Optimally controlled quantum molecular dynamics: A perturbation formulation and the existence of multiple solutions

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(Received 22 April 1992)

This work considers optimal control of quantum-mechanical systems within the framework of perturbation theory with respect to the controlling optical electric field. The control problem is expressed in terms of a cost functional including the physical objective, the penalties, and constraints. The resultant nonlinear variational equations are linearized by considering the lowest-order term in an expansion in powers of the optical-field strength. The optical field is found to satisfy a linear integral equation, and the solution may be expressed in terms of a generalized eigenvalue problem associated with the corresponding kernel. A full determination of the field is specified through the solution to the integral equation and the roots of an accompanying linearized spectral equation for a characteristic multiplier parameter. Each discrete value of the latter parameter corresponds to a particular solution to the variational equations. As a result, it is argued that under very general conditions there will be a denumerably infinite number of solutions to well-posed quantum-mechanical optimal-control problems.

PACS number(s): 03.65.−w, 34.30.+h

I. INTRODUCTION

There has been considerable recent interest in exploring the control of quantum-mechanical systems [1–3]. This interest stems from a long-standing desire to actively manipulate dynamical events at the atomic and molecular scale, as well as other applications. In general, control is envisioned to be achieved by the application of a tailored external (optical) field. Given that the phenomena are inherently quantum mechanical, the tailored fields achieve control by delicately manipulating constructive and destructive quantum wave interferences. The principles involved are rooted in the most elementary of quantum phenomena (e.g., the interference pattern generated by a double slit experiment), and experimental verification of these basic principles has been seen [4]. Depending on the complexity of the molecular control objective, the tailored fields may range from simple cw sources to complex coherent pulse shapes. Current theoretical work has made an initial exploration of a variety of control objectives involving rotational, vibrational, and electronic degrees of freedom [5–24].

The design calculations referred to above have generally been cast into an optimal control framework [25–28] that allows for the flexible introduction of control objectives and competing penalties (e.g., excessive optical-field fluence, access to undesirable molecular states, etc.) while satisfying Schrödinger's equation. The optimization then consists of minimizing a positive-semidefinite cost functional with respect to the sought-after unknown optical field. An important point in this process concerns the nonlinear nature of the resultant control problem. Although Schrödinger's equation is linear with respect to the wave function, as a control problem it is nonlinear since the unknown controlling field and the wave function enter quadratically. Furthermore, using a traditional quadratic cost functional, the variational optimizing equations lead to the Schrödinger equation and its coupled adjoint form, both containing a cubic nonlinearity reminiscent of the nonlinear Schrödinger equation [29]. It is curious that the latter equations are known to support solitonic and other types of unusual wave behavior in related areas of physics, although the full significance of this matter in the quantum control domain has not been explored. However, the rendering of the quantum control problem into an inherent nonlinear framework opens up the possibility of there being multiple optimal design solutions for the optical fields. This prospect has been verified empirically in actual numerical calculations, but until now, to the authors' knowledge, not carefully explored. The present paper and its planned companion [31] develop a perturbation-theory approach in quantum control theory that clearly reveals the nature of there being multiple solutions to quantum optimal-control problems. Although the formulation developed here could be implemented numerically, present interest is directed toward obtaining analytical and conceptual insight into the quantum control process.

Section II of the paper will succinctly summarize the optimal quantum control formulation by defining the cost functional and obtaining the resultant variational equations. Section III will introduce a perturbation expansion for the wave function and its adjoint (i.e., the Lagrange multiplier function entering the optimization process) in terms of an infinite series in the strength of the controlling field. As a result, the optimal-control formulation will be reduced to solving a "field equation" and a "spectral equation." Section IV will deal with the linearized

field equation, and similarly, Sec. V will deal with the linearized spectral equation. General conclusions will be drawn concerning the likelihood of finding multiple solutions to quantum optimal-control problems.

II. DERIVATION OF THE DYNAMICAL EQUATIONS

Consider a molecular system whose free motion is completely described through its time-independent Hamiltonian H_0 and its initial state characterized by the wave function $\tilde{\psi}$. If we apply an electrical field whose amplitude is denoted by $\mathcal{E}(t)$ to this molecule, then its evolution will deviate from its expected free molecular motion. A deviation can be manipulated by changing the field's frequency or temporal structure. In this way, it may be possible to relax or even to break certain bonds in the molecule or otherwise control its dynamical evolution. We can write the Hamiltonian of the molecule in the presence of the field as follows:

$$H=H_0+\mu\mathcal{E}(t) , \tag{2.1}$$

where μ stands for the time-independent dipole function of the molecule under consideration and the field amplitude varies only with time. The vector nature of the field is implicitly understood and $\mathcal{E}(t)$ is the scalar amplitude. We could equivalently use a purely magnetic or electromagnetic field. However, the only change would be in the structure of the field-molecular interaction. The formulation in Eq. (2.1) encompasses electronic, vibrational, or rotational degrees of freedom, and appropriate terms for nonlinear field effects could also be added.

As long as $\mathcal{E}(t)$ is given, there is nothing unusual about the forward dynamics of the system that is described via H and $\tilde{\psi}$. Standard methods of quantum dynamics would, in principle, solve the problem. However, the problem takes on a new perspective when we want to *design* a field such that the motion of the molecules follows a new route that is as close as possible to one we desire. The criteria for choosing an appropriate field poses an inverse problem formulated through optimal-control theory [25–28]. Optimal-control theory is implemented by the selection of an appropriate cost functional and the derivation of the corresponding Euler equations.

We now assume that the field-molecule interaction exists over the time interval $0<t\leq T$, and consider an observable that is characterized by a Hermitian operator $\hat{O}$. If we desire that the expectation value of $\hat{O}$ become as close as possible to a given target value represented by $\tilde{O}$, then the following objective term can be chosen as a part of the cost functional

$$\mathcal{J}_0=\tfrac{1}{2}[\langle\psi(T)|\hat{O}|\psi(T)\rangle-\tilde{O}]^2 . \tag{2.2}$$

The next step is the definition of the penalty terms. For this purpose, we consider only two different penalty terms in this work, one of which is aimed at suppressing the expectation value of an undesired observable operator denoted by $\hat{O}'$ during the field-molecule interaction via an appropriately chosen weight function denoted by $W_p(t)$. This can be expressed as

$$\mathcal{J}_p^{(1)}=\tfrac{1}{2}\int_0^T dt\ W_p(t)\langle\psi(t)|\hat{O}'|\psi(t)\rangle^2 ,$$
$$W_p(t)>0 \quad t\in[0,T] . \tag{2.3}$$

The second penalty term allows for the possibility of minimizing the field fluence. This term also includes an appropriate weight function denoted by $W_{\mathcal{E}}(t)$ and is given as follows:

$$\mathcal{J}_p^{(2)}=\tfrac{1}{2}\int_0^T dt\ W_{\mathcal{E}}(t)\mathcal{E}(t)^2, \quad W_{\mathcal{E}}(t)>0,\ t\in[0,T] . \tag{2.4}$$

Until now, the wave function has directly or indirectly entered the cost terms. However, it must satisfy the fundamental equation of quantum mechanics. The Schrödinger equation may be introduced explicitly in the cost functional as a constraint term via a Lagrange multiplier λ, which varies temporally and spatially (assuming a configuration-space representation). Therefore, by considering a real-valued contribution, we can write the following cost term:

$$\mathcal{J}_{c,d}=\int_0^T dt\left\langle\lambda(t)\left|i\hbar\frac{\partial}{\partial t}-H(t)\right|\psi(t)\right\rangle + \int_0^T dt\left\langle\lambda^*(t)\left|-i\hbar\frac{\partial}{\partial t}-H(t)\right|\psi^*(t)\right\rangle . \tag{2.5}$$

Now, we are at a point where the total cost term can be written as a sum of these individual cost terms as follows:

$$\mathcal{J}=\mathcal{J}_0+\mathcal{J}_p^{(1)}+\mathcal{J}_p^{(2)}+\mathcal{J}_{c,d} . \tag{2.6}$$

Although the first three terms were given explicit forms above, in practice there is additional flexibility to build in a variety of other physical cost terms. The dynamical equations of the system, which is optimally controlled through the above cost functional, are obtained by the stationary variational condition of $\mathcal{J}$

$$\delta\mathcal{J}=0 . \tag{2.7}$$

Since $\mathcal{J}$ depends on $\lambda(t)$, $\psi(t)$ in addition to the field amplitude $\mathcal{E}$, the variation of $\mathcal{J}$ can be expressed as a linear combination of the variations of these variables. Therefore, the coefficients of this linear combination must individually vanish. These equations can be reduced to the following form:

$$i\hbar\frac{\partial\psi(t)}{\partial t}=[H_0+\mu\mathcal{E}(t)]\psi(t) , \tag{2.8a}$$

$$\psi(0)=\tilde{\psi} , \tag{2.8b}$$

$$i\hbar\frac{\partial\lambda(t)}{\partial t}=[H_0+\mu\mathcal{E}(t)]\lambda(t) - W_p(t)\langle\psi(t)|\hat{O}'|\psi(t)\rangle\hat{O}'\psi(t) , \tag{2.9a}$$

$$\lambda(T)=\frac{i}{\hbar}\eta\hat{O}\psi(T) , \tag{2.9b}$$

$$\mathcal{E}(t)=\frac{2}{W_{\mathcal{E}}(t)}\mathrm{Re}[\langle\lambda(t)|\mu|\psi(t)\rangle] , \tag{2.10}$$

$$\langle\psi(T)|\hat{O}|\psi(T)\rangle=\tilde{O}+\eta , \tag{2.11}$$

where Re denotes the real part. The intermediate con-

stant variable η is introduced to facilitate the further analysis.

When the control problem is well posed, we could demand the exact achievement of the expectation value of $\hat{O}$ to the given value $\tilde{O}$ when $t=T$. Then, we would replace the objective term given by Eq. (2.2) with the following objective constraint term:

$$\mathcal{J}_{c,o}=\eta[\langle\psi(T)|\hat{O}|\psi(T)\rangle-\tilde{O}] , \tag{2.12}$$

where η is a constant Lagrange multiplier. The above variational formulation follows through for this case also. After similar intermediate steps, exactly the same equations given by the formulas from (2.8a) to (2.10) are obtained. The only difference is the nonexistence of η in the right-hand side of the Eq. (2.11), and thus we replace Eq. (2.11) with the following more general form:

$$\langle\psi(T)|\hat{O}|\psi(T)\rangle=\tilde{O}+\alpha\eta , \tag{2.13}$$

where the new parameter α is defined as

$$\alpha=\begin{cases}1 & \text{if } \mathcal{J}_0 \text{ is used (flexible case)}\\ 0 & \text{if } \mathcal{J}_{c,o} \text{ is used (constrained case)} .\end{cases} \tag{2.14}$$

In the case involving $\mathcal{J}_0$ the coefficient η just measures the deviation of the objective from its target value. In the analysis to follow in Secs. IV and V the coefficient η will play an important role in establishing the existence of multiple solutions to the optimal-control problem. As pointed out above, the cost functional prescribed here is physically reasonable, although other forms could be chosen. The purpose of this paper is to explore the existence of multiple solutions for Eqs. (2.8)–(2.11), and the form of these equations directly depends on the form of $\mathcal{J}$ and also the system Hamiltonian. A notable special case is control of a harmonic-oscillator system within Ehrenfest's theorem using a quadratic cost functional [8,11]. In this case there is a unique solution to the control problem. As shown below, the opposite circumstance arises in the more general case introduced here.

III. PERTURBATIVE REDUCTION OF THE DYNAMICAL EQUATIONS

If we temporarily assume that the field amplitude is known, then the Eqs. (2.8a) and (2.8b) would determine the unknown wave function $\psi(t)$. We now consider the field-molecule interaction contribution in Eq. (2.8a) as a perturbation. By using a dummy ordering parameter ν, which will be taken equal to unity later, we can proceed with

$$i\hbar\frac{\partial\psi(\nu,t)}{\partial t}=[H_0+\nu\mu\mathcal{E}(t)]\psi(\nu,t) , \tag{3.1a}$$

$$\psi(\nu,0)=\tilde{\psi} , \tag{3.1b}$$

$$\psi(\nu,t)=\sum_{j=0}^{\infty}\psi_j(t)\nu^j , \tag{3.2}$$

$$i\hbar\frac{\partial\psi_j(\nu,t)}{\partial t}=H_0\psi_j(t)+\mu\mathcal{E}(t)\psi_{j-1}(t) , \quad j\geq 0,\ \psi_{-1}\equiv 0 , \tag{3.3a}$$

$$\psi_j(0)=\tilde{\psi}\delta_{j0} \quad j\geq 0 . \tag{3.3b}$$

The formal solution of Eqs. (3.3a) and (3.3b) can be cast into the form

$$\psi_j(t)=\frac{(-i)^j}{\hbar^j}e^{-(i/\hbar)tH_0}\mathcal{S}_0^j\tilde{\psi} , \tag{3.4}$$

where $\mathcal{S}_0$ is defined to act on an arbitrary wave function $\hat{\psi}(t)$ without explicitly denoted spatial dependence as follows:

$$\mathcal{S}_0\hat{\psi}(t)=\int_0^t d\tau\,\mathcal{E}(\tau)Q_\mu(\tau)\hat{\psi}(\tau) . \tag{3.5}$$

The kernel of the above integral operator is defined in terms of the free propagator evolved dipole operator

$$Q_\mu(t)=e^{(i/\hbar)tH_0}\mu e^{-(i/\hbar)tH_0} . \tag{3.6}$$

If we now assume the normal case that μ is a bounded function of spatial variables and utilize the unitarity of the free propagator, we can write the following inequalities after some intermediate manipulations:

$$\|\psi_j(t)\|\leq\frac{\|\mu\|^j}{\hbar^j}\frac{\left[\int_0^t d\tau|\mathcal{E}(\tau)|\right]^j}{j!}, \quad j\geq 0 \tag{3.7}$$

$$\|\psi(t)\|\leq\exp\left[\frac{|\nu|\,\|\mu\|}{\hbar}\int_0^t d\tau|\mathcal{E}(\tau)|\right] , \tag{3.8}$$

where $\|\tilde{\psi}\|=1$ was assumed. Therefore, the perturbation expansion converges in every finite domain of the ordering parameter ν and for all values of the spatial variables during the field-molecule interaction time.

The boundedness assumption on μ is not a serious restriction in practical examples, since most molecular systems have bounded dipole functions. However, we may have to use unbounded dipole functions in cases where molecules dissociate as ions. This circumstance will force the perturbation expansion of the wave function in powers of ν to have a finite convergence radius. This means that we cannot guarantee that the point $\nu=1$ is included in the convergence domain. However, the convergence behavior could be enhanced by introducing a *known* reference field $\tilde{\mathcal{E}}$ and considering a new expansion about $[\mathcal{E}-\tilde{\mathcal{E}}]$. More generally, analytic continuation methods could be used to accelerate or make convergent the expansion if it is asymptotic. In practice all calculations are carried out over a finite domain and no true dipole function singularities would arise under these conditions. Finally, in the present paper we shall confine our attention to weak fields where the lowest order of perturbation theory suffices. This matter will not be treated further here, and henceforth we assume that we are only dealing with bounded field-molecule interactions.

Now, by again assuming the field amplitude is known, we can write the following generalized form of Eqs. (2.9a) and (2.9b) via a dummy ordering parameter ν to obtain a

perturbation expansion of the Lagrange multiplier function λ

$$i\hbar\frac{\partial\lambda(\nu,t)}{\partial t}=[H_0+\nu\mu\mathcal{E}(t)]\lambda(\nu,t)+\sum_{j=0}^{\infty}\mathcal{F}_j(t)\nu^j\ , \quad (3.9a)$$

$$\lambda(\nu,T)=\frac{i}{\hbar}\eta\hat{O}\sum_{j=0}^{\infty}\psi_j(T)\nu^j\ , \quad (3.9b)$$

where

$$\mathcal{F}_j=-W_p(t)\sum_{k=0}^{j}\sum_{l=0}^{j-k}\langle\psi_{j-k-l}(t)|\hat{O}|\psi_l(t)\rangle\hat{O}'\psi_k(t)\ , \quad j\geq 0\ . \quad (3.10)$$

The solution of the Eqs. (3.9) can be expressed in a series expansion as

$$\lambda(\nu,t)=\sum_{j=0}^{\infty}\lambda_j(t)\nu^j\ , \quad (3.11)$$

where the coefficients satisfy the following recursive partial differential equations

$$i\hbar\frac{\partial\lambda_j(t)}{\partial t}=H_0\lambda_j(t)+\mu\mathcal{E}(t)\lambda_{j-1}(t)+\mathcal{F}_j(t)\ , \quad (3.12a)$$

$$\lambda_j(T)=\frac{i}{\hbar}\eta\hat{O}\psi_j(T),\quad j\geq 0\ . \quad (3.12b)$$

After some intermediate manipulations we can explicitly write the solution of the last two equations above as follows:

$$\lambda_j(t)=\sum_{k=0}^{j}\left[\frac{i}{\hbar}\right]^{j-k+1}e^{(i/\hbar)(T-t)H_0}\mathcal{S}_T^{j-k}\times\left\{\eta\hat{O}\psi_k(T)+\int_t^T d\tau\, e^{-(i/\hbar)(T-\tau)H_0}\mathcal{F}_k(\tau)\right\}\quad j\geq 0 \quad (3.13)$$

where

$$\mathcal{S}_T\hat{\psi}=\int_t^T d\tau\,\mathcal{E}(\tau)Q_\mu(\tau)\hat{\psi}\ . \quad (3.14)$$

If we assume that both $\hat{O}$ and $\hat{O}'$ are bounded, then a detailed norm analysis similar to the case of the perturbation expansion of the wave function enables us to conclude the following inequality for the Lagrange multiplier function:

$$\|\lambda(t)\|\leq\left[\frac{|\eta|\,\|\hat{O}\|+\|\hat{O}'\|^2\int_0^T d\tau\,W_p(\tau)}{\hbar}\right]\times\exp\left[\frac{4|\nu|\,\|\mu\|}{\hbar}\int_0^T d\tau|\mathcal{E}(\tau)|\right]\ . \quad (3.15)$$

This result means that the perturbation expansion of the Lagrange multiplier function converges for all finite values of ν as long as μ, $\hat{O}$, and $\hat{O}'$ remain bounded.

If one of the operators $\hat{O}$ and $\hat{O}'$ is unbounded, then the convergence radius of the perturbation expansion for $\lambda(\nu,t)$ is reduced to a finite value and we can no longer guarantee that $\nu=1$ is inside the convergence domain even for the bounded dipole function case. To see this point, it is sufficient to investigate the behavior of $\hat{O}\psi$ without getting into a detailed analysis, since the behavior of $\lambda(\nu,t)$ is strongly related to the latter quantity

$$\|\hat{O}\psi(\nu,t)\|<\sum_{j=0}^{\infty}\sigma_j(t)\|\psi_j(t)\|\,|\nu|^j\ , \quad (3.16)$$

where

$$\sigma_j(t)=\frac{\|\hat{O}\psi_j(t)\|}{\|\psi_j(t)\|},\quad j\geq 0\ . \quad (3.17)$$

By using Eq. (3.7) one can replace Eq. (3.16) with the following:

$$\|\hat{O}\psi(\nu,t)\|<\sum_{j=0}^{\infty}\frac{\sigma_j(t)}{j!}\tilde{\nu}^j\ , \quad (3.18)$$

where

$$\tilde{\nu}=\frac{\|\mu\|\,|\nu|\int_0^t d\tau|\mathcal{E}(\tau)|}{\hbar}\ . \quad (3.19)$$

Since the sequence $\{\sigma_j\}_{j=0}^{\infty}$ is unbounded due to the unboundedness of $\hat{O}$, the asymptotic behavior of σ_j when j goes to infinity strongly affects the convergence nature of the expansion in Eq. (3.16). Depending on the asymptotic behavior of σ_j at large values of j, the convergence domain may shrink to being finite or even to the point $\nu=0$. This obviously is an undesired situation and it is necessary to eliminate these cases.

The removal of the unboundedness of the operators can be accomplished through the redefinition of the cost terms $\mathcal{J}_o$ and $\mathcal{J}_p^{(1)}$ as follows:

$$\mathcal{J}_o=\tfrac{1}{2}[\langle\psi(T)|\varphi_1(\hat{O})|\psi(T)\rangle-\varphi_1(\tilde{O})]^2\ , \quad (3.20a)$$

$$\mathcal{J}_p^{(1)}=\tfrac{1}{2}\int_0^T dt\,W_p(t)\langle\psi(t)|\varphi_2(\hat{O}')|\psi(t)\rangle^2,\quad W_p(t)>0 \quad (3.20b)$$

where φ_1 and φ_2 are appropriately chosen monotonic functions and $\varphi_1(x)$ and $\varphi_2(x)$ are bounded when x is real. Many of the comments below Eq. (3.8) about the perturbation series convergence also apply here. Henceforth we shall assume convergence of the expansion for $\lambda(t)$.

We now define the following temporal functions which, at the same time, depend on ν:

$$\Phi(\nu,t)=\frac{2}{W_{\mathcal{E}}}\mathrm{Re}[\langle\lambda(\nu,t)|\mu|\psi(\nu,t)\rangle]\ , \quad (3.21)$$

$$\Omega(\nu,t)=\langle\psi(\nu,t)|\hat{O}|\psi(\nu,t)\rangle\ . \quad (3.22)$$

The function Φ is the sought-after field $\mathcal{E}(t)$ and $\Omega(\nu,t)$ is the desired observable. The series expansions of these functions in powers of ν are

$$\Phi(\nu,t)=\sum_{j=0}^{\infty}\Phi_j(t)\nu^j\ , \quad (3.23)$$

$$\Omega(\nu,t)=\sum_{j=0}^{\infty}\Omega_j(t)\nu^j\ , \quad (3.24)$$

where

$$\Phi_j(t)=\frac{2}{W_{\mathcal{E}}(t)}\sum_{k=0}^{j}\mathrm{Re}[\langle\lambda_k(t)|\mu|\psi_{j-k}(t)\rangle],\quad j\geq 0 \tag{3.25}$$

$$\Omega_j(t)=\sum_{k=0}^{j}\langle\psi_k(t)|\hat{O}|\psi_{j-k}(t)\rangle,\quad j\geq 0\ . \tag{3.26}$$

By using these equations we can rewrite Eqs. (2.10) and (2.13) as follows:

$$\mathcal{E}(t)=\sum_{j=0}^{\infty}\Phi_j(t)\ , \tag{3.27}$$

$$\sum_{j=0}^{\infty}\Omega_j(T)=\tilde{O}+\alpha\eta\ . \tag{3.28}$$

We call these the field equation and spectral equation, respectively, due to reasons that will be made clear in the following sections. Hereafter we evaluate the relevant expressions at $\nu=1$ corresponding to the nominal system.

IV. LINEARIZED FIELD EQUATION

An examination of the structure of the perturbation expansion coefficients of $\psi(\nu,t)$ and $\lambda(\nu,t)$ in Eqs. (3.4) and (3.13), respectively, immediately reveals that $\psi_j(t)$ and $\lambda_j(t)$ are jth-order homogeneous functionals in terms of the field amplitude. This result implies that the function $\Phi_j(t)$ given by Eq. (3.25) is also a jth-order homogeneous functional on $\mathcal{E}(t)$. Hence the right-hand side of Eq. (3.27) is a well-ordered expansion with respect to the field amplitude. This equation determines the necessary field amplitude for optimal control of molecular motion. Therefore it can be denoted as the field equation.

To get a better understanding of the nature of the field equation, it is useful to investigate, at first, its linearized form. If we denote the solution of the linearized field equation by $\mathcal{E}_L$, we can simply derive the following equation from Eq. (3.25):

$$\mathcal{E}_L(t)=\Phi_0(t)+\Phi_1^{(L)}(t)\ , \tag{4.1}$$

where the only field-dependent term is denoted by $\Phi_1^{(L)}(t)$. The superscript (L) implies the substitution $\mathcal{E}_L(t)$ for the field amplitude in $\Phi_1(t)$. We may now identify

$$\Phi_0(t)=\frac{2}{W_{\mathcal{E}}(t)}\mathrm{Re}[\langle\lambda_0(t)|\mu|\psi_0(t)\rangle]\ , \tag{4.2}$$

and use the explicit expressions of $\psi_0(t)$ and $\lambda_0(t)$ given in Sec. III to deduce the following equation:

$$\Phi_0(t)=-\eta u_1(t)\ , \tag{4.3}$$

where

$$u_1(t)=\frac{2}{W_{\mathcal{E}}(t)}\mathrm{Im}\{\langle\tilde{\psi}|Q(T)Q_\mu(t)|\tilde{\psi}\rangle\}\ , \tag{4.4}$$

with Im denoting the imaginary part and

$$Q(t)=e^{(i/\hbar)tH_0}\hat{O}e^{-(i/\hbar)tH_0}\ . \tag{4.5}$$

The derivation of the explicit expression for $\Phi_1^{(L)}(t)$ necessitates long and tedious manipulations with the final result as follows:

$$\begin{aligned}\Phi_1^{(L)}(t)=&\int_0^t d\tau\,u_2(\tau,t)\mathcal{E}_L(\tau)+\int_t^T d\tau\,u_3(\tau,t)\mathcal{E}_L(\tau)\\&-\eta\int_0^t d\tau\,u_4(\tau,t)\mathcal{E}_L(\tau)\\&-\eta\int_t^T d\tau\,u_5(\tau,t)\mathcal{E}_L(\tau)\ ,\end{aligned} \tag{4.6}$$

where

$$u_j(\tau,t)=\frac{2}{W_{\mathcal{E}}(t)}\mathrm{Re}[\bar{u}_j(\tau,t)],\quad j=2,3,4,5 \tag{4.7}$$

and

$$\bar{u}_2(\tau,t)=v_1(\tau,t)+v_3(\tau,t)+v_5(\tau,t)+v_7(\tau,t)\ , \tag{4.8a}$$

$$\bar{u}_3(\tau,t)=v_2(\tau,t)+v_4(\tau,t)+v_6(\tau,t)+v_8(\tau,t)\ , \tag{4.8b}$$

$$\bar{u}_4(\tau,t)=v_9(\tau,t)+v_{11}(\tau,t)\ , \tag{4.8c}$$

$$\bar{u}_5(\tau,t)=v_{10}(\tau,t)+v_{11}(\tau,t)\ , \tag{4.8d}$$

and

$$\begin{aligned}v_1(\tau,t)=&-\frac{1}{\hbar^2}\int_t^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q_\mu(\tau)Q'(\tau_1)\tilde{P}Q'(\tau_1)\\&\times Q_\mu(t)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9a}$$

$$\begin{aligned}v_2(\tau,t)=&-\frac{1}{\hbar^2}\int_\tau^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q_\mu(\tau)Q'(\tau_1)\tilde{P}Q'(\tau_1)\\&\times Q_\mu(t)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9b}$$

$$\begin{aligned}v_3(\tau,t)=&\frac{1}{\hbar^2}\int_t^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)Q_\mu(\tau)\tilde{P}Q'(\tau_1)\\&\times Q_\mu(t)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9c}$$

$$\begin{aligned}v_4(\tau,t)=&\frac{1}{\hbar^2}\int_\tau^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)Q_\mu(\tau)\tilde{P}Q'(\tau_1)\\&\times Q_\mu(\tau)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9d}$$

$$\begin{aligned}v_5(\tau,t)=&\frac{1}{\hbar^2}\int_t^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)\tilde{P}Q_\mu(\tau)Q'(\tau_1)\\&\times Q_\mu(t)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9e}$$

$$\begin{aligned}v_6(\tau,t)=&\frac{1}{\hbar^2}\int_\tau^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)\tilde{P}Q_\mu(\tau)Q'(\tau_1)\\&\times Q_\mu(t)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9f}$$

$$\begin{aligned}v_7(\tau,t)=&\frac{1}{\hbar^2}\int_t^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)\tilde{P}Q'(\tau_1)Q_\mu(t)\\&\times Q_\mu(\tau)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9g}$$

$$\begin{aligned}v_8(\tau,t)=&\frac{1}{\hbar^2}\int_\tau^T d\tau_1 W_p(\tau_1)\langle\tilde{\psi}|Q'(\tau_1)\tilde{P}Q'(\tau_1)Q_\mu(t)\\&\times Q_\mu(\tau)|\tilde{\psi}\rangle\ ,\end{aligned} \tag{4.9h}$$

$$v_9(\tau,t)=\frac{1}{\hbar^2}\langle\tilde{\psi}|Q(T)Q_\mu(t)Q_\mu(\tau)|\tilde{\psi}\rangle\ , \tag{4.9i}$$

$$v_{10}(\tau,t)=\frac{1}{\hbar^2}\langle\tilde{\psi}|Q(T)Q_\mu(\tau)Q_\mu(t)|\tilde{\psi}\rangle\ , \tag{4.9j}$$

$$v_{11}(\tau,t)=\frac{1}{\hbar^2}\langle\tilde{\psi}|Q_\mu(\tau)Q(T)Q_\mu(t)|\tilde{\psi}\rangle\ , \tag{4.9k}$$

and

$$Q(t)' = e^{(i/\hbar)tH_0}\hat{O}\,' e^{-(i/\hbar)tH_0} , \tag{4.10}$$

$$\tilde{P} = |\tilde{\psi}\rangle\langle\tilde{\psi}| . \tag{4.11}$$

It is clear that the linearized field equation for $\mathcal{E}_L$ is a linear integral equation. To put this equation into a more amenable form, we can use the integral operators defined as

$$\mathcal{M}f(t) \equiv \int_0^t d\tau\, u_2(\tau,t) f(\tau) + \int_t^T d\tau\, u_3(\tau,t) f(\tau) - f(t) , \tag{4.12}$$

$$\mathcal{N}f(t) = \int_0^t d\tau\, u_4(\tau,t) f(\tau) + \int_t^T d\tau\, u_5(\tau,t) f(\tau) , \tag{4.13}$$

where $f(t)$ is a square integrable function over the interval $[0,T]$. By using the triangular identity for two-dimensional integration and integration by parts, and after some intermediate manipulations, one can show that the kernels of these integral operators are symmetric. In other words,

$$(f(t),\mathcal{M}g(t)) = (\mathcal{M}f(t),g(t)) , \tag{4.14}$$

$$(f(t),\mathcal{N}g(t)) = (\mathcal{N}f(t),g(t)) , \tag{4.15}$$

where $f(t)$ and $g(t)$ are square integrable under the weight function $W_{\mathcal{E}}(t)$ over the time interval $[0,T]$ and the new scalar product is defined as

$$(f(t),g(t)) \equiv \int_0^T dt\; W_{\mathcal{E}}(t) f(t) g(t) . \tag{4.16}$$

Therefore, we can rewrite the linearized field equation in terms of these Hermitian operators as follows:

$$\mathcal{M}\mathcal{E}_L(t) - \eta\mathcal{N}\mathcal{E}_L(t) = \eta u_1(t) . \tag{4.17}$$

We now investigate the definiteness of $\mathcal{N}$. We can proceed for this purpose by evaluating its diagonal matrix elements

$$\begin{aligned}(f(t),\mathcal{N}f(t)) = {} & \frac{2}{\hbar^2}\{f(t)\tilde{\psi}, Q(T)Q_1(t)f(t)\tilde{\psi}\} \\ & + \frac{2}{\hbar^2}\{f(t)\tilde{\psi}, Q(T)Q_2(t)f(t)\tilde{\psi}\} \\ & + \frac{2}{\hbar^2}\mathrm{Re}[\langle Q_3(T)\tilde{\psi}|Q(T)|Q_3(T)\tilde{\psi}\rangle] ,\end{aligned} \tag{4.18}$$

where

$$Q_1(t)f(t)\bar{\psi} \equiv Q_\mu(t)\int_0^t d\tau\, Q_\mu(\tau) f(\tau)\bar{\psi} , \tag{4.19}$$

$$Q_2(t)f(t)\bar{\psi} \equiv \int_0^t d\tau\, Q_\mu(\tau) Q_\mu(\tau) f(\tau)\bar{\psi} , \tag{4.20}$$

$$Q_3(T) \equiv \int_0^T dt\; Q_\mu(t) . \tag{4.21}$$

Here the new scalar product $\{,\}$ is defined on the Cartesian product of the Hilbert spaces for wave functions and for the weighted [under $W_{\mathcal{E}}(t)$] square-integrable functions of time over the interaction period. Its explicit definition is written

$$\{f(t)\bar{\psi}_1, g(t)\bar{\psi}_2\} \equiv \mathrm{Re}\left[\int_0^T dt\; W_{\mathcal{E}}(t) f(t) g(t) \langle\bar{\psi}_1|\bar{\psi}_2\rangle\right] , \tag{4.22}$$

where $f(t)$, $g(t)$, $\bar{\psi}_1$, and $\bar{\psi}_2$ are arbitrary functions in their corresponding Hilbert spaces. Now, it is quite easily seen that $\mathcal{N}$ is a (positive or negative) definite integral operator when $\hat{O}$ is (positive or negative) definite. Since there is a flexibility in the definition of the objective cost term, the designer of the optimal control problem can always choose a positive-definite $\hat{O}$ operator without much loss of generality or inconvenience. This, however, enables us to deal with a real-valued spectrum for the weighted eigenvalue problem appearing in the linearized field equation. Henceforth, we assume that $\hat{O}$ (therefore $\mathcal{N}$) is positive definite.

To explore the solution to Eq. (4.17), consider the following generalized eigenvalue problem:

$$\mathcal{M}e_k = \eta_k \mathcal{N}e_k , \quad k \geq 1 \tag{4.23}$$

$$(e_j, \mathcal{N}e_k) = \delta_{j,k} , \quad j,k \geq 1 \tag{4.24}$$

with eigenfunctions e_k and eigenvalues η_k. The above eigenfunctions form a complete basis set for functions that are square integrable with respect to $W_{\mathcal{E}}(t)$ over the interval $[0,T]$. [The existence and the discreteness of the relevant spectrum can be shown via the theory of linear integral operators [30]. Usually one considers unit operator weighted eigenvalue problems, and we can transform the eigenvalue problem in Eq. (4.23) to this type through a transformation with $\mathcal{N}^{1/2}$ since $\mathcal{N}$ is positive definite. The existence of a symmetric and nonsingular kernel (i.e., Hilbert-Schmidt kernel) in $\mathcal{M}$ enables us to prove the discreteness of the spectrum given in Eq. (4.23).] Hence any function in this Hilbert space can be uniquely expanded in a linear combination of these functions. This result can be employed to write the solution of the linearized field equation for the case where η_L is outside the above spectrum

$$\mathcal{E}_L(t) = \eta_L \sum_{k=1}^{\infty} \frac{(e_k,u_1)}{\eta_k - \eta_L} e_k(t) . \tag{4.25}$$

As long as $u_1(t)$ does not become orthogonal to any $e_k(t)$ and η_L is outside the above spectrum, $\mathcal{E}_L(t)$ depends on only a single as yet undetermined parameter η_L. However, if the following equation holds,

$$(e_K, u_1) = 0, \quad K = k_1, k_2, \ldots \geq 1 , \tag{4.26}$$

then the associated coefficients of Eq. (4.25) become arbitrary when k is equal to $k_1, k_2, \ldots$, and η_L can be equal to the corresponding eigenvalues. Hence, the solution of the linearized field equation contains additional undetermined arbitrary parameters in this case. This special case and the determination of η_L will be treated in the next section.

V. LINEARIZED SPECTRAL EQUATION

As we have seen in the last section, the solution of the linearized field equation includes one arbitrary parameter

η_L. To remove this arbitrariness we can use the previously defined spectral equation after its linearization.

Let us consider Eq. (3.24) with $\nu=1$. Since one can easily prove that the perturbation expansion coefficients of $\Omega(\nu,t)$ are homogeneous functionals in the field amplitude, the left side of Eq. (3.28) is well ordered with respect to the powers of $\mathcal{E}$. Hence we can easily write the linearized spectral equation as follows:

$$\Omega_0(T)+\Omega_1^{(L)}(T)=\tilde{O}+\alpha\eta_L \ , \tag{5.1}$$

where the superscripts or subscripts imply that the unknowns are to be determined as the solutions of the linearized equations and $\Omega_0(T)$ does not depend on the field amplitude. Now, we can write the following explicit expressions for $\Omega_0(T)$ and $\Omega_1^{(L)}(T)$ after a careful analysis,

$$\Omega_0(T)=\langle\tilde{\psi}|Q(T)|\tilde{\psi}\rangle \ , \tag{5.2a}$$

$$\Omega_1^{(L)}(T)=(u_1(t),\mathcal{E}_L(t)) \ , \tag{5.2b}$$

and Eq. (4.25) makes it possible to finalize the following form for the linearized spectral equation:

$$\rho(\eta_L)=\alpha+\{\tilde{O}-\langle\tilde{\psi}|Q(T)|\tilde{\psi}\rangle\}\frac{1}{\eta_L} \ , \tag{5.3}$$

where

$$\rho(\eta_L)\equiv\sum_{k=0}^{\infty}\frac{(e_k,u_1)^2}{\eta_k-\eta_L} \ , \tag{5.4}$$

and we assumed that none of the coefficients appearing in the eigenfunction expansion of $u_1(t)$ with respect to the set $\{e_k\}_{k=1}^{k=\infty}$ vanish. We see that $\rho(\eta_L)$ is a meromorphic function whose poles are simple and located at the eigenvalues of the integral operator $\mathcal{M}$ under the weight operator $\mathcal{N}$. The function $\rho(\eta_L)$ increases monotonically from $-\infty$ to ∞ between any two consecutive poles as η_L monotonically increases. Since the right side of the linearized spectral equation is a hyperbola with a vertical asymptote located at $\eta_L=0$ and a horizontal one whose ordinate is α, it produces an infinite number of solutions for η_L. Let us denote these values by $\eta_L^{(k)}, k\geq 1$. Then one can establish a one-to-one correspondence between $\eta_L^{(k)}$ and η_k defined in Eq. (4.23). Since every different point in the spectrum $\eta_L^{(k)}$ defines a different field amplitude, there will be an infinite number of optimal functions to be used as the field. These possibilities are given through the following equation:

$$\mathcal{E}_L^{(k)}(t)=\eta_L^{(k)}\sum_{j=1}^{\infty}\frac{(e_j,u_1)}{\eta_j-\eta_L^{(k)}}e_j(t) \ . \tag{5.5}$$

Let us now consider the case where $(e_n,u_1)=0$ but all other coefficients survive (the case of additional vectors e_j orthogonal to u_1 is similar). In this case, $\rho(\eta_L)$ has a missing pole located between η_{n-1} and η_{n+1}. However, otherwise it has the same properties as before. The lack of a vertical asymptote in the structure of $\rho(\eta_L)$ obviously causes a decrease in the number of solutions although they are still infinite. In this case, we can write the solution for the field amplitude as follows:

$$\mathcal{E}_L^{(j)}(t)=Ae_n(t)+\eta_L^{(j)}\sum_{\substack{k=1\\k\neq n}}\frac{(e_k,u_1)}{\eta_k-\eta_L^{(j)}}e_k(t) \ , \tag{5.6}$$

where A is an arbitrary constant at this point. Substitution of Eq. (5.6) into Eq. (5.2b) again leads to the same linearized spectral Eqs. (5.3) and (5.4) and no problem arises for $j\neq n$. In the case $j=n$ there are two possibilities. First, if $A=0$ then we see that Eq. (5.6) will satisfy the field Eq. (4.17) with $\eta_L^{(n)}$ simply being the missing root of Eqs. (5.3) and (5.4). If $A\neq 0$, then substitution of Eq. (5.6) into (4.17) demands that $\eta_L^{(n)}=\eta_n$. However, this requirement in turn leaves Eqs. (5.3) and (5.4) as being only satisfied by the adjustment of $\tilde{O}$, which was already prescribed initially in the control problem. Thus in general we conclude that if $(e_n,u_1)=0$, then $A=0$. Treatment of the missing root could also be affected by redefining H_0 to alter $\{e_k\}$, or possibly going to higher-order perturbation theory.

VI. CONCLUSION

The primary goal of this paper is to establish the existence of multiple solutions to quantum-mechanical optimal-control problems. The analysis of this objective was carried out starting with a rather general optimizing cost functional and proceeding with a perturbation expansion of the resultant Euler equations. The perturbation expansion for the wave function and the corresponding Lagrange multiplier function lead to the field and spectral equations. These equations were then linearized with respect to the field. Under rather mild conditions and assumptions, it was concluded that an infinite number of solutions to the quantum-mechanical optimal-control problem will generally exist. In practice, each of these solutions will have certain levels of merit with regard to the corresponding value of the cost functional. Solutions that do not correspond to the true minimum of the cost functional may nonetheless be quite satisfactory physically. From another perspective, the existence of multiple solutions merely opens up the prospect of introducing additional costs and constraints into the cost functional to ultimately further discriminate among the multiple solutions. Another interesting issue to explore is whether multiple solutions will exist for other less general choices for the cost functional.

Although the identification of multiple solutions to the optimal-control problem is the primary purpose of the present paper, perturbation theory may nonetheless provide a practical means for computationally approaching quantum-control problems. Naturally, the solutions must not violate the perturbation-theory assumptions, and care is needed to satisfy the boundedness criteria introduced for the various operators involved. One attraction of this approach is that the solution for the field in

Eq. (5.5) does not require iteration (except for the constant $\eta_L^{(k)}$), and it remains for further work to establish the computational viability of the perturbation approach. A companion paper is planned to analyze the higher-order perturbation corrections further.

ACKNOWLEDGMENTS

The authors acknowledge support from the Army Research Office, the Air Force Office of Scientific Research, and the Office of Naval Research.

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