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Semiclassical Path-Integral Approach to Nonlinear Spectroscopy

Vadim Khidekel, Vladimir Chernyak, and Shaul Mukamel
Department of Chemistry, University of Rochester, Rochester, NY 14627

A semiclassical expansion for linear and nonlinear optical response functions is constructed. Quantum corrections to classical response functions are represented in terms of classical response functions of higher orders. The technique allows us to expand the two separate paths required in a quantum mechanical formalism using a single classical reference path.

I. INTRODUCTION

Spectroscopic signals are related to the molecular polarization induced by the external radiation field:

$$P(\mathbf{r},t) = \mathrm{Tr}[V\rho(t)] \equiv \langle\langle V|\rho(t)\rangle\rangle, \tag{1}$$

where $|\rho(t)\rangle\rangle = \sum_{jk}\rho_{ik}(t)|jk\rangle\rangle$ is the density matrix of a molecule driven by the electric field, and the ket $|jk\rangle\rangle$ denotes the Liouville-space operator $|j\rangle\langle k|$ [1].

Expanding $\rho(t)$ in powers of electric field we obtain for the nth order contribution

$$P^{(n)}(\mathbf{r},t) = \int_0^\infty dt_n \int_0^\infty dt_{n-1}\cdots\int_0^\infty dt_1\, R^{(n)}(t,t_n,\ldots,t_1)E(\mathbf{r},t_n)\cdots E(\mathbf{r},t_1).$$

Here $R^{(n)}(t,t_n,\ldots,t_1)$ is the nth order *response function*, given by [2]

$$R^{(n)}(t,t_1,\ldots,t_n) = \left(\frac{i}{\hbar}\right)^n \left\langle \widehat{P}_+(t)\widehat{P}_-(t_1)\cdots\widehat{P}_-(t_n)\right\rangle, \tag{2}$$

where $\widehat{P}_+ = \frac{1}{2}(\widehat{P}_L + \widehat{P}_R)$, $\widehat{P}_- = \widehat{P}_L - \widehat{P}_R$, and $\widehat{P}_L$ and $\widehat{P}_R$ are the polarization operators that act on the ket (left) and bra (right) of the density matrix. The operator $P_+(t)$ corresponds to the observation time, the operators $P_-(t_j)$ represent interactions with the external field at times t_j, and $\langle\cdots\rangle$ denote the averaging with the equilibrium density matrix ρ_0. We assume an arbitrary form of the polarization operator $P = P(q)$, where q denotes all nuclear coordinates. Using a path-integral representation, we have

$$R^{(n)}(t,t_1,\ldots,t_n) = \left(\frac{i}{\hbar}\right)^n \int dq_L(0)dq_R(0)\rho_0(q_L,q_R)\int \mathcal{D}[q_L(\tau)]\mathcal{D}[q_R(\tau)]P_+(q_L,q_R,t)$$
$$\times P_-(q_L,q_R,t_1)\cdots P_-(q_L,q_R,t_n)\exp\left\{\tfrac{i}{\hbar}S[q_L(\tau)] - \tfrac{i}{\hbar}S[q_R(\tau)]\right\}, \tag{3}$$

where the left trajectory $q_L(\tau)$ and the right trajectory $q_R(\tau)$ describe the evolution of the bra and ket of the density matrix $\rho[q_L(t),q_R(t)]$. The integration is taken over all possible trajectories $q_L(\tau)$ and $q_R(\tau)$ and $S[q(\tau)] = \int_0^\tau L(q,\tau')d\tau'$ is the action, L being the Lagrangian.

Response functions can be calculated exactly either by formula (3) or as sums over eigenstates of the system. However, in practice this can be done only for simple quantum systems. We therefore look for some reference models that can be solved either analytically or numerically. The exact solution is then constructed as an expansion in a small parameter.

In this paper we use the classical response function calculated by neglecting all quantum effects as a reference. A host of methods exist for the analysis of the classical response, from direct numerical calculations to derivation of analytical solutions of various models. Quantum effects are then incorporated semiclassically as an expansion in $\hbar$.

The method that we apply has several advantages. In the standard approach, by substituting in Eq. (3) the definitions of the operators P_+ and P_-, we express the response function as a sum of 2^n terms, each corresponding to a distinct Liouville-space path [1]. This often results in a problem of large cancelations among different paths, which may become a serious obstacle for numerical calculations. On the contrary, keeping the operators P_+ and P_- and preserving the response function as a single term, we avoid this difficulty.

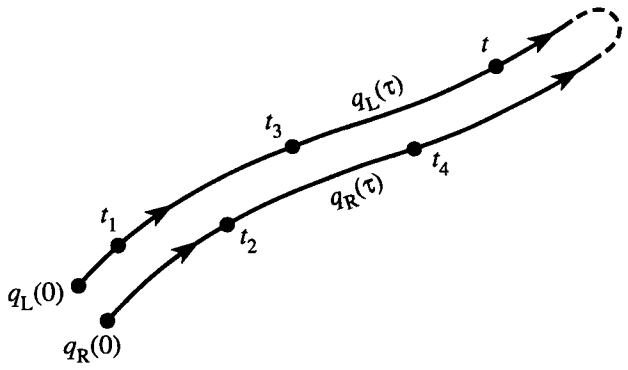

Fig. 1. The Keldysh time loop. Going along the loop, we can arrange all the operators in the proper order.

The second new feature of our method is that we do not consider the left and the right trajectories $q_L(\tau)$ and $q_R(\tau)$ separately (see Fig. 1) but change the variables to their half-sum $q = \frac{1}{2}(q_L + q_R)$ and the difference $q_- = q_L - q_R$. The integral with respect to $q_L(\tau), q_R(\tau)$ is then replaced by the integral with respect to $q(\tau), q_-(\tau)$ and we can expand all the expressions in powers of q_-. The leading term of this expansion gives the classical response function, and the following terms provide quantum corrections proportional to powers of $\hbar$. We therefore need to calculate only one classical trajectory of the system, which is given by $q(\tau)$. The main result of the article is that these quantum corrections can be expressed in terms of higher-order classical response functions calculated along this average trajectory $q(\tau)$. Our derivation of the semiclassical approximation is advantageous over the stationary-phase method, often used for that purpose. The stationary-phase method applies when the left and the right trajectories are far apart but fails when they are close, where the Keldysh action, $S^{(K)} \equiv S[q_L(\tau)] - S[q_R(\tau)]$, which figures in (3), becomes small.

II. THE CLASSICAL RESPONSE FUNCTION

Changing the variables $q_L(\tau)$ and $q_R(\tau)$ in (3) to $q(\tau)$ and $q_-(\tau)$ and expanding all factors in $q_-(t)$ keeping only the leading terms, we obtain

$$P_+(q, q_-, t) \equiv \frac{1}{2}(P(q_L, t) + P(q_R, t)) \approx P(q, t), \tag{4}$$

$$P_-(q, q_-, t) \equiv P(q_L, t) - P(q_R, t) \approx P'(q, t), \tag{5}$$

$$\exp\left\{\tfrac{i}{\hbar}S[q_L(t)] - \tfrac{i}{\hbar}S[q_R(t)]\right\} \approx \exp\left\{\frac{i}{\hbar}\frac{\delta S}{\delta q}q_-\right\}, \tag{6}$$

where $P'(q,t) \equiv \partial P(q,t)/\partial q$. Substituting these expressions in Eq. (3) and noting that as $\hbar \to 0$ the quantum density matrix tends to the classical phase-space density, $\rho_c(q,p)$ as

$$\rho(q, q_-) = \int \rho_c(q,p) e^{-\frac{i}{\hbar}pq_-} dp,$$

we finally get

$$R^{(n)}_{\rm class}(t,t_1,\ldots,t_n)=\Big(\frac{i}{\hbar}\Big)^n\int dq_0dp_0\rho(q_0,p_0)\int\mathcal{D}[q(\tau)]P(q,t)P'(q,t_1)\cdots P'(q,t_n)$$
$$\times\int\mathcal{D}[q_-(t)]q_-(t_1)\cdots q_-(t_n)\exp\Big\{\frac{i}{\hbar}\Big(\frac{\delta S}{\delta q}-p_0\Big)q_-\Big\},\qquad(7)$$

where $q_0\equiv q(0)$ and $p_0\equiv p(0)$.

We will show now that (7) represents the classical nonlinear response. First, the factors $q_-(t_k)$ can be replaced by $i\hbar\frac{\partial}{\partial p_0}(t_k)$ acting on the integrand. Integrating by parts with respect to the variable p_0, we see that the integral with respect to q_- reduces to the delta function $\delta(\delta S/\delta q)$. We should keep in mind that this is a multidimensional delta function. The path integral is understood as a limit of a finite sum when the length of each time interval tends to zero; the dimensionality of the delta function equals the number of these time intervals. It is easy to see that $\frac{\delta S}{\delta q}=0$ results in the classical equation of motion. By the variation principle, the classical trajectory nullifies the first variation derivative of the action. If, for example, $H=\frac{1}{2}m\dot{q}^2+U(q)$, then $\frac{\delta S}{\delta q}=m\ddot{q}+U'(q)$, and the condition $\frac{\delta S}{\delta q}=0$ gives the classical equation of motion.

This delta function eliminates the path integral with respect to $\mathcal{D}q(\tau)$ (its dimensionality matches that of the δ-function) and we obtain the following expression for the classical nonlinear response function

$$R^{(n)}_{\rm class}(t,t_1,\ldots,t_n)=\int dq_0dp_0\Big[P(q,t)P'(q,t_1)\cdots P'(q,t_n)\frac{\partial^n\rho(q_0,p_0)}{\partial p(t_1)\cdots\partial p(t_n)}\Big],\qquad(8)$$

where all quantities are now calculated along the classical trajectory $q=q(t)$. This formula may be used in numerical calculations: once we obtain the classical trajectories of the system $q=q(t)$ and $p=p(t)$ (either numerically or analytically), we know all the operators $P(q,t_k)$, and the response function can be calculated by averaging with respect to the equilibrium phase-space density. We can also rewrite this formula in a different form that resembles the Fluctuation-Dissipation Theorem and has some clear numerical advantages [3].

III. QUANTUM CORRECTIONS TO OPTICAL RESPONSE FUNCTIONS

If a system is harmonic (i.e. the action is quadratic in nuclear coordinates), and the dipole operator is linear in coordinates and momenta, then all nonlinear response functions vanish, and the system behaves completely classically. There are two possible sources that generate distinct quantum corrections to the nonlinear response: (i) nonlinear dependence of the dipole operator on coordinate and (ii) anharmonicity of the potential. A third quantum correction comes from the expansion of the equilibrium density matrix. We thus have

$$R^{(n)}(t,t_1,\ldots,t_n)=R^{(n)}_{\rm class}(t,t_1,\ldots,t_n)+\Delta R^{(n)}_{\rm eq}+\Delta R^{(n)}_{\rm dip}+\Delta R^{(n)}_{\rm anh},$$

where $R^{(n)}_{\rm class}$ is the classical response function, calculated in the preceding section, $\Delta R^{(n)}_{\rm eq}$ comes from quantum corrections to the equilibrium density matrix, $\Delta R^{(n)}_{\rm dip}$ describes a nonlinear dependence of the dipole operator on coordinates, and $\Delta R^{(n)}_{\rm anh}$ arises from anharmonic

terms in the potential. The calculation of these terms is presented in Appendices A–C, and they are given by Eqs. (9), (10), and (19), respectively. Below we present the correction for the particular case of linear response ($n = 1$) and the linear dependence of the polarization operator on the coordinate, $P(q) = aq$. The correction $\Delta R_{\rm eq}^{(n)}$ is given by (9), the term $\Delta R_{\rm dip}^{(n)}$ vanishes identically in the case $P(q) = aq$, and

$$\Delta R_{\rm anh}^{(1)}(t,t_1) = a^2\hbar^2 \int dq_0 dp_0\, \rho(q_0,p_0) \int d\tau_0 \Big\{ \int d\tau_1 \mathfrak{R}^{(4)}(\tau_1;\tau_0,\tau_0,\tau_0,\tau_1;q_0,p_0) \frac{\delta[q(t)U'''(\tau_0)]}{\delta q(\tau_1)}$$
$$+ \cdots + \int d\tau_1 d\tau_2 d\tau_3 d\tau_4\, \mathfrak{R}^{(1)}(\tau_1;\tau_0;q_0,p_0)\mathfrak{R}^{(1)}(\tau_2;\tau_0;q_0,p_0)$$
$$\times \mathfrak{R}^{(1)}(\tau_3;\tau_0;q_0,p_0)\mathfrak{R}^{(1)}(\tau_4;t_1;q_0,p_0) \frac{\delta^4[q(t)U'''(\tau_0)]}{\delta q(\tau_1)\cdots\delta q(\tau_4)} \Big\}$$

In this equation $\mathfrak{R}^{(k)}(\tau';\tau_1,\ldots,\tau_k;q_0,p_0)$ denotes the kth order classical response of the system to an external field coupled *linearly* to the coordinate, given that the initial point of the trajectory is (q_0,p_0). This illustrates how quantum corrections at a given order can be expressed in terms of classical response function of higher orders. In the case of linear response, the correction contains response functions up to the fourth order.

In conclusion, we will consider another possible reference problem. An example is the Brownian oscillator model [1], when nuclear motions are harmonic. The analysis of this model may be connected with the instantaneous mode technique [4–7] used for studying molecular dynamics and solvation processes. An important peculiarity of the harmonic system is that the bookkeeping (left and right trajectories separately versus one "average" trajectory) are both exact in this case. The results can then be generalized by introducing anharmonicity to the system and treating it perturbatively. Numerical methods that allow the calculation of path integrals for anharmonic systems [8] can then be used.

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Appendix A: Quantum Correction due to the Expansion of the Equilibrium Density Matrix

Following [9], we write,

$$\rho(q,q_-) = \int \rho_c(q,p) e^{-\frac{i}{\hbar}pq_-} \Big\{ 1 - \hbar^2\beta^3\Phi(q,p) \Big\} dp,$$

where

$$\Phi(q,p) \equiv \frac{7}{24}\Big[\Big(\frac{\partial H}{\partial p}\Big)^2 \frac{\partial^2 H}{\partial q^2} + \frac{\partial^2 H}{\partial p^2}\Big(\frac{\partial H}{\partial q}\Big)^2\Big] + \frac{\beta}{8}\frac{\partial^2 H}{\partial p^2}\frac{\partial^2 H}{\partial q^2}.$$

Substituting this expansion into Eq. (8), we obtain the quantum corrections to the order $\hbar^2$ for the classical response, $\Delta R_{\rm eq}^{(n)}$,

$$\Delta R^{(n)}_{\rm eq}(t,t_1,\ldots,t_n)=\hbar^2\beta^3\int dq_0dp_0\Big[P(q,t)P'(q,t_1)\cdots P'(q,t_n)\frac{\partial^n[\rho(q_0,p_0)\Phi(q_0,p_0)]}{\partial p(t_1)\cdots\partial p(t_n)}\Big]. \quad (9)$$

Appendix B: Quantum Correction due to Nonlinearity of Dipole Operator

We start with the expansions (4), (5) of the operators P_+, P_- in powers of $q_-(t)$ an keep the lowest two terms in each,

$$P_+(q,q_-,t)=P(q,t)+\frac{P''(q,t)}{2}(q_-)^2,$$
$$P_-(q,q_-,t)=P'(q,t)+\frac{P'''(q,t)}{6}(q_-)^3.$$

Substituting these expressions in Eq. (7), we get two additional powers of q_- in the integrand. Hence, in the nth response we will have $(n+2)$th derivative of the density function, which gives the $\hbar^2$ factor

$$\Delta R^{(n)}_{\rm dip}(t,t_1,\ldots,t_n)=\hbar^2\int dq_0dp_0\Big[P''(q,t)P'(q,t_1)\cdots P'(q,t_n)\frac{\partial^{n+2}\rho(q_0,p_0)}{\partial p(t)^2\partial p(t_1)\cdots\partial p(t_n)}$$
$$+P(q,t)\sum_{j=1}^{n}P'(q,t_1)\cdots P'''(q,t_j)\cdots P'(q,t_n)\frac{\partial^{n+2}\rho(q_0,p_0)}{\partial p(t_1)\cdots\partial p(t_j)^3\cdots\partial p(t_n)}\Big]. \quad (10)$$

Appendix C: Quantum Correction due to Anharmonicity of the Potential

Taking into account the next term in the expansion (6), we obtain

$$\exp\Big\{\frac{i}{\hbar}S[q_L(t)]-\frac{i}{\hbar}S[q_R(t)]\Big\}\approx\exp\Big\{\frac{i}{\hbar}\Big(\frac{\delta S}{\delta q}q_-+\frac{\delta^3S}{\delta q^3}\frac{(q_-)^3}{6}\Big)\Big\}.$$

We then substitute this into the integral (3). To calculate this integral we first add a new variable $f(\tau)$ and rewrite $R^{(n)}$ in the form

$$R^{(n)}(t,t_1,\ldots,t_n)=\int\mathcal{D}[f(\tau)]\delta\Big(\frac{\delta S}{\delta q}-p_0-f(\tau)\Big)$$
$$\times\Big(\frac{i}{\hbar}\Big)^n\int dq_0dp_0\rho(q_0,p_0)\int\mathcal{D}[q_+(\tau)]\mathcal{D}[q_-(\tau)]P(q,t)P'(q,t_1)\cdots P'(q,t_n)$$
$$\times\exp\Big\{\frac{i}{\hbar}\int f(\tau)q_-(\tau)d\tau+\frac{i}{6\hbar}\int U'''[q(\tau)](q_-(\tau))^3+\ldots\Big\}. \quad (11)$$

We can now use the delta function $\delta[\delta S/\delta q-p_0-f(\tau)]$ to calculate in (11) the integral with respect to q and get

$$R^{(n)}(t,t_1,\ldots,t_n)=\Big(\frac{i}{\hbar}\Big)^n\int dq_0dp_0\rho(q_0,p_0)\int\mathcal{D}[q_-(\tau)]\mathcal{D}[f(\tau)]$$
$$\times\exp\Big\{\frac{i}{\hbar}\int f(\tau)q_-(\tau)d\tau\Big\}F(q,q_-,t,t_1,\ldots,t_n)\Big|_{\frac{\delta S}{\delta q}=f(\tau)}, \quad (12)$$

where

$$F(q,q_-,t,t_1,\dots,t_n) = P(q,t)P'(q,t_1)\cdots P'(q,t_n)\,q_-(t_1)\cdots q_-(t_n) \times \exp\left\{\frac{i}{6\hbar}\int U'''[q(\tau)](q_-(\tau))^3+\dots\right\}. \quad (13)$$

Here the coordinate $q(\tau)$ is calculated along the trajectory that deviates from the classical trajectory $\frac{\delta S}{\delta q}=0$. We thus denote this deviation $\delta q(\tau)$, that is, $q(\tau)=q_c(\tau)+\delta q(\tau)$, where $q_c(\tau)$ stands for the classical trajectory, and expand the function F of (13) in the Taylor series in this deviation:

$$F(q_c+\delta q) = F(q_c)+\int\frac{\delta F(q_c)}{\delta q(\tau')}\delta q(\tau')d\tau' + \int\frac{\delta^2F(q_c)}{\delta q(\tau')\delta q(\tau'')}\frac{\delta q(\tau')\delta q(\tau'')}{2}d\tau' d\tau''+\dots \quad (14)$$

The function $f(\tau)$ plays the role of an additional external force. [Indeed, for the Hamiltonian $H(p,q)=\frac{p^2}{2m}+U(q)$, it will be replaced by $H_1(p,q)=\frac{p^2}{2m}+U(q)+qf(\tau)$.] We may thus consider $\delta q(\tau)$ as a response of the system to this external force, and write an expansion in powers of $f(\tau)$:

$$\delta q(\tau') = \sum_{k=1}^{\infty}\frac{1}{k!}\int d\tau_1\dots d\tau_k\,\mathfrak{R}^{(k)}(\tau';\tau_1,\dots,\tau_k;q_0,p_0)f(\tau_1)\dots f(\tau_k). \quad (15)$$

$\mathfrak{R}^{(k)}(\tau';\tau_1,\dots,\tau_k;q_0,p_0)$ denotes the kth classical response of the system to the external field coupled *linearly* to the coordinate. Note that it also depends on the initial point of the trajectory.

We will study the contribution of each term in the expansion (14) separately. The leading term gives no contribution to the response. Consider the term linear in $\delta q(\tau)$. We thus rewrite the response function (12) substituting $\int\frac{\delta F(q_c)}{\delta q(\tau')}\delta q(\tau')d\tau'$ for the function F, where $\delta q(\tau')$ is represented by the series (15). This contribution can be written as

$$\left(\frac{i}{\hbar}\right)^n\int dq_0dp_0\rho(q_0,p_0)\sum_{k=1}^{\infty}\frac{1}{k!}\int d\tau' d\tau_1\dots d\tau_k\,\mathfrak{R}^{(k)}(\tau';\tau_1,\dots,\tau_n;q_0,p_0) \times\frac{\delta}{\delta q(\tau')}\Big[P(q,t)P'(q,t_1)\cdots P'(q,t_n)I_{nk}(\tau_1,\dots,\tau_k,t_1,\dots,t_n)\Big], \quad (16)$$

where the integral I_{nk} denotes the standard block

$$I_{nk}(\tau_1,\dots,\tau_k,t_1,\dots,t_n) \equiv \int\mathcal{D}[q_-(\tau)]\mathcal{D}[f(\tau)]f(\tau_1)\dots f(\tau_k)\,q_-(t_1)\cdots q_-(t_n) \times\exp\left\{\frac{i}{\hbar}\int f(\tau)q_-(\tau)d\tau\right\}\exp\left\{\frac{i}{6\hbar}\int U'''[q(\tau)](q_-(\tau))^3d\tau+\dots\right\}. \quad (17)$$

These integrals can be calculated explicitly,

$$I_{nk}(\tau_1,\dots,\tau_k,t_1,\dots,t_n) = \hbar^k\left[\frac{\delta^k}{\delta q_-(\tau_1)\dots\delta q_-(\tau_k)}q_-(t_1)\cdots q_-(t_n)\exp\left\{\frac{i}{6\hbar}\int U'''[q(\tau)](q_-(\tau))^3d\tau+\dots\right\}\right]_{q_-(\tau)=0}.$$

All the integrals I_{nk} with $k < n$, that is, when the number of τ-derivatives in (17) is less than the number of the q_- factors, vanish. The first surviving term is $k = n$, the next one is for $k = n + 3$. We then have

$$I_{nn}(\tau_1, \ldots, \tau_n, t_1, \ldots, t_n) = \hbar^n \delta(t_1 - \tau_1) \cdots \delta(t_n - \tau_n),$$
$$I_{n,n+3}(\tau_1, \ldots, \tau_{n+3}, t_1, \ldots, t_n)$$
$$= \hbar^{n+2} U'''[q(\tau_0)] \delta(t_1 - \tau_1) \cdots \delta(t_n - \tau_n) \delta(\tau_0 - \tau_{n+1}) \delta(\tau_0 - \tau_{n+2}) \delta(\tau_0 - \tau_{n+3}).$$

When substituted into (16), these two terms give

$$k = n: \qquad \int dq_0 dp_0 \rho(q_0, p_0) \int d\tau' \mathfrak{R}^{(n)}(\tau'; t_1, \ldots, t_n; q_0, p_0)$$
$$\times \frac{\delta}{\delta q(\tau')} \Big[P(q,t) P'(q,t_1) \cdots P'(q,t_n) \Big].$$

$$k = n + 3: \quad \hbar^2 \int dq_0 dp_0 \rho(q_0, p_0) \int d\tau_0 d\tau' \, \mathfrak{R}^{(n+3)}(\tau'; \tau_0, \tau_0, \tau_0, t_1, \ldots, t_n; q_0, p_0)$$
$$\times \frac{\delta}{\delta q(\tau')} \Big[P(q,t) P'(q,t_1) \cdots P'(q,t_n) U'''(q(\tau_0)) \Big].$$

The first formula represents the contribution to the classical response, whereas the second one to the first quantum correction, having the order $\hbar^2$.

In a similar way we calculate other terms in (14) that have higher powers of δq. Gathering all the contributions from different orders in δq together we can write a representation of the classical response and the first quantum correction. We have

$$R^{(n)}_{\text{class}}(t; t_1, \ldots, t_n) = \int dq_0 dp_0 \, \rho(q_0, p_0) \int d\tau_0 \sum_{k=1}^{n} \int d\tau_1 \ldots d\tau_k \sum_{j_1, \ldots, j_k = 1}^{j_1 + \cdots + j_k = n} \sum_{\lambda}$$
$$\times \mathfrak{R}^{(j_1)}\Big(\tau_1; s_1^{(\lambda)}, \ldots, s_{j_1}^{(\lambda)}; q_0, p_0\Big) \mathfrak{R}^{(j_2)}\Big(\tau_2; s_{j_1+1}^{(\lambda)}, \ldots, s_{j_1+j_2}^{(\lambda)}; q_0, p_0\Big)$$
$$\times \cdots \times \mathfrak{R}^{(j_k)}\Big(\tau_k; s_{j_1+\cdots+j_{k-1}+1}^{(\lambda)}, \ldots, s_{j_1+\cdots+j_k}^{(\lambda)}; q_0, p_0\Big)$$
$$\times \frac{1}{k!} \frac{\delta^k}{\delta q(\tau_1) \cdots \delta q(\tau_k)} \Big[P(q,t) P'(q,t_1) \cdots P'(q,t_n) \Big]. \tag{18}$$

$$\Delta R^{(n)}_{\text{anh}}(t; t_1, \ldots, t_n) = \hbar^2 \int dq_0 dp_0 \, \rho(q_0, p_0) \int d\tau_0 \sum_{k=1}^{n+3} \int d\tau_1 \ldots d\tau_k \sum_{j_1, \ldots, j_k = 1}^{j_1 + \cdots + j_k = n+3} \sum_{\lambda}$$
$$\times \mathfrak{R}^{(j_1)}\Big(\tau_1; s_1^{(\lambda)}, \ldots, s_{j_1}^{(\lambda)}; q_0, p_0\Big) \mathfrak{R}^{(j_2)}\Big(\tau_2; s_{j_1+1}^{(\lambda)}, \ldots, s_{j_1+j_2}^{(\lambda)}; q_0, p_0\Big)$$
$$\times \cdots \times \mathfrak{R}^{(j_k)}\Big(\tau_k; s_{j_1+\cdots+j_{k-1}+1}^{(\lambda)}, \ldots, s_{j_1+\cdots+j_k}^{(\lambda)}; q_0, p_0\Big)$$
$$\times \frac{1}{k!} \frac{\delta^k}{\delta q(\tau_1) \cdots \delta q(\tau_k)} \Big[P(q,t) P'(q,t_1) \cdots P'(q,t_n) U'''(\tau_0) \Big]. \tag{19}$$

Here λ denotes all possible ways to divide the set of times $(t_1, \ldots, t_n, \tau_0, \tau_0, \tau_0)$ in k groups so that in each there will be j_k times and within each group they are time-ordered. Having done this, we denote these times by $s_1^{(\lambda)}, \ldots, s_{j_1}^{(\lambda)}, s_{j_1+1}^{(\lambda)}, \ldots, s_{j_1+j_2}^{(\lambda)}, s_{j_1+\cdots+j_{k-1}+1}^{(\lambda)}, \ldots, s_{j_1+\cdots+j_k}^{(\lambda)}$.

These two formulas need some additional clarification. We see that the summation with respect to k, which comes from summing all the contributions in (14), is always finite and determined by the order of the response function to be calculated.

Eq. (18) allows us to express the classical response function for the nonlinear dipole operator in terms of classical responses written for linear coupling with the field.

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