Quantum Optimal Control Theory in the Linear Response Formalism

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Quantum optimal control theory (QOCT) aims at finding an external field that drives a quantum system in such a way that optimally achieves some predefined target. In practice this normally means optimizing the value of some observable, so called merit function. In consequence, a key part of the theory is a set of equations, which provides the gradient of the merit function with respect to parameters that control the shape of the driving field. We show that these equations can be straightforwardly derived using the standard linear response theory, only requiring a minor generalization – the unperturbed Hamiltonian is allowed to be time-dependent. As a result, the aforementioned gradients are identified with certain response functions. This identification leads to a natural reformulation of QOCT in term of the Keldysh contour formalism of the quantum many-body theory. In particular, the gradients of the merit function can be calculated using the diagrammatic technique for non-equilibrium Green’s functions, which should be helpful in the application of QOCT to computationally difficult many-electron problems.

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I. INTRODUCTION

Quantum Optimal Control Theory (QOCT) [1, 2] is concerned with finding a time-dependent external field that drives a given quantum system to optimally achieve some predefined target, that depends on the manner in which the system evolves [3]. For example, a target can be the population of some excited state at the final time of the propagation – but many other options are possible. The theory can be regarded as a branch of the classical control theories developed mostly in the fields of mathematics and engineering [4, 5]. The quantum discipline was born in the late 80s [6–8], as the most complete theoretical framework capable of addressing the nascent experimental field of quantum control (or coherent control) [9]. The range of applications of QOCT is growing very fast, thanks to the progress in the ultrafast laser pulse generation and pulse shaping techniques [10], as well as to the development of adaptive feedback control schemes [11, 12]. Typical examples of applications are the control of the population of excited states in molecules [12], optimization of high-harmonic generation [13], optimization of selective photo-dissociation of molecules [14], optimization of multi-photon ionization of atoms [15], enhancement of electron transfer in dye-sensitized solar cells [16], etc.

At the formal level, the central problem of QOCT is to maximize an expectation value of some operator, usually known as a metrit (or target) function, whose input is the external field that needs to be optimally shaped. The field is normally parameterized either by a discrete set of real-valued “control” parameters, or, in a more general setting, by continuous functions of time. In the latter case, one usually speaks of target functionals. In most cases, the optimization algorithm will require both the computation of the merit function and of its gradient with respect to control parameters. Therefore an expression and computational strategy for this gradient constitutes one of the most important parts of QOCT.

The usual derivation of expressions for the gradient of the merit function proceeds via the definition of a Lagrangian functional, and of a “Lagrange multiplier” wave function (see, for example, Refs. [7, 17]). It leads to an expression for the gradient that involves the forward propagation of the system wave function, and the backwards propagation of the new Lagrange multiplier wave function. At this point it is worth noting that the presence of forward and backwards time propagations is a general feature of the quantum kinetic theory which can be conveniently formulated as a propagation along the Keldysh-Schwinger closed-time contour [18, 19]. Therefore it is natural to expect that there is a connection between QOCT and the Keldysh contour formulation of the quantum dynamics. In the present work we make this connection explicit by re-examining the derivation of the expression of the gradient (or functional derivative) of the target functional.

Our main simple observation is that the differentiation of a target observable with respect to a control parameter is identical to computing a change of that observable induced by a corresponding perturbation in the
Hamiltonian. Thus, the problem of calculating the gradient of the merit function reduces to a generalized form of linear response theory (LRT), in which the unperturbed Hamiltonian is no longer static but depends on time. The formalism of LRT can then be directly applied, and we straightforwardly recover the very same expressions that one reaches in the “traditional” way. However, these expressions can then be regarded as response functions represented by certain retarded correlation functions. We emphasize that this re-derivation is not a mere academic exercise, since the new interpretation of the gradient as a response function suggests immediately the use of the known approximations to this object. In particular by relating the retarded response function to a contour-ordered correlation function we can apply well developed methods and approximations of the non-equilibrium many-body perturbation theory to QOCT for many-electron systems [18, 21, 21].

The latter is a specially important aspect, since the computational tractable scheme, in combination with QOCT. It is necessary to have a predictive (ab initio) yet computationally tractable scheme, in combination with QOCT. Here we propose a new possibility, based on non-equilibrium and time-dependent density-functional theory [23]. Here the direct control of electrons is an area of growing interest, due to the advances in laser pulses of strong intensity and ultra-short durations, in the atto-second range – the scale of the electronic movements. In order to theoretically study a direct control of electronic motion, it is necessary to have a predictive (ab initio) yet computational tractable scheme, in combination with QOCT. Some possibilities have been recently put forward, such as (multi-configuration) time-dependent Hartree Fock [22] and time-dependent density-functional theory [23]. Here we propose a new possibility, based on non-equilibrium many-body Green’s functions theory.

The structure of the paper is the following. In Sec. II we derive the gradient QOCT equations in the formalism of LRT. To make this paper self-contained, the slightly generalized basic LRT results needed for this purpose are presented in Appendix A. Sec. III elaborates on the equations derived in Sec. II by proposing a QOCT scheme for many-body systems, based on the Keldysh contour formalism and on standard approximations in non-equilibrium many-body Green’s functions theory.

II. THE BASIC QOCT EQUATIONS IN THE LINEAR RESPONSE THEORY LANGUAGE

Let us consider a quantum system described by its density matrix \( \hat{\rho}(t) \) and governed, in the time interval \([t_0, t_f]\), by a von Neumann equation in the form:

\[
\frac{\partial}{\partial t} \hat{\rho}(t) = -i \left[ \hat{H}[u](t), \hat{\rho}(t) \right], \tag{1}
\]

\[
\hat{\rho}(t_0) = \hat{\rho}_0, \tag{2}
\]

where the Hamiltonian is given by [24]:

\[
\hat{H}[u](t) = \hat{H} + \epsilon[u](t) \hat{V}. \tag{3}
\]

The Hamiltonian piece \( \hat{H} \) is static, and \( \epsilon[u](t) \) is a time-dependent function whose precise form is determined by a set of parameters that we will denote, collectively, \( u \). The operator \( \hat{V} \) represents the coupling of the system with an external field, e.g. if we think of an atom or molecule irradiated by a laser pulse, the dipole operator. Evidently, a particular choice of the control \( u \) leads to a system evolution, \( u \to \hat{\rho}[u](t) \).

We wish to find the values of \( u \) that maximize the value of the expectation value of some observable \( \hat{A} \) at the end of the propagation. In other words, we want to find the maximum of the function:

\[
G[u] = \text{Tr} \{ \hat{\rho}[u](t_f) \hat{A} \}. \tag{4}
\]

In order to find the maximum, the best way is to be able to compute the gradient of \( G \). The problem that we face, therefore, is that of finding a suitable expression for this gradient.

Assuming that there is only one parameter \( u \) (the generalization to more than one is trivial):

\[
\frac{\partial G}{\partial u}[u] = \lim_{\Delta u \to 0} \Delta u^{-1} \left( G[u + \Delta u] - G[u] \right). \tag{5}
\]

Note that \( \dot{\hat{\rho}}[u] \) corresponds to the propagation of the system with the Hamiltonian given in Eq. (8), whereas \( \dot{\hat{\rho}}[u + \Delta u] \) corresponds to the propagation of the system with the Hamiltonian

\[
\hat{H}[u + \Delta u](t) = \hat{H}[u](t) + \Delta u \frac{\partial}{\partial u}[u] \hat{V}, \tag{6}
\]

to first order in \( \Delta u \). Now we can use directly the LRT result introduced in appendix A by making the identifications:

\[
\hat{H}_0(t) = \hat{H}[u](t), \quad f(t) = \Delta u \frac{\partial}{\partial u}[u] \hat{V}, \tag{7}
\]

Therefore, we just need to apply Eqs. (A12) and (A13) to arrive at:

\[
\frac{\partial G}{\partial u}[u] = \int_{t_0}^{t_f} d\tau \frac{\partial \epsilon}{\partial u}[u](\tau) \chi_{\hat{A},\hat{V}}(t_f, \tau), \tag{8}
\]

where

\[
\chi_{\hat{A},\hat{V}}(t_f, \tau) = -i\theta(t_f - \tau) \text{Tr} \{ \dot{\hat{\rho}}(t_0) \left[ \hat{A}_H(t_f), \hat{V}_H(\tau) \right] \} \tag{9}
\]

is the response function for the \( (\hat{A}, \hat{V}) \) operators. Inside the commutator, these operators appear in the Heisenberg representation, defined by:

\[
\hat{O}_H(t) = \hat{U}(t, t_0) \hat{O} \hat{U}^\dagger(t, t_0), \tag{10}
\]

for any observable \( \hat{O} \), and where \( \hat{U}(t, t_0) \) is the propagator corresponding to the \( \hat{H}[u](t) \) Hamiltonian. Eq. (9) clearly manifests how the gradient is nothing else than a response function – albeit a generalized one. It corresponds to the response of a system driven by a time-dependent Hamiltonian, to a modification of this Hamiltonian. It remains now to see how this result is equivalent
to the expressions obtained in a different manner with the usual QOCT technique. For that purpose, we define an operator:

\[ \hat{A}[u](\tau) = \hat{U}(\tau) \hat{A} \hat{U}^{-1}(\tau), \]

where \( \hat{U}(\tau) \) is the unitary propagator. The time evolution of the density matrix takes the form of the QOCT equations naturally follow from our approach. In the next section we will obtain a functional derivative; in fact, this derivative will be that in which it is a function of expectation values of observables. In this case the functional derivative is nothing else than the response function, i.e. Eq. (8) is the definition of a Lagrangian function). Algorithmically, the computation of the gradient is performed with two consecutive propagations, one forwards for the original system equations, and one backwards in order to obtain \( \hat{A}[u](t) \). These propagations provide the necessary ingredients to compute Eq. (15). In the next section we will make a link of these forward and backwards propagations to the formulation of the quantum dynamics via the Keldysh contour formalism.

It is also easy to see that all variations and generalizations of the QOCT equations naturally follow from our linear response approach.

A. Pure states

For the case of a pure state dynamics the density matrix takes the form \( \hat{\rho}[u](t) = |\Psi[u](t)\rangle \langle \Psi[u](t)| \) where the wave function \( |\Psi[u](t)\rangle \) evolves from a given initial state \( |\Psi[u](t_0)\rangle = |\Psi_0\rangle \) according to the Schrödinger equation

\[ \frac{\partial}{\partial t} |\Psi[u](t)\rangle = -i [\hat{H}[u](t), |\Psi[u](t)\rangle]. \]

The gradient of the merit function is given by the general expression in the form:

\[ \frac{\delta G}{\delta \epsilon} = \chi_{\hat{A},\hat{V}}(t_f, t). \]

This can be rewritten, for the pure state case, as:

\[ \frac{\delta G}{\delta \epsilon} = 2i \text{Im} \langle \chi[u](t) | \hat{V} | \Psi[u](t) \rangle, \]

where \( \chi[u](t) \) is the solution to Eqs. (20) and (21).

B. Continuous parameters

The case in which the control function \( \epsilon(t) \) is not parameterized, but one does the search in the whole space of continuous functions, can also be treated essentially in the same manner. In this case, instead of a gradient we will obtain a functional derivative; in fact, this derivative is nothing else than the response function, i.e. Eq. (15) is

\[ \frac{\partial G}{\partial \epsilon} = \chi_{\hat{A},\hat{V}}(t_f, t). \]

where \( |\chi[u](t)\rangle \) is defined by the expression

\[ |\chi[u](t)\rangle = \hat{U}(t,t_f) \hat{A} |\Psi[u](t_f)\rangle. \]
D. Time-dependent targets

A more interesting generalization is that in which the function to optimize depends on the expectation value of the operator at all times during the propagation, and not only at the final time \( t_f \): Once again, this case can also be put in response-function language in a rather straightforward manner. Let us consider for example the pure-state case:

\[
G[u] = \int_{t_0}^{t_f} dt \, g(t) \langle \Psi[u](t)|A|\Psi[u](t) \rangle ,
\]

where \( g(t) \) is some weight function. The application of the LRT equations leads now to:

\[
\frac{\partial G}{\partial u}[u] = \int_{t_0}^{t_f} \int_{t_0}^{\infty} dt \, g(t) \frac{\partial}{\partial u}[u](\tau) \chi_{A,V}(t, \tau) .
\]

Here the response function \( \chi_{A,V}(t, \tau) \) is given by Eq. \( \ref{eq:chi} \). Following the same route as in derivation of Eq. \( \ref{eq:chi} \) in Sec. IIIA we rewrite Eq. \( \ref{eq:chi_deriv} \) as:

\[
\frac{\partial G}{\partial u}[u] = 2i \int_{t_0}^{t_f} d\tau \, \frac{\partial}{\partial u}[u](\tau) \langle \chi[u](\tau)|\hat{V}|\Psi[u](\tau) \rangle ,
\]

where \( \chi[u](\tau) \) is defined by the following integral

\[
|\chi[u](\tau)\rangle = \int_{\tau}^{t_f} dt \, g(t) \hat{U}(t, \tau) \hat{A}|\Psi[u](t)\rangle ,
\]

which can be put in the equivalent differential form:

\[
\frac{\partial}{\partial \tau} |\chi[u](\tau)\rangle = -i \hat{H}[u](\tau)|\chi[u](\tau)\rangle - g(\tau) \hat{A}|\Psi[u](\tau)\rangle .
\]

These are once again the backwards QOCT equations, in the case of “time-dependent targets”.

III. QOCT IN TERMS OF THE KELDYSH CONTOUR FORMALISM

The new point of view on QOCT proposed in the previous section naturally suggests new approximation strategies for control problems in interacting many-electron systems. As we will now show the QOCT equations can be expressed in terms of correlations functions defined on a Keldysh \([\ref{18}] \) closed time contour. This allows for an immediate application of the powerful machinery of non-equilibrium Green’s functions theory to the coherent control problem.

Let us reconsider the key equation for the gradient of the merit function, Eq. \( \ref{eq:merit} \), and write it explicitly as follows:

\[
\frac{\partial G}{\partial u}[u] = -i \int_{t_0}^{t_f} d\tau \, \frac{\partial}{\partial u}[u](\tau) \text{Tr}\{\hat{\rho}(t_0) \hat{A}_H(t_f) \hat{V}_H(\tau)\} \\
- i \int_{t_f}^{t_0} d\tau \frac{\partial}{\partial u}[u](\tau) \text{Tr}\{\hat{\rho}(t_0) \hat{V}_H(\tau) \hat{A}_H(t_f)\} .
\]

The two integrals in this equation can be composed into a single integral over the Keldysh contour \( C \) depicted in Fig. \( \ref{fig:keldysh} \). This contour starts at \( t_0 \), goes forward in time to \( t_f \), and then comes back to the origin. Therefore by using the standard definition of a contour-ordered correlation function

\[
\chi_{A,V}^C(\tau, \tau') = -i \text{Tr}\{\hat{\rho}(t_0) T_C [\hat{A}_H(\tau) \hat{V}_H(\tau')]\}
\]

where \( T_C \) is the chronological ordering operator on the contour \( C \), we can cast Eq. \( \ref{eq:merit} \) into the following compact form

\[
\frac{\partial G}{\partial u}[u] = \int_{C} d\tau \, \frac{\partial}{\partial u}[u](\tau) \chi_{A,V}^C(t_f, \tau) ,
\]

The main advantage of the representation \( \ref{eq:merit_c} \) is that for interacting many-body systems the contour-ordered correlation functions can be calculated using the standard diagrammatic technique for non-equilibrium Keldysh Green’s functions (see, e. g., Refs. \([18, 21, 21, 25–28]\) ). In other words, by employing the well developed machinery/approximations of the non-equilibrium Green’s functions theory (NEGFT) we can express the gradients of the merit function as a functional of the contour ordered one-particle Green’s functions.

To illustrate above statements we consider the simplest case when both the control field \( V \) and the observable of interest \( A \) are represented by one-particle operators. In this case the correlation function \( \chi_{A,V}^C(t_f, \tau) \) entering Eq. \( \ref{eq:merit_c} \) is given by:

\[
\chi_{A,V}^C(t_f, \tau) = \begin{array}{c}
A \\
\begin{array}{c}
K \\
\end{array}
\end{array} \\
\begin{array}{c}
V \\
\begin{array}{c}
\tau \\
\end{array}
\end{array}
\]

where \( K \) is the exact two-particle Green’s function. Now we can take our favorite many-body approximation, such as Hartree-Fock, second-Born, \( T \)-matrix, random phase approximation (RPA), etc., to get an explicit and practically feasible expression. For example, at the RPA/GW level the correlation function reduces to the two following
terms:

$$\chi^C_{A,V}(t_f,\tau) = \begin{array}{c}
\text{A} \\
\text{V}
\end{array} + t_f \begin{array}{c}
\text{W} \\
\text{V}
\end{array} \tau \tau_1 \tau_2$$

(36)

Analytically, this diagram translates to:

$$\chi^C_{A,V}(t_f,\tau) = \text{tr}\{\hat{A}G(t_f,\tau)\tilde{V}G(\tau,t_f)\}$$

$$+ \int d\tau_1 d\tau_2 \int d\tau_1 d\tau_2 \text{tr}\{\hat{A}G(t_f,\tau)\hat{n}(\tau_1)G(\tau,t_f)\}$$

$$\times W(\tau_1,\tau_1;\tau_2,\tau_2)\text{tr}\{\hat{n}(\tau_2)G(\tau_2,\tau)\hat{A}G(\tau,\tau_2)\}$$

(37)

where $G(\tau_1,\tau_2) = G(\tau_1,\tau_1;\tau_2,\tau_2)$ is the one-particle contour Green’s function, $W(\tau_1,\tau_1;\tau_2,\tau_2)$ is a dynamically screened Coulomb interaction, $\hat{n}(\tau)$ is a one-particle density operator, and all traces are taken over a one-particle Hilbert space.

Equation (37) shows that for the practical calculation of the correlation function $\chi^C_{A,V}(t_f,\tau)$, and thus the gradient of Eq. (34) we need the contour ordered Green’s function $G$ and the screened interaction $W$. The latter is given by the RPA integral equation:

$$\begin{array}{c}
\text{A} \\
\text{V}
\end{array} = \begin{array}{c}
\text{V} \\
\text{V}
\end{array} + \begin{array}{c}
\text{V} \\
\text{V}
\end{array} \text{W}_\tau \tau_1 \tau_2$$

(38)

while the former is calculated by propagating the Kadanoff-Baym equation: $\hat{G}_0$,

$$\left(i\frac{\partial}{\partial \tau_1} - \hat{h}(1)\right) G(1,2) = \delta(1,2) + \int d\beta \Sigma(1,3)G(3,2),$$

(39)

and its conjugate on the time contour. In Eq. (39) $\hat{h}(1) = \hat{h}(\tau_1,\tau_1)$ is the one-particle Hamiltonian which also includes the Hartree potential, and the self energy is given by the GW diagram:

$$\Sigma(1,2) = G(1,2)W(2,1)$$

(40)

More technical details can be found, for example, in Ref. [27]. At this point it is worth to comment on one technical issue. Most currently existing implementations of the Kadanoff-Baym equations [24,28] assume that the dynamics starts from the thermal equilibrium state at some temperature $T = 1/\beta$. The equilibrium initial conditions are technically convenient because they can be treated by a slight modification of the Keldysh contour. Namely, one attaches a “vertical track” going from $t_0$ to $t_0 - i\beta$ from the backward branch of the contour, and imposes antiperiodic Martin-Schwinger boundary conditions $G(t_0 - i\beta,\tau) = -G(t_0,\tau)$ on the Green’s function. If this formalism is employed then all time integrations in Eqs. (33) and (39) are along the modified contour including the vertical track. However, this does not influence the calculation of the gradient of Eq. (34) as it requires only the correlation function on the real time, forwards and backwards branches of the contour. We would like to emphasize that the use of equilibrium/ground state initial conditions is not a fundamental restriction of NEGFT. It is also possible to formulate the theory for a general initial state [21,22,24,30] although we are not aware of any practical implementation of this formalism.

We conclude this section by noting the following remarkable fact regarding the Keldysh contour formulation of QOCT for interacting many-body systems. If the quantum dynamics is described within NEGFT the implementation of QOCT does not require solving any additional equation. All ingredients required to calculate the merit function gradients are already known from the solution of the Kadanoff-Baym equations. For example at the RPA/GW level of the theory one only needs to plug the known functions $G$ and $W$ into Eqs. (33) and (31), perform the integrations, and close the optimization loop.

IV. CONCLUSIONS

We have shown how the key equations of QOCT can be easily derived by employing the formalism of linear response theory. These equations provide the gradient of the target functional with respect to the external field which has to be optimally shaped. In the light of the linear response interpretation, the gradient is in fact the response function of the driven system. First of all, this derivation is valuable methodologically as it explains the internal structure of the coherent control theory using one of the most common techniques in theoretical physics, thus making QOCT more clear and accessible to a broad audience. In addition to that our LRT representation immediately suggests a reformulation of QOCT equations in terms of the Keldysh contour-ordered correlation functions. The theory of non-equilibrium Green’s functions (NEGFT) may then be directly applied to derive new approximation strategies for control problem in interacting many-electron systems. We stress out that the implementation of QOCT looks especially simple, if the quantum dynamics is described within NEGFT, as it is frequently done in practice for many-body systems. To calculate the merit function gradients there is no need to solve any additional equation, since all the required quantities are already known from the solution of the Kadanoff-Baym equations. Work along this line is in progress.
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Appendix A: Generalized Kubo formula

Let us consider a system governed by a total Hamiltonian \( \hat{H}(t) \) that is split as:
\[
\hat{H}(t) = \hat{H}_0(t) + f(t)\hat{V},
\]
given some real time-dependent function \( f(t) \) supported in the time interval \([t_0, t_f] \). To formulate a generalized LRT we need to solve the equation of motion for the density matrix \( \hat{\rho}(t) \)
\[
i \frac{\partial}{\partial t} \hat{\rho}(t) = [\hat{H}_0(t), \hat{\rho}(t)] + [f(t)\hat{V}, \hat{\rho}(t)]
\]
for some given initial \( \hat{\rho}(t_0) \), by considering the second term as a “perturbation”, while allowing the first term, \( \hat{H}_0 \), to be time dependent.

We search for a solution in the following form
\[
\hat{\rho}(t) = \hat{\rho}_0(t) + \hat{\rho}_1(t),
\]
where \( \hat{\rho}_0(t) \) solves Eq. (A2) with \( f(t) = 0 \) and the initial condition \( \hat{\rho}_0(t_0) = \hat{\rho}(t_0) \), and \( \hat{\rho}_1(t) \) is a solution to the linearized equation
\[
i \frac{\partial}{\partial t} \hat{\rho}_1(t) = [\hat{H}_0(t), \hat{\rho}_1(t)] + [f(t)\hat{V}, \hat{\rho}_0(t)]
\]
with the initial condition \( \hat{\rho}_1(t_0) = 0 \).

It is convenient to introduce a propagator \( \hat{U}(t, t') \) for the unperturbed evolution
\[
\hat{U}(t, t') = \tilde{T}e^{-i \int_{t'}^{t} dt' \hat{H}_0(t')} ,
\]
where \( \tilde{T} \) is the usual time-ordering operator. Equation (A5) is a formal solution to the equations
\[
i \frac{\partial}{\partial t} \hat{U}(t, t') = \hat{H}_0(t)\hat{U}(t, t'),
\]
\[
i \frac{\partial}{\partial t'} \hat{U}(t, t') = -\hat{U}(t, t')\hat{H}_0(t')
\]
with the boundary condition \( \hat{U}(t, t) = \hat{I} \).

Using Eqs. (A6) we immediately find both the unperturbed density matrix \( \hat{\rho}_0(t) \) and the solution \( \hat{\rho}_1(t) \) of the linearized equation (A4):
\[
\hat{\rho}_0(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}(t_0, t),
\]
\[
\hat{\rho}_1(t) = -i \int_{t_0}^{t} d\tau \hat{U}(\tau, t)[f(\tau)\hat{V}, \hat{\rho}_0(\tau)]\hat{U}(\tau, t).
\]

It is easy to check that \( \hat{\rho}_1(t) \) of Eq. (A8) is the solution to Eq. (A4). Indeed, the differentiation with respect to the upper limit of the \( \tau \)-integral in Eq. (A8) yields the second term in the right hand side in Eq. (A4), while the \( t \)-derivatives of the propagators in Eq. (A8) produce the first term, \( [\hat{H}_0(t), \hat{\rho}_1(t)] \).

Now one can calculate the change \( \delta A(t) \) of the expectation value for any observable \( \hat{A} \), which is induced by the perturbation [the second term in the Hamiltonian \( \hat{A} \)]:
\[
\delta A(t) = \text{Tr} \{ \hat{\rho}_1(t) \hat{A} \}.
\]

Inserting \( \hat{\rho}_1(t) \) of Eq. (A8) into Eq. (A9) and rearranging terms we get the result
\[
\delta A(t) = -i \int_{t_0}^{t} d\tau f(\tau) \text{Tr} \{ \hat{\rho}(t_0) \{ \hat{A} \hat{H}(t), \hat{V}_H(t) \} \},
\]
where operators \( \hat{O} \) in the Heisenberg representation are defined as follows
\[
\hat{O}_H(t) := \hat{U}(t_0, t)\hat{O}\hat{U}(t, t_0) \equiv \hat{U}^\dagger(t, t_0)\hat{O}\hat{U}(t, t_0).
\]

Equation (A10) suggests the definition of the \( \hat{A}, \hat{V} \) response function as:
\[
\chi_{\hat{A}, \hat{V}}(t, t') = -i\partial(t - t')\text{Tr} \{ \hat{\rho}(t_0) \{ \hat{A} \hat{H}(t), \hat{V}_H(t') \} \}
\]
so that:
\[
\delta A(t) = \int_{t_0}^{\infty} d\tau f(\tau)\chi_{\hat{A}, \hat{V}}(t, \tau).
\]

The response function of Eq. (A13) has the standard form of Kubo’s formula [31]. The only minor difference is that for a time-dependent unperturbed Hamiltonian \( \hat{H}_0(t) \) the Heisenberg operators, Eq. (A11), are defined via the time-ordered exponential of Eq. (A5).

Finally, we note that the QOCT equations can also be derived in yet another different but equivalent manner by making use of the following identity for the quantum mechanical propagator associated to a Hamiltonian that depends on a parameter \( \lambda \):
\[
\frac{\partial}{\partial \lambda} \hat{U}_\lambda(t_f, t_0) = -i \int_{t_0}^{t_f} dt' \hat{U}_\lambda(t, t')\frac{\partial}{\partial \lambda} \hat{H}_\lambda(t)\hat{U}_\lambda(t, t_0).
\]

With this identity, it is straightforward to compute the derivative of:
\[
G[u] = \langle \Psi[u](t_f)|\hat{A}|\Psi[u](t_f)\rangle
= \langle \Psi_0|\hat{U}_u(t_f, t_0)|\hat{A}|\hat{U}_u(t_f, t_0)|\Psi_0\rangle,
\]
where \( \hat{U}_u(t_0, t_f) \) is the propagator determined by the Hamiltonian \( \hat{H}[u](t) \).
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