact analytical inversion of the integral equation shows that the detuning-independent $\pi/2$ pulse amplitude is given by a delta function. The equation also provides a means to calculate numerically approximate $\pi/2$ pulses for broadband excitation.

Introduction

The transient response of a system of atoms or spins to a coherent pulsed excitation may be predicted by the solution of a Maxwell-Bloch equation. When the sample of such a system is "thin", the reaction of the induced field back upon the exciting field may be ignored, and then it suffices to solve the Bloch equation alone. The equation has been solved for various amplitude and/or phase modulated pulses by direct numerical integration and for certain pulse profiles analytically.[1] In many instances, however, what one is ultimately interested in is not how the system will respond to an excitation field but how to drive the system to respond as one would like with a minimum expenditure of pulse power. The problem posed here is then quite analogous to inverse scattering (IS), a method for determining the shape of the scattering potential (the pulsed field) from the observed scattering data (the excitation profile). A major break through in IS is the discovery of IS transform[2,3] (IST) and a very broad class of evolution equations has been solved analytically by this method.[4] It finds applications in diverse areas of physics,[5] and of particular interest here are the applications to processes during interaction between ultrashort pulses and resonant media in magnetic resonance imaging[6,7] and coherent optics[8,9]. Lamb transformed the Bloch equation into a form resembling a time-independent Schrödinger equation,[8] enabling one to apply the whole arsenal of IS theories to deduce the shape of the exciting field. A family of amplitude modulated $2N\pi$ ($N=1,2,\cdots$) soliton pulses for a two-level system has been found by the IST.[6,7]

On the other hand, there is another important class of IS problems that has been extensively studied—scattering by central potentials. It actually predates IST, yet it appears that little applications of the radial problem have been made to similar problems in field-matter interaction processes. I report in this paper the discovery that $\pi/2$ rotation of a Bloch vector can precisely be treated as a quantum scattering by a central potential. Then from the analogy between a pulse and a central potential scatterer, the shape of the pulse can be determined from the standard IS procedure of constructing potentials from phase shifts of radial functions due to the potentials. Inparticular, the procedure will be applied to obtaining broadband[10] $\pi/2$ pulses, which play an important role incoherent optics and spectroscopy.

In the next section a brief review is given on the previous works of inversion of the Bloch equation by IST. Then in section III a new method for inverting the equation by applying IS for central potentials is developed. The validity of the formulation is demonstrated by showing analytically that it yields a delta-function pulse envelope for the $\pi/2$ pulse, which is identical to the result obtained by applying IST. Section IV concludes with a summary of the main results of this paper along with a discussion on some further points of the results.

Inverse Scattering on the Entire Axis and the Inversion of the Bloch Equation

The interaction of a pulsed electromagnetic field with a two-level system is described by the Bloch equation, which in a rotating frame and without relaxation, is given by

$$\dot{\mathbf{M}}=-\mathbf{\Omega}\times\mathbf{M}, \tag{1}$$

where $\mathbf{M}=(M_x, M_y, M_z)$ with the components satisfying $M_x^2+M_y^2+M_z^2=1$ is a Bloch vector and $\mathbf{\Omega}=(\omega_1(t), 0, \Delta\omega)$ with $\Delta\omega$ and $\omega_1(t)$ being, respectively, the detuning and the amplitude of the driving field. As usual, the overdot denotes differentiation with respect to time.

The Bloch equation can be transformed into a linear differential equation[8]

$$\ddot{\varphi}+\frac{1}{4}(\Delta\omega^2+\omega_1^2+2i\dot{\omega}_1)\varphi=0 \tag{2}$$

by introducing a non-zero differentiable function $\varphi(t)$ defined by

$$\eta+\frac{\omega_1}{\Delta\omega}=\frac{2i\dot{\varphi}}{\Delta\omega\varphi}, \tag{3}$$

where

$$\eta\equiv\frac{M_x+iM_y}{M_z-1} \tag{4}$$

Equation (2) is in a Sturm-Liouville form and with the change of variables $t\leftrightarrow x$ may be recognized immediately as a one-dimensional Schrödinger equation with the potential V and energy E given by

$$V=-\frac{1}{4}(\omega_1^2+2i\dot{\omega}_1), \tag{5}$$

$$E=\frac{1}{4}\Delta\omega^2. \tag{6}$$

The goal of IS is to construct V from the scattering data (the asymptotic behavior of φ as $t\to\infty$). Assume that initially ($t\to-\infty$) the Bloch vector has the equilibrium value, $\mathbf{M}=(0, 0, -1)$. Suppose further that one wishes to bring it back to the equilibrium position after applying the pulse regardless of the magnitude of the detuning, so that $M_z=-1$, or equivalently, $\eta=1$ as $t\to\infty$. This corresponds to seeking an ideal broadband $2N\pi$ pulse. In the quantum scattering language the restoration to the initial equilibrium value of the Bloch vector after the passage of a $2N\pi$ pulse corresponds to the transmission of an incident wave without reflection. And the potentials responsible for this phenomena are well-known reflectionless potentials.[11] As detailed in Refs. 6 and, 7 for *amplitude* modulation one may consider only the real part of V and make the ansatz

$$\omega_1(t)=2\sqrt{-V(t)}. \tag{7}$$

With V reflectionless potentials one gets the amplitude modulated broadband $2N\pi$ pulses given in Refs. 6 and 7 The purely amplitude modulated hyperbolic secant 2π pulse that exhibits self-induced transparency[12] (SIT) is but one of the pulses that may be derived from such a family of reflectionless potentials. Anapplication of IST to SIT is discussed in a paper by Haus.[13]

To apply the method reviewed above to pulse areas other than $2N\pi$ recall that since ω_1 (and hence V) vanishes as $t\to\infty$, $\eta(t)$ must be such that the asymptotic solution $\varphi(t)$ is a linear combination of exp $(\pm i\Delta\omega t/2)$. Difficulties arise, however, for these other pulse areas, since $\eta(t)$ no longer is a constant but in general is a function of $\Delta\omega$ and t. It turns out that for $\pi/2$ pulses the asymptotic solutions do have the right form, and it can be shown by an exact analytic solution of a pertinent Gel'fand-Levitan-Marchenko (GLM) equation that initially the pulse has a δ-function profile.[14] When evolution of the scattering data is considered, one can obtain in principle an infinite number of pulse shapes. A numerical study on this initial value problem is being carried out by the author.

Inverse Scattering Theory for Central Potentials and $\pi/2$ Pulse Shaping

Tranformation of the Bloch equation into a radial problem. Now I attempt a new approach to obtain the shape of the pulses by applying the inverse theories developed for scattering by central potentials. To this end note that it is not illegitimate to set the initial time at $t=0$. Then with the obvious change of variables $T\leftrightarrow r$ nothing prevents one from regarding Eq. (2) as a radial equation for the three-dimensional scattering by a central field:

$$\left[\frac{d^2}{dr^2}+E-V(r)-\frac{l(l+1)}{r^2}\right]y_l=0. \tag{8}$$

The regular solution satisfies the boundary condition $y_l(0)=0$, and the asymptotic form it takes is given by

$$y_l \overset{r\to\infty}{\sim} \sin\left(kr-\frac{1}{2}l\pi+\delta_l\right), \tag{9}$$

where δ_l is a phase shift.

The relation between φ and η may be inverted to give

$$\varphi(t)=\exp\left\{-\frac{i}{2}\int_0^t[\Delta\omega\eta(t')+\omega_1(t')]dt'\right\}. \tag{10}$$

However, it is not an acceptable solution to Eq. (2), now interpreted as a radial equation, because it is not regular at the origin. This problem can be circumvented: since the detuning can be either positive or negative, the wave function may be decomposed as

$$\varphi_\pm(t)=\exp\left\{-\frac{i}{2}\int_0^t[\pm|\Delta\omega|\eta_\pm(t')+\omega_1(t')]dt'\right\}, \tag{11}$$

where $\eta_\pm(t)=\eta(\pm|\Delta\omega|;t)$. Both wave functions satisfy Eq. (2) with the same energy. Then the most general formal solution to Eq. (2) that vanishes at the origin is

$$\varphi(t)=N\left\{\exp\left[i\int_0^t k\eta_+(t')dt'\right]-\exp\left[-i\int_0^t k\eta_-(t')dt'\right]\right\}$$
$$\exp\left[-\frac{i}{2}\int_0^t\omega_1(t')dt'\right], \tag{12}$$

where N is a normalization constant and $k=|\Delta\omega|/2$.

Suppose now we seek a pulse that takes the Bloch vector from $\mathbf{M}=(0, 0, -1)$ to $\mathbf{M}=(1, 0, 0)$ at the end of the pulse $t=t_p$ regardless of $\Delta\omega$, namely a detuning-independent $\pi/2$ pulse. (If the tail of the pulse is not rigorously zero but is negligible at $t>t_p$, the subsequent results hold essentially true.) At a later time $t>t_p$ the magnetization vector will have-precessed due to the detuning to give $M_x=\cos\Delta\omega(t-t_p)$ and $M_y=\sin\Delta\omega(t-t_p)$, and hence

$$\eta(t)=\frac{i\ \sin\Delta\omega(t-t_p)}{\cos\Delta\omega(t-t_p)-1}. \tag{13}$$

With this asymptotic form of $\eta(t)$, both exponential functions in the braces of Eq. (12) give rise to a factor $\sin k(t-t_p)$. The pulse area

$$\int_0^t\omega_1(t')dt'=\frac{\pi}{2},\ t>t_p \tag{14}$$

is just the total flip angle, so the last exponential function may be absorbed in the normalization constant. Consequently, one has asymptotically

$$\varphi(t)\sim\sin\ k(t-t_p), \tag{15}$$

which indeed is the asymptotic form of the regular solution of the radial Schrödinger equation, Eq. (9), and the phase shift is given by

$$\delta_l=-kt_p+\frac{1}{2}l\pi. \tag{16}$$

Another way to get the phas shift is, since Eq. (2) and Eq. (8) are identified, to use the continuity condition of $\varphi(t)$ and the asymptotic solution $\sin(kt-1/2l\pi+\delta_l)$ and their first derivatives at $t=t_p$. Thus, equating the logarithmic derivatives at $t=t_p$, one has

$$\left.\frac{\dot\varphi}{\varphi}\right|_{t=t_p}=ik\eta(t_p)\frac{\exp\left[i\int_0^{t_p}k\eta_+(t')dt'\right]+\exp\left[-i\int_0^{t_p}k\eta_-(t')dt'\right]}{\exp\left[i\int_0^{t_p}k\eta_+(t')dt'\right]-\exp\left[-i\int_0^{t_p}k\eta_-(t')dt'\right]}$$
$$=\frac{k}{\tan(kt_p-\frac{1}{2}l\pi+\delta_l)}, \tag{17}$$

and consequently

$$\delta_l=-kt_p+\frac{1}{2}l\pi+\tan^{-1}A, \tag{18}$$

where

$$A=\frac{-i}{\eta(t_p)}\ \frac{\exp\left[i\int_0^{t_p}k\eta_+(t')dt'\right]-\exp\left[-i\int_0^{t_p}k\eta_-(t')dt'\right]}{\exp\left[i\int_0^{t_p}k\eta_+(t')dt'\right]+\exp\left[-i\int_0^{t_p}k\eta_-(t')dt'\right]}=0. \tag{19}$$

In the last equality $\eta(t_p)=\infty$ is used. The inverse tangent term contributes $n\pi$ to the phase shift, n being the number of bound states. However, there are no poles in the S-matrix element $S(k)=\exp(2i\delta_0)$ on the positive imaginary axis of the complex-k plane. It follows therefore that there are no bound states and the phase shift again reduces to Eq. (16).

Analytical $\pi/2$ pulse shape by exact inversion. Given the scattering data as a phase shift, the potential may be extracted from various inverse methods such as the Gel'fand-Levitan theory and the Born and the semiclassical approximations. Many of the practical inversion methods have been reviewed by Buck.[15] The approach taken here is to use the well-known formula[16]

$$\sin\delta_l=-k\int_0^\infty j_l(kr)V(r)y_{l,k}(r)r\ dr, \tag{20}$$

where $j_l(kr)$ is a spherical Bessel function. Inverse solution to the equation by an analytical method is difficult and the straightforward numerical approach, parametrizing the potential and varying the parameters until a satisfactory fit to the phase shift is obtained, may be adopted. Fortunately, however, the problem can be simplified substantially on the following physical grounds: If in Eq. (2) the potential is zero for all $r\geq 0$, the wave function is given by $\varphi(r)\sim\sin kr$. On the other hand, in the absence of the scattering potential the phase shift must be zero, so the asymptotic form of the regular solution of Eq. (8) becomes $y_l\sim\sin(kr-1/2l\pi)$. To identify Eq. (2) with Eq. (8) it is thus required that $l=0$

(the s-wave scattering). Consequently, for $\pi/2$ pulse shaping the only relevant scattering data is the phase shift $\delta_0 = -kt_p$, and the determination of the potential reduces to solving

$$\sin kt_p = \int_0^\infty \sin kr' V(r')\varphi(r')dr'. \tag{21}$$

Now the inverse problem is amenable to an exact analysis. One can recognize Eq. (21) as a Fourier sine transform and the inverse transform is given by

$$\begin{aligned} V(r)\varphi(r) &= \frac{2}{\pi}\int_0^\infty \sin kr \sin kt_p\, dk \\ &= \frac{1}{2\pi}\int_0^\infty dk[e^{i(r-t_p)k} + e^{-i(r-t_p)k} - e^{i(r+t_p)k} - e^{-i(r+t_p)k}] \\ &= \delta_+(t_p - r) + \delta_+(r - t_p) - \delta_+(-t_p - r) - \delta_+(t_p + r) \\ &= \frac{1}{2\pi i}\left[P\frac{1}{t_p - r} + P\frac{1}{r - t_p} - P\frac{1}{-t_p - r} - P\frac{1}{t_p + r}\right] \\ &+ \frac{1}{2}[\delta(t_p - r) + \delta(r - t_p) - \delta(-t_p - r) - \delta(t_p + r)]. \end{aligned} \tag{22}$$

In the above, the definition

$$\delta_+(\omega) = \frac{1}{2\pi}\lim_{t\to\infty}\int_0^t d\tau e^{-i\omega\tau} = \frac{1}{2\pi i}P\frac{1}{\omega} + \frac{1}{2}\delta(\omega) \tag{23}$$

is used. $P(1/x)$ is the principal part of $1/x$. Eq. (22) is further reduced to

$$V(r)\varphi(r) = \delta(r - t_p) \tag{24}$$

by using the property $\delta(-x) = \delta(x)$ and from the fact that r, $t_p > 0$. Or, one could get Eq. (24) intuitively from the structure of Eq. (21).

Since a physically acceptable wave function is finite everywhere, it is $V(r)$ that has the δ-function characteristic. So we may put the potential in the form

$$V(r) = f(r)\delta(r - t_p) \tag{25}$$

and the wave function within the range of the potential in the form

$$\varphi(r) = \frac{g(r)}{f(r)}, \tag{26}$$

subject to the conditions $\varphi(0) = 0$ and $g(t_p) = 1$. Furthermore, because of the δ-function character of the potential the incident wave virtually cannot penetrate the potential well, a situation of potential scattering.[16] It in turn means that $f(t_p) \to \infty$. In principle, there can be an infinite number of potential-wave function pairs that satisfy these conditions. But, from the relation[17]

$$[\delta(x)]^2 = \lim_{K\to\infty}\left[\frac{1}{2\pi}\int_{-K/2}^{K/2} e^{ikx}dx\right]^2 = \lim_{K\to\infty} K\delta(x) \tag{27}$$

it is reasonable to put

$$V(r) = A[\delta(r - t_p)]^2. \tag{28}$$

The constant A can be determined from Eq. (14) to give $A = -(\pi/4)^2$. Therefore, the desired potential is

$$V(r) = -\left[\frac{\pi}{4}\delta(r - t_p)\right]^2, \tag{29}$$

and consequently the pulse amplitude is

$$\omega_1(t) = \frac{\pi}{2}\delta(t - t_p), \tag{30}$$

in agreement with the earlier result.[14] Note that in arriving at these conclusions it was not required to know the explicit form of the wave function.

The consistency of the results can also be checked by solving the direct scattering problem. Let us consider, as a representation of the δ-function potential given by Eq. (29), an infinitely deep spherical square well potential. For a spherical square well potential of any depth, the Schrödinger equation can be solved exactly and the s-wave phase shift is given by $\delta_0 = -kr_0 + \tan^{-1}$, $(k/\kappa \tan\kappa r_0)$, where r_0 is the width of the potential well and $\kappa = [2m(E + V_0)/\hbar^2]^{1/2}$, V_0 being the depth of the well.[16] In the usual notation of this paper $r_0 = t_p$ and $\kappa = (k^2 + \omega_1^2/4)^{1/2}$. Note that in the limit of a $\pi/2$ "delta" pulse, $\omega_1 \to \infty$, but $\omega_1 t_p = \pi/2$. The phase shift then becomes $\delta_0 = -kt_p$, which is identical to the one obtained above.

Summary and Discussions

Previous works on inverting the Bloch equations were based on the methods of one-dimensional IS on the entire real axis. It is equally legitimate to regard the problem as one on the positive real axis (*i.e.* a radial problem). This paper demonstrates that indeed $\pi/2$ pulse shaping can be precisely connected to the inverse scattering of central potentials. It was possible, by formulating the problem in the latter manner, to immediately take advantage of the extensive information available for the radial problem, culminating in the derivation of Eq. (21). An exact analytical inversion of Eq. (21) shows that the detuning-independent $\pi/2$ pulse profile is given by a delta-function unlike the $2N\pi$ pulses, which take the form of solitons. Previously, the perfectly uniform excitation profile a delta pulse gives could be explained only in linear response theory, where the excitation profile is given by a Fourier transform of the pulse shape (See the discussion in Ref. [1(b)], for example). However, linear response theory holds in the limits of weak applied fields or small flip angles. We have seen that IS offers a rigorous explanation for the nonlinear response of a system to a coherent pulse. Appropriately, the related technique of IST has been termed the nonlinear Fourier transform.[3]

Pulses with the delta-function profile have long been extensively used due to its conceptual simplicity, although technical limitations force one to generate and manipulate them only in an approximate manner. Furthermore, although the analysis in this paper shows that the delta-function profile is the only exact detuning-independent shape for a $\pi/2$ pulse, it is not a broadband pulse because of its (infinitely) large amplitude. One hopes to get over the drawbacks of the delta pulse and its finite-amplitude approximation by pulse shaping. For most practical applications it suffices to find (most likely by means of numerical optimization) pulses that have reasonably slowly varying envelopes and perform well over a reasonably wide range of bandwidth. Eq. (21) can also be used as a definite means for such an investigation. Both GLM equation and Eq. (21) yield an identical δ-function solution, so it seems that these approaches are complementary to each other at least for $\pi/2$ pulse shaping. It would be illuminating to compare the numerical results from these two approaches. Work along this line is under way.

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Theoretical Studies of Surface Diffusion: Multidimensional TST and Effect of Surface Vibrations

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We present a theoretical formulation of diffusion process on solid surface based on multidimensional transition state theory (TST). Surface diffusion of single adatom results from hopping processes on corrugated potential surface and is affected by surface vibrations of surface atoms. The rate of rare events such as hopping between lattice sites can be calculated by transition state theory. In order to include the interactions of the adatom with surface vibrations, it is assumed that the coordinates of adatom are coupled to the bath of harmonic oscillators whose frequencies are those of surface phonon modes. When nearest neighbor surface atoms are considered, we can construct Hamiltonians which contain terms for interactions of adatom with surface vibrations for the well minimum and the saddle point configurations, respectively. The escape rate constants, thus the surface diffusion parameters, are obtained by normal mode analysis of the force constant matrix based on the Hamiltonian. The analysis is applied to the diffusion coefficients of W, Ir, Pt and Ta atoms on the bcc(110) plane of W in the zero-coverage limit. The results of the calculations are encouraging considering the limitations of the model considered in the study.

Introduction

Diffusion of atoms and molecules adsorbed on solid surfaces is an important and interesting phenomena both from a conceptual and a practical points of view.[1,2] It is the primary mechanism of mass transport on solid surfaces. Surface diffusion plays a key role in the growth of thin films, the formation of epitaxial layers, and the catalytic reaction occurring on metal surfaces.

The migration of adsorbed atoms on solid surfaces have been studied extensively both experimentally and theoretically. In recent years, the development of the field ion microscope (FIM) allows one to image the metal substrate surface in atomic resolution.[1,4-6] Several elementary atomic processes on surface have been studied in detail with FIM: surface diffusion of single adatoms and small clusters, adatom-ada-