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Linear theory for optimal control of molecular wave packets

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A linear theory for optimizing optical fields to achieve a molecular configuration at a chosen time is formulated with an emphasis on the symmetric transformation between time domain and space domain representations. Based on two different measures of control, the yield and achievement functions, two parallel but distinct optimization schemes are derived in a unified algebraic format. Connections are then established to a more conventional optimization procedure as well as the optimization procedure for squeezing wave packets used by Averbukh and Shapiro [Phys. Rev. A **47**, 5086 (1993)]. A numerical example of the production of localized wave packets (i.e., squeezed states) demonstrates the effectiveness and feasibility of the proposed scheme. [S1050-2947(97)02506-7]

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I. INTRODUCTION

Numerous proposals for the quantum control of matter have been suggested [1–7], among which optimal control theory has been employed to predict the time-varying light field that best drives the quantum dynamics of a system toward a desired outcome [8–14]. An approach is developed in this paper to unify various optimization procedures for quantum control of wave packets in the linear-response regime. One particularly interesting application of the theory is the prediction of the light field capable of producing spatially squeezed states [15–19].

The paper is organized as follows. In Sec. II A, a symmetric algebraic structure linking the time and coordinate domain representations is explored based on the linear nature of optimal control. In Sec. II B, two different measures of control are compared and examined, which further leads to two parallel versions of optimization. In Sec. II C, the optimization scheme for squeezing wave packets used by Averbukh and Shapiro [19] is reformulated using the simplified notation and unified format developed here. A numerical example is given in Sec. III and a discussion in Sec. IV concludes the paper.

II. THEORY

A. Algebra and notation

We consider a molecular system described by the two-level Hamiltonian

$$H=H_g|g\rangle\langle g|+(H_e+\hbar\omega_{eg})|e\rangle\langle e|, \tag{2.1}$$

where H_e and H_g are the ground- and excited-state Hamiltonians, respectively. The molecule, initially in its ground state $|g\rangle$ at $t=0$, is excited to state $|e\rangle$ at time T by a laser pulse whose electric field is

$$E_0(t)=E(t)e^{-\omega_{eg}t}+E^*(t)e^{i\omega_{eg}t}. \tag{2.2}$$

Under the rotating-wave approximation, the excited-state wave function is given in the linear-response regime by [8,14]

$$\phi_e(T,x)=\int_0^T\frac{i}{\hbar}\langle x|e^{-iH_e(T-t)/\hbar}\mu e^{-iH_gt/\hbar}|g\rangle E(t)dt, \tag{2.3}$$

where μ is the transition dipole moment. Formally, this equation can be cast in a compact expression as

$$\phi(x)=\int_0^T U(x,t)E(t)dt\equiv U(x,t)\cdot E(t), \tag{2.4}$$

where the subscript e and the observation time T in $\phi_e(T,x)$ can be omitted without causing confusion. Here the dot denotes a time integral from 0 to T and $U(x,t)$ is a linear transformation from the laser electric field in the time domain to the excited-state wave function in the coordinate domain, explicitly defined as

$$U(x,t)=\frac{i}{\hbar}\langle x|e^{-iH_e(T-t)/\hbar}\mu e^{-iH_gt/\hbar}|g\rangle. \tag{2.5}$$

Clearly, this transformation establishes a one-to-one correspondence between the excited-state wave function $\phi(x)$ and the applied electric field $E(t)$.

Within this format, the expectation value of an operator $\hat{A}$ evaluated for the excited-state wave function ϕ is written as

$$\overline{A}=\langle\phi|\hat{A}|\phi\rangle=\int\int E^*(t)\langle U(x,t)|\hat{A}(x,x')\times|U(x',t')\rangle E(t')dt\,dt'\equiv E^*\cdot\widetilde{A}\cdot E, \tag{2.6}$$

where $\widetilde{A}$ is the time-domain counterpart of $\hat{A}$, i.e.,

$$\widetilde{A}=\langle U|\hat{A}|U\rangle. \tag{2.7}$$

Here $\widetilde{A}$ denotes the expectation value of an operator that takes the form of $\widetilde{A}$ in the time-domain representation and $\hat{A}$ in the coordinate-domain representation. As an example, when $\hat{A}$ is the identity operator $\hat{I}$ defined on the excited-state manifold, we have

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$$N=\langle\phi|\hat{I}|\phi\rangle=E^*\cdot\langle U|U\rangle\cdot E=E^*\cdot\tilde{N}\cdot E, \tag{2.8}$$

where N denotes the excited-state population and $\tilde{N}$ is its time-domain operator.

Next, the inverse transformation of U is introduced as

$$E(t)=[U(x,t)]^{-1}|\phi(x)\rangle=S(t,x)|\phi(x)\rangle, \tag{2.9}$$

where S satisfies $\int_0^T U(x',t)S(t,x)dt=\delta(x'-x)$. Then, the total incident energy is given by

$$Q=\int_0^T |E|^2 dt=E^*\cdot E=\langle\phi|S^+\cdot S|\phi\rangle=\langle\phi|\hat{Q}|\phi\rangle, \tag{2.10}$$

which defines the spatial operator as

$$\hat{Q}=S^+\cdot S=(U\cdot U^+)^{-1}. \tag{2.11}$$

With the help of S, the reverse transformation of Eq. (2.7) can be established as

$$\hat{A}=S^+\cdot\tilde{A}\cdot S. \tag{2.12}$$

As can be seen from the above relations, a perfect time-coordinate symmetry is preserved and is embodied in the following pairs of functions: $E(t)$ and $\phi(x)$, $S(t,x)$ and $U(x,t)$, and $\tilde{N}(t,t')$ and $\hat{Q}(x,x')$.

Because of the importance of $\hat{Q}$ in our theory, an explicit expression in the Hilbert space of eigenstates is presented here in addition to the formal definition in Eq. (2.11). Assuming that the initial wave function is a ground eigenstate with eigenenergy ϵ_g, the excited wave function is expanded in terms of eigenstates $|n\rangle$ on the excited electronic manifold, giving

$$\phi(x)=\sum_n \langle x|n\rangle\langle n|g\rangle\int_0^T \frac{i}{\hbar}e^{-i\epsilon_n(T-t)/\hbar}\mu e^{-i\epsilon_g t/\hbar}E(t)dt, \tag{2.13}$$

with ϵ_n being the eigenenergy of state $|n\rangle$. Then, the inverse of $\hat{Q}$ becomes

$$\hat{Q}^{-1}=U\cdot U^+=\sum_{n,m}|n\rangle\langle n|g\rangle \times\langle g|m\rangle\langle m|\left\{\frac{i}{\hbar(\epsilon_n-\epsilon_m)}[e^{-i(\epsilon_n-\epsilon_m)T/\hbar}-1]\right\}, \tag{2.14}$$

in which terms with $n=m$ are understood as the limit of $\epsilon_n\to\epsilon_m$.

B. Optimization procedure

To define the objective of control, we choose a target operator $\hat{A}$, which, in principle, can be any desired outcome, such as a wave packet in phase space or a projection operator onto a particular product channel [9,13]. As shown in Eq. (2.6), the corresponding target operator in the time domain is simply $\tilde{A}$, better known as the material response function [13]. To maximize the expectation value of the target operator, we can either increase the overall population on the excited state or improve the efficiency of the excited-state wave function in matching the target. This physical consideration leads us to construct a cost functional [11–13]

$$J(T)=\overline{A}-\eta N-\lambda Q, \tag{2.15}$$

where η and λ represent a weight, or penalty, on the excited-state population and the incident radiation energy, respectively. The variables η and λ can also be treated as Lagrange multipliers, which are adjusted to yield the desired constraints on the excited-state population N or the incident radiation energy Q, respectively. However, as far as the first stage of optimization is concerned, the same results are obtained whether η and λ are treated as weights or as Lagrange multipliers. We therefore will not distinguish between these two viewpoints hereafter unless we specifically so indicate.

Corresponding to the two mechanisms to enhance the control, two different measures of control are introduced: a yield function defined with respect to the incident energy,

$$y=\frac{E^*\cdot\tilde{A}\cdot E}{E^*\cdot E}=\frac{\overline{A}}{Q} \tag{2.16}$$

and an achievement function defined with respect to the excited-state population,

$$a=\frac{\langle\phi|\hat{A}|\phi\rangle}{\langle\phi|\phi\rangle}=\frac{\overline{A}}{N}. \tag{2.17}$$

[We point out here that the achievement used in Ref. [13] is the square root of the one defined by Eq. (2.17).] Consequently, we have the choice of maximizing the yield function or the achievement function. These two equivalent, though different, optimization scenarios are described in the following.

1. First optimization scheme

Given a constraint on or equivalently a weight assigned to the incident radiation energy Q, the achievement function is maximized with respect to the excited-state wave function. To this end, the cost functional is expressed in terms of the wave function, giving

$$J[\phi(t)]=\langle\phi|[\hat{A}-\lambda\hat{Q}-\eta]|\phi\rangle. \tag{2.18}$$

Then, taking the functional derivative $\delta J[\phi(t)]/\delta\phi^*(t)$ leads to an eigenequation

$$(\hat{A}-\lambda\hat{Q})|\phi\rangle=\eta|\phi\rangle. \tag{2.19}$$

Consequently, the maximum eigenvalue η of this equation gives the yield

$$y=\lambda+\frac{\eta}{Q} \tag{2.20}$$

and the achievement

$$a=\eta+\lambda Q, \tag{2.21}$$

where the total radiation energy is $Q=\langle\phi|\hat{Q}|\phi\rangle$ and the excited-state population is normalized as $N=\langle\phi|\phi\rangle=1$.

Also, the corresponding eigenvector is the normalized optimal wave function, which can be converted to the optimal field via the transformation (2.9). As stated earlier, for a constraint on the incident radiation energy Q, the weight λ in Eq. (2.18) can be understood as a Lagrange multiplier that is adjusted to meet the constraint on Q while the achievement is maximized.

2. Second optimization scheme

Given a constraint on or equivalently a weight assigned to the excited-state population N, the yield function is maximized with respect to the electric field. Similarly, the cost functional is expressed in terms of the optical field,

$$J[E(t)]=E^{*}\cdot[\tilde{A}-\lambda-\eta\tilde{N}]\cdot E, \tag{2.22}$$

the extremum of which is given by

$$(\tilde{A}-\eta\tilde{N})\cdot E=\lambda\cdot E. \tag{2.23}$$

Again, the maximum eigenvalue λ of the above eigenequation results in the yield

$$y=\lambda+\eta N \tag{2.24}$$

and the achievement

$$a=\eta+\frac{\lambda}{N}, \tag{2.25}$$

where the excited-state population is $N=E\cdot\tilde{N}\cdot E$ and the incident radiation energy is normalized as $Q=E^{*}\cdot E=1$.

It is clear from the above that there exists an almost exact parallel between the two optimization schemes. In fact, a one-to-one correspondence can be established between the wave-function solution to Eq. (2.19) for a given λ and the electric-field solution to Eq. (2.23) for a corresponding η, or vice versa.

Both schemes of optimization have been proposed in the literature from seemingly different perspectives [20]. If the excited-state population η assumes no weight, i.e., $\eta=0$, the second scheme becomes exactly the weak-field version of the optimization formalism developed earlier [8,13,14] and the eigenequation (2.23) now reduces to

$$\tilde{A}\cdot E=\lambda E, \tag{2.26}$$

which implies that the yield is maximized with respect to the field regardless of the excited-state population. Another relevant earlier procedure will be explained in the next subsection.

C. Optimization procedure by Averbukh and Shapiro

To design laser fields for the generation of spatially squeezed molecular wave packets [15–18], Averbukh and Shapiro [19] put forth a different optimization procedure based on optimal control theory. We will show here that their formulation is essentially the first optimization scheme presented in the preceding subsection. The presentation below follows closely the original derivation in Ref. [19], but with a simpler and more transparent treatment. Such a simplification is made possible because of the compact notation and the optimization concepts developed in the preceding two subsections.

The object of optimal squeezing, as stated in Ref. [19], is to produce as high a localization in coordinate space as possible at the end of the optimization interval T, while limiting the optical pulse bandwidth. Therefore, the objective functional is introduced as

$$J_0(T)=\overline{x^2}-\overline{x}^2+\lambda\int_0^T|E(t)|^2dt, \tag{2.27}$$

which is essentially a generalized form of the cost functional with the spatial spreading of the wave packet as the target operator. Due to the nonlinear term $\overline{x}^2$, we first minimize J_0 with $\overline{x}$ fixed. To this end, a cost functional similar to Eq. (2.18) is constructed as

$$J[\phi(t)]=\overline{x^2}-\eta N-\eta_1\overline{x}+\lambda Q, \tag{2.28}$$

where an additional Lagrange multiplier η_1 is included to lift the constraint on $\overline{x}$. Then, taking a functional derivative results in

$$(\hat{x}^2-\eta_1\hat{x}+\lambda\hat{Q})|\phi\rangle=\eta|\phi\rangle, \tag{2.29}$$

an eigenequation that gives the optimal wave function as the largest eigenvalue solution. As usual, the Lagrange multiplier η_1 is varied to yield the desired center $\overline{x}$ of wave packet. Finally, on substituting the eigensolution Eq. (2.29) back into Eq. (2.26), we immediately obtain

$$J_0(T)=\eta+\eta_1\overline{x}-\overline{x}^2, \tag{2.30}$$

which measures the success in squeezing the molecular wave packet.

III. AN ILLUSTRATIVE EXAMPLE

To illustrate the optimization procedure described in the preceding section, we will study the electronic excitation of a molecular system modeled as a simple displaced harmonic oscillator. More specifically, the ground- and excited-state Hamiltonians defined in the two-level-system Hamiltonian (2.1) are given, respectively, by

$$H_g=\frac{p^2}{2m}+\frac{1}{2}m\omega^2(x+d)^2 \tag{3.1}$$

and

$$H_e=\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2. \tag{3.2}$$

The advantage of using such a simple system is the availability of the quantum propagator expressed in the closed form

$$\langle x|e^{-iH_et}|\phi_g\rangle=\exp\left\{ip(t)[x-x(t)]-\frac{[x-x(t)]^2}{2\alpha_0^2}-i\theta(t)/\hbar\right\}, \tag{3.3}$$

where $p(t)=m\omega d\sin(\omega t)$, $x(t)=-d\cos(\omega t)$, $\alpha(t)=(m\omega^2 d^2/4)\sin(2\omega t)+(\epsilon+\omega\hbar/2)t$, and $\alpha_0^2=\hbar/m\omega$. Here ϕ_g is the ground-state wave function given as $\phi_g=\exp[-(x+d)^2/2\alpha_0^2]$, with $d=5\alpha_0$. For the sake of simplicity, unit values are assumed for mass, frequency, and the Planck constant $\hbar$ in the calculation.

For a realistic system, it is unlikely that an analytical expression for the quantum propagator can be found as is found for the case of the simple harmonic oscillator. Then quantum-dynamics methods must be employed to propagate the system numerically in order to calculate the transformation matrix $U(x,t)$. Alternatively, one can solve for the eigenstates of the system and make use of the relation (2.13) to obtain the information. In fact, for the stability of the inversion in Eq. (2.11), the eigenstate representation (2.14) is preferred.

To demonstrate the ability to predict the light pulse needed to produce a localized state, a spatially localized Gaussian function is chosen as the target wave function,

$$\phi(T)=\frac{1}{\sqrt{2\pi\alpha^2}}\,e^{-(x-x_0)^2/2\alpha^2}, \tag{3.4}$$

where α denotes the width of the wave packet. The momentum distribution is not specified since an extremely localized wave packet in coordinate space will be correlated to a widely spread wave packet in momentum space according to the uncertainty principle. The target time is chosen as $T=5$ and the parameters for the target wave function in Eq. (3.4) are $x_0=5$ and $\alpha^2=0.01$.

As stated in Sec. II C, though the scheme suggested by Averbukh and Shapiro allows for the calculation of electric fields needed for squeezing wave packets, the numerical procedure is complicated due to the nonlinearity in the object targets. Alternatively, with the help of a localized target wave function, the optimization formalism in Sec. II B can effectively achieve the same goal as minimizing the width of wave packet, but with less numerical effort. In addition to squeezed states, various shapes of wave packets can be produced in this fashion, such as a wave packet with two localized peaks, which is useful in demonstrating the so-called Schrödinger cat states [6,21]. Therefore, the first optimization scheme as described by Eqs. (2.17)–(2.21) will be adopted here for the calculation.

To implement the optimization procedure, the relevant functions and operators are discretized in both the time and coordinate domains, resulting in a vector and matrix notation. For example, the transformation $U(x,t)$ is expressed as a matrix and is inverted to obtain S; then $\tilde{N}$ is obtained by matrix multiplication according to Eq. (2.11). To proceed, the matrix equation (2.19) is diagonalized for a given λ, hence the largest eigenvalue η gives the corresponding yield and achievement according to Eqs. (2.20) and (2.21) and the corresponding eigenvector $\phi(t)$ gives the optimal wave function, which in turn is solved for the optimal field from Eq. (2.9).

In Fig. 1, the yield and achievement are plotted as functions of the weight λ. As the weight of the incident radiation energy η increases, the yield y increases accordingly, whereas the achievement a decreases. Notice the linear dependence of the yield on λ at large values of λ, a result of Eq. (2.20) when the first term becomes dominant. This observation indicates that more electric energy is used to excite the ground-state wave function in order to enhance the expectation value of the target without further squeezing the wave packet. On the other extreme, with a small value of λ, a localized wave packet is produced by exciting the ground-state wave function from a non-Franck-Condon region, which is implied by the increase in achievement and the decrease in yield. For a better understanding of wave-packet focusing and rephasing, some relevant discussions have been presented based on semiclassical arguments [14,22] and physical considerations [19,23–25].

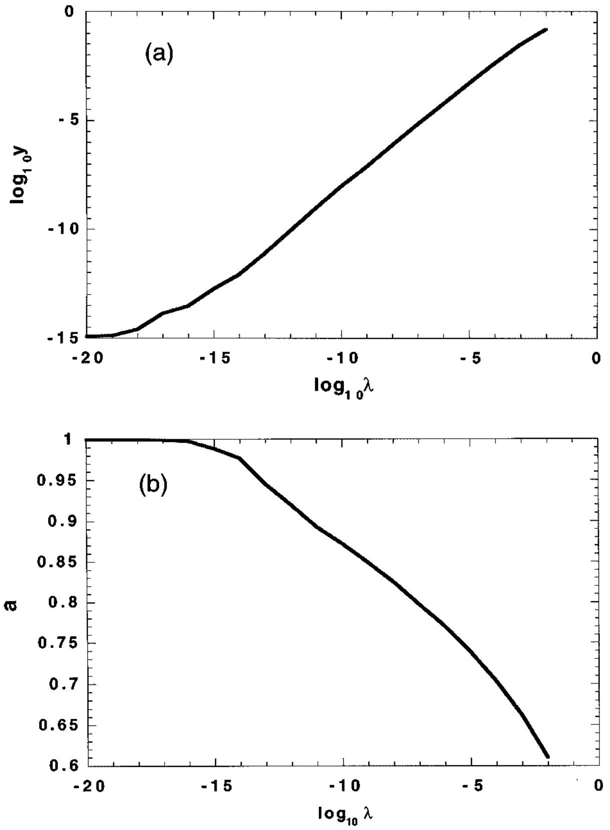

FIG. 1. (a) Yield y and (b) achievement a as functions of the weight λ. The optimization procedure follows the first scheme described in Sec. II B, applied to the displaced harmonic oscillator described in Sec. III [cf. Eqs. (3.1)–(3.4)].

To further understand the mechanism of focusing wave packets, the optimal field and wave function computed for $\lambda=0.001$ are shown in Figs. 2(a) and 2(b), respectively. Such a highly localized state is produced by the interference of two wave packets, one moving inward and the other moving outward, induced by the two distinguishable subpulses shown in Fig. 2(a). It becomes even clearer in Fig. 2(b), where a delocalized wave function is shown as a result of reversing the phase relation between the two optical subpulses. This phenomena is clearly the manifestation of the same physical principle underlying the well-known wave-packet interferometry experiments [26].

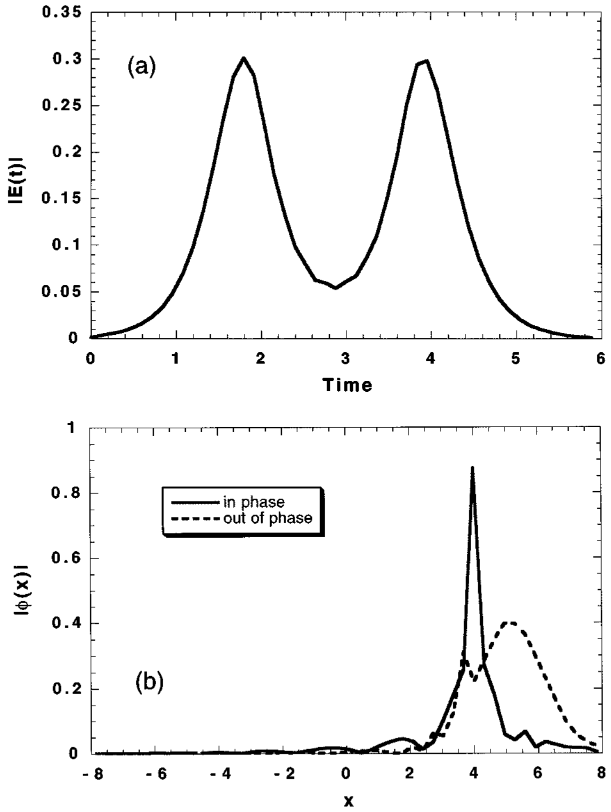

FIG. 2. Amplitude of the (a) optimal field and (b) wave function for $\lambda = 0.001$. The optimization procedure is the same as that described for Fig. 1. In (b) the curve denoted by *in phase* is the result of the optimal field given in (a), whereas the curve denoted by *out of phase* is the result of reversing the phase relation between the two subpulses of the optimal field.

For comparison, the results computed from the more conventional optimization scheme [13,14] described by Eq. (2.26) is shown in Fig. 3, where Fig. 3(a) is the optimal field and Fig. 3(b) is the wave function at the target time. As indicated in Eq. (2.26), there is no adjustable weight as in Eqs. (2.19) and (2.22), so there exists a unique solution to every objective. Also, it is found that the width of the target wave function α no longer makes any difference once $\alpha < 0.1$, hence there is clearly a limit to squeezing the wave packet through this approach. In this case, the most narrow wave packet predicted by Eq. (2.26) is not as narrow as that predicted according to Eq. (2.19).

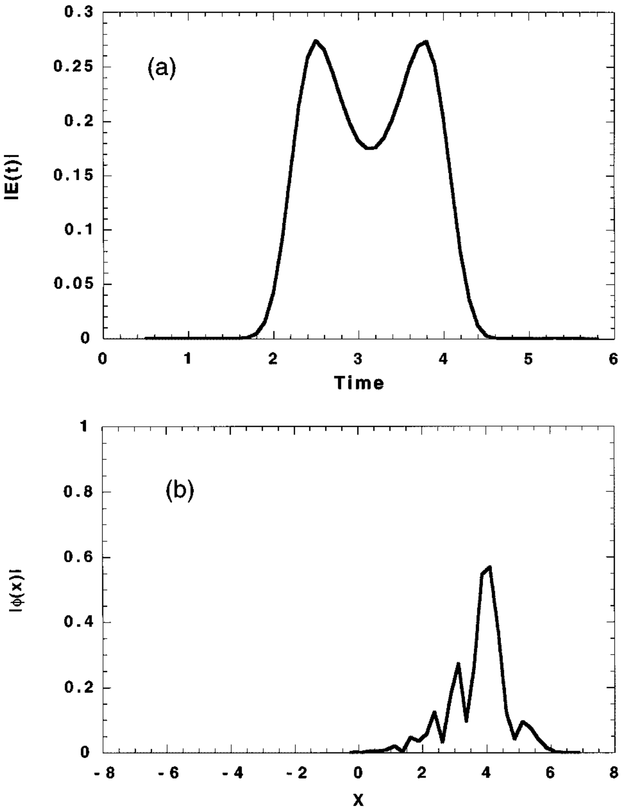

FIG. 3. Amplitude of the (a) optimal field and (b) wave function. The conventional optimization procedure given by Eq. (2.24) is adopted for this calculation. Note that the optimal wave packet is not as narrow as that in Fig. 2.

IV. CONCLUSION

The formalism presented in this paper, by virtue of a compact algebraic format, allows existing theories to be clarified and simplified and adds further insights and additional theories to our understanding of the subject. Equivalent mathematically, the two proposed optimization procedures are both flexible enough to be applied to a large number of problems. It is therefore a matter of desired objective and practical convenience as to which one is preferred. For example, when mixed initial states and dissipation are present [13,27], the second scheme is preferable because the time domain operators $\widetilde{A}$ and $\widetilde{N}$ are easily recast in terms of the density matrix. Such extensions and other more practical applications are left for future studies.

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