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Semiclassical formalism of optical absorption

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A semiclassical formalism for the optical absorption in a coupled electron-ion system is developed. The formalism assumes (a) an initial periodic trajectory whose frequency is much lower than electronic energies, and (b) a short-memory condition, i.e., the excited-state trajectories diverge away from the initial one within one period. The result shows nonadiabatic features such as level broadening, sidebands, and tails in nonclassical regimes. The formalism is demonstrated on a model for polyacetylene and can account for unusual absorption data.

I. INTRODUCTION

The semiclassical description of many-body quantum theory has been a useful approach in the study of molecules,[1-4] solid state,[5,6] nuclear matter,[7] elementary particles,[8] and more.[9,10] In general, a nonlinear interaction is treated by an expansion in $\hbar$, the zeroth order being the classical equations. The expansion in $\hbar$ requires care since nonanalytic terms in $\hbar$ usually arise. The most efficient way of deriving these expansions is by using functional integrals.[9,10]

A coupled electron-ion system is a natural application since the heavy ions correspond to near-classical variables. A conventional description of such a system is "adiabatic dynamics" (AD):[3,5] At any given time the electronic spectra are solved as if the ions were frozen; this allows for a full quantum description of the electrons. The ions then evolve by a classical equation which includes a force from the electron-ion interaction. The AD is valid for a periodic state when its frequency ω_B is much smaller than the lowest electronic transition energy. The feasibility of this condition is due to the large ratio of ion to electron masses.

An external electromagnetic field poses new difficulties for the AD description. While the initial state can be properly described by AD, the electric field may excite a state for which AD is not valid for all times. In particular, we consider photoexcited states for which the adiabatic potential, as a function of the ion coordinates, is near a maximum (turning point), while the minimum is far, or even infinitely far, from that of the ground state. Such unstable excitations occur in photoinduced fission of molecules or nuclei, photoexcitation during molecular collisions, or photoexcitation of a well-separated electron-hole pair in semiconductors. Another difficulty of AD relates to the concept of a "transition time," i.e., at what "time" does an electron jump from an initial to an excited state. Since the ion trajectories depend on time, so do the excitation energies $\Delta E_e(t)$ to a state e. Classically, a transition time τ is expected when $\Delta E_e(\tau)=\hbar\omega$, where ω is the frequency of the external field. It is not obvious what the uncertainty in this transition time is when nonadiabatic effects are included. Furthermore, when there are two such nearby transition times there could be a nonclassical interference between them. This is the situation near a classical turning point.

We note that the conventional Franck-Condon[11] approximation is not sufficient to handle these cases; in particular, it leads to spurious divergences at the turning points. Nonadiabatic absorption may also be inferred from precise derivations of electron densities of states;[12,13] such derivations, however, are in general not feasible for many-body systems.

Transitions between bound states of anharmonic molecules, via optical absorption or electron-transfer reaction, were studied extensively by Warshel and Hwang (WH).[14-16] These transitions were studied both by semiclassical techniques and by simplified expressions[17] in terms of ΔE_e; the two approaches gave comparable results only for harmonic systems.[15,16] The simplified forms were not derived rigorously, yet they seem to be the only practical method for dealing with anharmonic molecules with many degrees of freedom.[14-16]

To resolve the aforementioned conceptual and practical issues we have developed[18] a semiclassical formalism which is presented here in detail. The conditions for this formalism are defined in terms of the AD scheme for the initial and excited states: (a) The adiabatic condition, i.e., the electron-energy differences are much larger than $\hbar\omega_B$. The relevant electron energies are the excitation energy from the initial state ΔE_e, the spacing to other excited states $\Delta E_e'-\Delta E_e$, and the energy $\hbar\omega_{\max}-\hbar\omega_{\min}$

spanned by $\Delta E_e(\tau)$ in one period. The latter large amplitude condition $\omega_{\max}-\omega_{\min}\gg\omega_B$ also guarantees a large spacing $\Delta E_e'-\Delta E_e$ during most of the period. (b) A short-memory condition, i.e., the adiabatic dynamics for the excited state leads to a trajectory which rapidly (within one period) diverges away from the initial trajectory. Similar conditions for a nonperiodic trajectory with a turning point can be defined in terms on a curvature ω_B at the turning point.

Within these assumptions we derive a simple yet powerful expression for the real part of the conductivity $\mathrm{Re}\sigma(\omega)$. This expression is similar to the simplified forms that were previously assumed.[14-17] Note, however, that WH (Refs. 15–17) consider transitions between bound states, while our derivation applies to an essentially different situation, i.e., the excited state is unbound with a rapid decay (short-memory condition). The requirement for harmonic potentials[15,16] is therefore not necessary in our case.

In Sec. II we define the problem and examine properties of adiabatic wave functions. In Sec. III we consider a heuristic derivation in which a fully adiabatic formalism with a unique ion trajectory is assumed. We then argue that a plausible coarse-graining scheme leads to a more reliable result. In Sec. IV we evaluate $\mathrm{Re}\sigma(\omega)$ from first principles by a functional integral over ion trajectories. Transition times are then identified as stationary phase points. Use of the above assumptions restricts the excited-state trajectory to times close to the nearest transition times. This short-memory feature then leads to our central result, Eq. (40). After analyzing some general properties of our result in Sec. V, we demonstrate in Sec. VI an application to an electron-phonon model for polyacetylene[5] and its nonlinear oscillations.[6] The results show a combination of classical features near the turning points $\omega=\omega_{\min}$ or $\omega=\omega_{\max}$, and of quantum features like level broadening, sidebands, and tails in nonclassical regimes. Parameters appropriate to *trans*-$(\mathrm{CH})_x$ can account for the observed pronounced tail of the ground-state absorption[19-21] and for unusual photoinduced absorption data.[22-26]

II. MODEL

Consider a general Hamiltonian for an electron-ion system

$$\mathcal{H}(x;p,q)=p^2/2M+v(q)+h(x;q)\ . \tag{1}$$

Here $q=(q_2,q_2,\ldots)$; $p=(p_1,p_2,\ldots)$; M and $V(q)$ are the coordinates, momenta, mass, and potential energy of the ions, respectively; $x=(x_1,x_2,\ldots)$ are the electron coordinates; and $h(x;q)$ includes the electron kinetic energy, electron-electron interactions, and electron-ion interactions. We wish to evaluate the optical absorption of a given eigenstate of Eq. (1). This corresponds to evaluating the linear response to an interaction Hamiltonian,

$$\mathcal{H}_{\mathrm{ex}}=(2i/\omega)J(x)\mathcal{E}_0\cos\omega t\ , \tag{2}$$

where $2\mathcal{E}_0\cos\omega t$ is an external electric field and $J(x)$ is the electronic current operator.

In the following, we use extensively the adiabatic wave functions, i.e., all the x dependence is contained in the eigenfunctions of

$$h(x;q)\psi(x;q)=E(q)\psi(x;q)\ , \tag{3}$$

where q is considered as a parameter. If $h(x;q)$ does not include direct electron-electron interactions, then $\psi(x;q)$ is a Slater determinant and $E(q)$ is a sum over single-particle energies. The present formalism, however, is sufficiently general to allow for electron-electron interactions in $h(x;q)$.

The initial state is $\psi_B(x;q)$ with eigenvalue $E_B(q)$, while the states excited by the electric field are $\psi_e(x;q)$ with eigenvalues $E_e(q)$. In the absence of electron-electron interactions ψ_e are particle-hole excitations.

To evaluate the effect of $\mathcal{H}_{\mathrm{ex}}$, as well as to clarify the validity of the adiabatic wave function, we need to solve the time-dependent equation where both q and the external interaction $\mathcal{H}_{\mathrm{ex}}$ are time dependent,

$$i\hbar\frac{\partial}{\partial t}\psi(x,t;q)=[h(x;q)+\mathcal{H}_{\mathrm{ex}}(x,t)]\psi(x,t;q)\ . \tag{4}$$

The solution can be expanded as

$$\psi(x,t;q)=c_B(t)\psi_B(x;q)+\sum_e c_e(t)\psi_e(x;q)\ , \tag{5}$$

with initial conditions $c_B(t_1)=1$, $c_e(t_1)=0$. Note that we expand in a complete set which itself evolves in time via $q(t)$. The trajectory $q(t)$ is assumed here to vary slowly with a frequency of order $\omega_B\ll\omega$.

Substituting Eq. (5) in (4) and projecting onto the states $\psi_B(x;q)$ and $\psi_e(x;q)$ yields the coupled equations

$$\begin{aligned} i\hbar\frac{\partial c_B}{\partial t}&=E_Bc_B-i\hbar c_B\langle\psi_B|\dot\psi_B\rangle\\ &\quad-i\hbar\sum_e c_e\langle\psi_B|\dot\psi_e\rangle+O(\mathcal{E}_0c_e)\ ,\\ i\hbar\frac{\partial c_e}{\partial t}&=E_ec_e+(2i/\omega)c_B\mathcal{E}_0\mu_e\cos\omega t-i\hbar c_B\langle\psi_e|\dot\psi_B\rangle\\ &\quad-i\hbar\sum_{e'}c_{e'}\langle\psi_e|\dot\psi_{e'}\rangle+O(\mathcal{E}_0c_e)\ , \end{aligned} \tag{6}$$

where

$$\mu_e(q(t))=\langle\psi_e(x;q(t))|J(x)|\psi_B(x;q(t))\rangle \tag{7}$$

and $\dot\psi_B=\partial\psi_B(x;q(t))/\partial t$, etc. Since c_e is generated either by small nonadiabatic terms or by the electric field, terms of order $\mathcal{E}_0c_e$ are neglected in Eq. (6). The terms like $\langle\psi_B|\dot\psi_B\rangle$ and $\langle\psi_e|\dot\psi_B\rangle$ in Eq. (6) oscillate with a frequency $\sim\omega_B$, which is small compared with $(E_e-E_B)/\hbar$ or with ω. These terms have two effects: first, off-diagonal terms lead to transitions between states. When $\mathcal{E}_0=0$ these terms act as an external field with a low frequency $\sim\omega_B$; the transition probability is then exponentially small [see Eq. (51)]. When $\mathcal{E}_0\neq0$, a state e can be generated by first exciting a state e' ($e'\neq e$) via $\mathcal{H}_{\mathrm{ex}}$ and then tunneling to the state e by the nonadiabatic overlap $\langle\psi_e|\dot\psi_{e'}\rangle$. We therefore need an adiabatic condition on the excited state, i.e., it is far from other states.

$|E_{e'}-E_e| \gg \hbar\omega_B$.

The second nonadiabatic effect is due to diagonal terms in Eq. (6), which shifts E_B by $-i\hbar\langle \psi_B | \dot{\psi}_B \rangle$ and similarly for E_e. Since ψ_B is normalized at all $q(t)$, $\mathrm{Re}\langle \psi_B | \dot{\psi}_B \rangle = 0$ and we can renormalize the adiabatic energy levels by

$$\tilde{E}_B = E_B + \hbar\,\mathrm{Im}\langle \psi_B | \dot{\psi}_B \rangle \ ,$$
$$\tilde{E}_e = E_e + \hbar\,\mathrm{Im}\langle \psi_e | \dot{\psi}_e \rangle \ . \tag{8}$$

The corrections to E_B and E_e are small, of order $\hbar\omega_B$. The other nonadiabatic corrections, which were neglected above, are exponentially small; hence, it is consistent to maintain the more significant linear corrections in Eq. (8). Note also that these corrections vanish for real eigenfunctions.

We conclude that (a) for $\mathcal{E}_0 = 0$, the states of Eq. (3) are a good approximation when $\omega_B \ll E_e - E_B$, i.e., the mixing of the initial and excited states is exponentially small; (b) a field $\mathcal{E}_0$ induces transitions between these states via the equations

$$i\hbar\frac{\partial c_B}{\partial t} = \tilde{E}_B\{q(t)\}c_B \ ,$$
$$i\hbar\frac{\partial c_e}{\partial t} = \tilde{E}_e\{q(t)\}c_e + (i/\omega)c_B\mu_e(q(t))\mathcal{E}_0\exp(-i\omega t) \ , \tag{9}$$

where $E_B\{q(t)\} = E_B(q,\dot{q})$ and $E_e\{q(t)\} = E_e(q,\dot{q})$ allow for a dependence on both $q(t)$ and $\dot{q}(t)$. A single excited state e is involved, for which $E_e \simeq E_B + \hbar\omega$. Other excited states e' with $|E_{e'}-E_e| \gg \hbar\omega_B$ are neglected; a term with $\exp(+i\omega t)$, which is far from resonance (i.e., at energy $2\hbar\omega$ from $E_e - E_B$) was also neglected. The solution of Eq. (9) is

$$c_e(t_2) = (\mathcal{E}_0/\hbar\omega)\int_{t_1}^{t_2} dt\,\mu_e(q(t))\exp\left[-i\omega t - i\int_{t_1}^{t}\tilde{E}_B\{q(t')\}dt'/\hbar - i\int_{t}^{t_2}\tilde{E}_e\{q(t')\}dt'/\hbar\right] . \tag{10}$$

We can interpret the integration variable t as a transition time—the exponent involves $\tilde{E}_B$ for $t' < t$ and $\tilde{E}_e$ for $t' > t$. The transition time can be anywhere in the range (t_1, t_2); the transition probability, however, is maximized when the integrand has a slowly varying phase. Since μ_e varies slowly, varying the phase with respect to t and setting it to zero gives the stationary-phase (SP) transition time

$$\hbar\omega = \tilde{E}_e\{q(t)\} - \tilde{E}_B\{q(t)\} \ . \tag{11}$$

Allowing for the ion kinetic energy in the final form for $\mathrm{Re}\sigma(\omega)$ (Sec. IV) modifies Eq. (11) by $\sim(\hbar\omega_B)^2$ terms [see Eq. (34)]. When $q(t)$ is periodic, ω in Eq. (11) has a maximal value $\omega_{\max}$ and a minimal one $\omega_{\min}$. Equation (11) has then two solutions when ω is this classical regime $\omega_{\min} < \omega < \omega_{\max}$, one solution at the turning points $\omega = \omega_{\min}$ or $\omega = \omega_{\max}$ and no solutions in the nonclassical regime $\omega > \omega_{\max}$ or $\omega < \omega_{\min}$. In the following sections we use Eq. (10) directly without assuming SP-type derivations. The concept of a transition time is, however, useful for deriving and understanding our results for $\mathrm{Re}\sigma(\omega)$.

III. ADIABATIC FORMALISM

In this section a simplified heuristic derivation of our result is given. A first-principles derivation with the role of each assumption explained is given in Sec. IV.

The AD process focuses on a single "self-consistent" trajectory $q_B(t)$ which satisfies classical ion dynamics. The initial state is defined with $\mathcal{E}_0 = 0$ and the electrons propagate with the "energy" $\tilde{E}_B(q,\dot{q})$ of Eq. (8). This defines an effective Lagrangian for the ions [see also below Eq. (24)],

$$\mathcal{L}_{\mathrm{eff}} = \tfrac{1}{2}M\dot{q}^{\,2} - V(q) - E_B(q) - \hbar\,\mathrm{Im}\langle \psi_B(x;q) | \dot{\psi}_B(x;q) \rangle \ . \tag{12}$$

Replacing $\dot{\psi}_B(x;q) = \dot{q}\,\partial\psi_B(x;q)/\partial q$, the last term in (12) has the form of a vector potential coupled to the velocity $\dot{q}$. The Euler-Lagrange equation for $\mathcal{L}_{\mathrm{eff}}$ is

$$M\frac{\partial^2 q}{\partial t^2} = -\frac{\partial}{\partial q}[V(q) + E_B(q)]$$
$$-2\hbar\,\mathrm{Im}\left\langle \frac{\partial\psi_B(x;q)}{\partial q} \middle| \frac{\partial\psi_B(x;q)}{\partial t} \right\rangle . \tag{13}$$

A solution of this equation defines an AD trajectory $q_B(t)$. Note that this is a vector equation which involves a Lorenz-like force via $\dot{\psi}_B = \dot{q}\,\partial\psi_B/\partial q$. This force relates to the ion momentum $-i\hbar\partial/\partial q$, which, in the state $\psi_B(x;q)$, acquires an additional term.

The self-consistent solution $q_B(t)$ can be used in Eq. (3) to find higher-energy excited states $\psi_e(x;q)$. These states are not self-consistent with q_B, i.e., Eq. (13) with subscript B replaced by e is not solved by $q_B(t)$. Nevertheless, the set $\{\psi_B, \psi_e\}$ is a useful complete set in which the exact solution can be expanded. We consider a periodic trajectory $q_B(t)$ with frequency ω_B as a generic case which involves turning points, i.e., times for which $\dot{q}_B(t) = 0$. Nonperiodic solutions can be treated similarly, except that ω_B then measures the curvature at a turning point.

A particular self-consistent trajectory is the adiabatic ground state, which has a static, time-independent q_B. If the ions remain static in the excited states one can apply the golden rule [or see below Eq. (20)] and obtain

$$\mathrm{Re}\sigma^{\mathrm{static}}(\omega) = (\pi/\omega)\sum_e |\mu_e|^2\delta(\hbar\omega - E_e + E_B) \ . \tag{14}$$

One is tempted then to use this expression even for a slowly varying $q_B(t)$ by time averaging a period T_B along the trajectory

$$\mathrm{Re}\sigma^{(0)}(\omega) = (\pi/\omega)\sum_e \int_0^{T_B} dt\,|\mu_e(t)|^2\delta(\hbar\omega - \Delta\tilde{E}_e(t))/T_B \ , \tag{15}$$

where, for short,

$$\Delta\tilde{E}_e(t)=\tilde{E}_e\{q_B(t)\}-\tilde{E}_B\{q_B(t)\}\ ,$$
$$\mu_e(t)=\mu_e(q_B(t))\ . \tag{16}$$

Equation (15) yields absorption only in the classical energy range $\omega_{\min}<\omega<\omega_{\max}$. At the turning points $\omega=\omega_{\min}$ or $\omega=\omega_{\max}$, Eq. (14) diverges. The form (15) is similar to the Franck-Condon result,[11] except that the initial-state wave function is replaced here by integrating the classical range of $q_B(t)$.

For a proper derivation of $\mathrm{Re}\sigma(\omega)$ we relate it to the energy absorption rate. An electric field $2\mathcal{E}_0\cos\omega t$ and the current $\langle J\rangle=\mathcal{E}_0\sigma(\omega)\exp(i\omega t)+\mathrm{H.c.}$ yield a time-averaged dissipation rate of $2\mathcal{E}_0^2\mathrm{Re}\sigma(\omega)$. The absorbed energy on the other hand is

$$\hbar\omega\int dx\,|\sum_e c_e(t_2)\psi_e(x;q_B)|^2\ ,$$

where $c_e(t_2)$ is given by Eq. (10) for $q=q_B(t)$. Hence

$$\mathrm{Re}\sigma(\omega)=\lim[2\hbar\omega(t_2-t_1)]^{-1}\sum_e\int_{t_1}^{t_2}dt\,\mu_e(t)\exp\left[-i\omega t+i\int_{t_1}^{t}\Delta\tilde{E}_e(t')dt'/\hbar\right]\Bigg|^2\ , \tag{17}$$

where the limit $t_2-t_1\rightarrow\infty$ is implied. Consider $t_1=-N_1T_B$, $t_2=N_2T_B$ with $N_2,N_1\rightarrow\infty$. Using the periodicity of $\mu_e(t)$ and of $\Delta E_e(t)$, the integral in Eq. (17) can be written as

$$\exp(i\omega_m N_1T_B)\sum_{n=-N_1}^{N_2-1}\exp[-i(\omega-\omega_m)nT_B]I(\omega)\ , \tag{18}$$

where $\hbar\omega_m=\int_0^{T_B}\Delta E_e(t)dt/T_B$ is the mean transition energy and

$$I_e(\omega)=\int_0^{T_B}dt\,\mu_e(t)\exp\left[-i\omega t+i\int_0^{t}dt'\frac{\Delta\tilde{E}_e(t')}{\hbar}\right]\ . \tag{19}$$

The limit of the sum in Eq. (18) is $\sum_k 2\pi\delta((\omega-\omega_m)T_B+2\pi k)$. The δ functions constrain the complex conjugate of (18) to have a factor of $N_1+N_2=(t_2-t_1)/T_B$. Thus, finally,

$$\mathrm{Re}\sigma^{(1)}(\omega)$$
$$=\sum_e\sum_{k=-\infty}^{\infty}\pi\delta(\omega-\omega_m+k\omega_B)|I_e(\omega)|^2/(\hbar\omega T_B^2)\ . \tag{20}$$

$I_e(\omega)$ is a smooth function (see Sec. V) whose main intensity is in the range of ΔE_e. This envelope function is modulated by the relatively dense set of δ functions. This sharp structure is a result of restricting the excited state to follow the same trajectory $q_B(t)$ of the initial state, which in turn implies long-time correlation between initial and excited trajectories. We expect this correlation to be seriously violated by the AD of the excited state and by nonadiabatic corrections so that coarse graining on a range of ω_B could be a better approximation. Hence, $\sum_k\delta(\omega-\omega_m+k\omega_B)$ is replaced by its average $1/\omega_B$ and our central result [Eq. (40) below] is obtained.

Note that in the static limit of $T_B\rightarrow\infty$ we obtain

$$|I(\omega)|^2\rightarrow 2\pi T_B|\mu_e|^2\delta(\omega-\Delta E_e/\hbar)$$

and hence the result, Eq. (14). In Sec. IV we present a systematic derivation of $\mathrm{Re}\sigma(\omega)$, in which the meaning of coarse graining is clarified.

IV. SHORT-MEMORY FORMALISM

Functional integrals provide an efficient conceptual and practical framework for treating electron and ion coordinates on distinct levels. In particular, the electrons can propagate in the Schrödinger picture, while the ions are described by a functional integral.

Consider the electron probability $K(x_2,t_2;x_1,t_1;q(t))$ for propagating from x_1 at time t_1 to x_2 at time t_2, while the ions are moving along an arbitrary trajectory $q(t)$. If, in addition, the ions propagate from $q(t_1)=q_1$ to $q(t_2)=q_2$ the total transition probability is

$$\mathcal{E}_0M(x_2,q_2,t_2;x_1,q_1,t_1)/\hbar\omega$$
$$\equiv\int_{q_1}^{q_2}\mathcal{D}qK(x_2,t_2;x_1,t_1;q(t))$$
$$\times\exp\left[i\int_{t_1}^{t_2}[\tfrac{1}{2}M\dot{q}^2-V(q)]dt\right]\ , \tag{21}$$

where $\mathcal{D}q$ is a functional integral[9,10] on the trajectories $q(t)$. $K(x_2,t_2;x_1,t_1;q(t))$ can be represented as a functional integral with the action corresponding to $h(x;q)+\mathcal{H}_{\mathrm{ex}}(x)$; instead, however, we can find this propagator by solving the Schrödinger equation. At this stage we use our first assumption, i.e., that AD is a valid description of the initial state. As shown in Sec. II, the initial wave function of Eq. (1) then has the form $\psi_B(x;q)\phi_B^{(n)}(q)$, where $\psi_B(x;q)$ solves Eq. (3) and $\phi_B^{(n)}(q)$ are eigenfunctions of the remaining q-dependent terms in (1) [see Eq. (25)]. Note that the subscript B refers to a chosen initial state of Eq. (3) and does not (yet) define a self-consistent trajectory as in Sec. III.

We wish to evaluate the probability, to first order in $\mathcal{E}_0$, that the perturbation $\mathcal{H}_{\mathrm{ex}}$ excites the system to a state orthogonal to $\psi_B(x;q)\phi_B^{(n)}(q)$. These excited states can be chosen as the set $\psi_e(x;q)\phi_e^{(m)}(q)$, where $\phi_e^{(m)}(q)$ are ion eigenfunctions in the excited state. This does *not* imply that we assume AD for the excited states; the set $\psi_e(x;q)\phi_e^{(m)}(q)$ is merely a convenient complete set which is orthogonal to $\psi_B(x;q)\phi_B^{(n)}(q)$ and in which an exact eigenfunction can be expanded. [$\psi_B(x;q)\phi_B^{(n')}(q)$ with $n'\neq n$ is also orthogonal to $\psi_B(x;q)\phi_B^{(n)}(q)$; however, $\mathcal{H}_{\mathrm{ex}}$ does not couple these states.]

The electronic wave function evolves via Eq. (4), where $q(t)$ is now an arbitrary trajectory. The initial wave function $\psi_B(x;q_1)$ at time t_1 evolves to an excited state $\psi_e(x;q_2)$ at time t_2 with the probability $c_e(t)$ of Eq. (5), which in terms of the electron propagator is

$$c_e(q(t))=\int dx_1 dx_2 \psi_e(x_2;q_2) \times K(x_2,t_2;x_1,t_1;q(t))\psi_B(x_1,q_1) \; . \tag{22}$$

This defines a transition probability in a mixed representation, i.e., electrons in eigenfunction space change from B to e, while ions in position space change from q_1 to q_2,

$$\mathcal{E}_0 M_e(q_2,t_2;q_1,t_1)/\hbar\omega = \int_{q_1}^{q_2} \mathcal{D}q\, c_e(q(t)) \exp\left[i\int_{t_1}^{t_2} [\tfrac{1}{2}M\dot{q}^2 - V(q)]dt/\hbar \right] \; . \tag{23}$$

We assume now that the dominant trajectories in (23) are slowly varying with frequencies near ω_B such that Eq. (10) for $c_e(q(t))$ is valid. This is justified by the AD condition on the initial state and on the relevant portion of the excited state, the latter being within one period from a jump time (see below). Thus we need $\hbar\omega_B \ll E_e - E_B \simeq \hbar\omega$, while other excited states e' are well separated from E_e, i.e., $\hbar\omega_B \ll |E_{e'} - E_e|$. Note that there are no constraints on the excited-state trajectories beyond one period; also there is no AD condition on the states e' being far from $E_B + \hbar\omega$.

We define $K_B(q_2,t_2;q_1,t_1)$ for $t_2 > t_1$ as the ion propagator with potential $\tilde{E}_B(q,\dot{q}) + V(q)$,

$$K_B(q_2,t_2;q_1,t_1)=\int_{q_1}^{q_2} \mathcal{D}q \exp\left[i\int_{t_1}^{t_2} [\tfrac{1}{2}M\dot{q}^2 - \tilde{E}_B(q,\dot{q}) - V(q)]dt/\hbar \right] \; . \tag{24}$$

When Eq. (10) is substituted in Eq. (23), the ion propagation until the excitation time t corresponds to the propagator Eq. (24). The exponent in Eq. (24) defines an effective Lagrangian for the ions as in Eq. (12).

The Hamiltonian is obtained from the momentum

$$p_B = M\dot{q} - \hbar\,\mathrm{Im}\langle \psi_B(x;q) | \partial\psi_B(x;q)/\partial q \rangle \; . \tag{25}$$

Since $p_B = -i\hbar\partial/\partial q$, its expectation value in a state $\psi_B(x;q)\phi(q)$ yields the two terms in Eq. (25). The Hamiltonian is, therefore,

$$\mathcal{H}_B = \frac{1}{2M}\left[p_B + \hbar\,\mathrm{Im}\left\langle \psi_B \left| \frac{\partial}{\partial q}\psi_B \right.\right\rangle \right]^2 + E_B(q) + V(q) \; , \tag{26}$$

and the corresponding Schrödinger equation is

$$\left[-\frac{\hbar^2}{2M}\left[\frac{\partial}{\partial q} + i\,\mathrm{Im}\left\langle \psi_B(x;q) \left| \frac{\partial}{\partial q}\psi_B(x;q) \right.\right\rangle \right]^2 + E_B(q) + V(q) \right] \phi_B^{(n)}(q) = E_B^{(n)}\phi_B^{(n)}(q) \; . \tag{27}$$

We define an excited-state propagator $K_e(q_2,t_2;q_1,t_1)$ as in Eq. (24), with $\tilde{E}_B$ replaced by $\tilde{E}_e$. A trajectory $q(t)$ in Eq. (23) can be decomposed to a path from (q_1,t_1) to $(\bar{q},t)$ with a propagator K_B and then a path from $(\bar{q},t)$ to (q_2,t_2) with a propagator K_e. Equations (10) and (23) then yield

$$M_e(q_2,t_2;q_1,t_1) = \int_{t_1}^{t_2} dt \exp(-i\omega t) \times \int d\bar{q}\, \mu(\bar{q}) K_B(\bar{q},t;q_1,t_1) \times K_e(q_2,t_2;\bar{q},t) \; . \tag{28}$$

The transition probability involves integrating (28) with the initial and final wave functions $\phi_B^{(n)}(q_1)$ and $\phi_e^{(m)}(q_2)$ and summing on all final states $\{e,m\}$. The argument preceding Eq. (17), now yields the absorption rate

$$\begin{aligned}\mathrm{Re}\sigma(\omega) &= \lim[2\hbar\omega(t_2-t_1)]^{-1}\sum_{e,m}\left| \int\int dq_1 dq_2 [\phi_e^{(m)}(q_2)]^* M_e(q_2,t_2;q_1,t_1)\psi_B^{(n)}(q_1) \right|^2 \\ &= \lim[2\hbar\omega(t_2-t_1)]^{-1}\sum_{e}\int\int\int dq_1 dq_2 dq_3 [\psi_B^{(n)}(q_3)]^* M_e^*(q_2,t_2;q_3,t_1) M_e(q_2,t_2;q_1,t_1)\psi_B^{(n)}(q_1) \; ,\end{aligned} \tag{29}$$

where completeness of the states $\psi_e^{(m)}(q)$ was used and the limit $t_2 - t_1 \to \infty$ is implied.

Substituting (28) in (29) yields a product of four propagators, as illustrated in Fig. 1(a). This can be reduced to products of three propagators by using the closure[9,10] for $t' < t$,

$$\int dq_2 K_e(q_2,t_2;\bar{q},t) K_e^*(q_2,t_2;\bar{q}',t') = K_e^*(\bar{q},t;\bar{q}',t') \; . \tag{30}$$

When $t' > t$, the right-hand side of (30) is replaced by $K_e(\bar{q}',t';\bar{q},t)$. The resulting two terms, as illustrated in Fig. 1(b), correspond to

$$\begin{aligned}\mathrm{Re}\sigma(\omega) = \lim[2\hbar\omega(t_2-t_1)]^{-1}\sum_{e}\int dq_1 dq_3 [\psi_B^{(n)}(q_3)]^* \psi_B^{(n)}(q_1) \int\int d\bar{q}\, d\bar{q}' \mu(\bar{q})\mu^*(\bar{q}') \\ \times \int_{t_1}^{t_2} dt\, e^{-i\omega t}\left[\int_{t_1}^{t} dt' e^{i\omega t'} K_B(\bar{q},t;q_1,t_1) K_e^*(\bar{q},t;\bar{q}',t') K_B^*(\bar{q}',t';q_3,t_1) \right. \\ \left. + \int_{t}^{t_2} dt' e^{i\omega t'} K_B(\bar{q},t;q_1,t_1) K_e(\bar{q}',t';\bar{q},t) K_B^*(\bar{q}',t';q_3,t_1) \right] \; .\end{aligned} \tag{31}$$

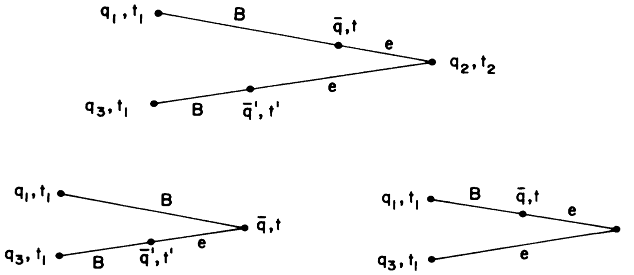

FIG. 1. Schematic representation of an optical absorption process, with B being the initial-state propagator [Eq. (24)] and e an excited state propagator. (a) Representation of Eq. (29) after substituting Eq. (28). (b) Representation of the equivalent two terms in Eq. (31).

To gain insight into the structure of Eq. (31) we consider the semiclassical limit ($\hbar \rightarrow 0$) in which the integrals are dominated by SP points. Each propagator has a phase which is the classical action $S(q,t;q_1,t_1)$; we use[3,10] $\partial S/\partial q = p$ and $-\partial S/\partial t = H$, where $p = p_B$ and $H = H_B$ on the initial trajectory [Eqs. (25) and (26)] and $p = p_e$, $H = H_e$ on the excited trajectory [Eqs. (25) and (26)] with B replaced by e. The SP condition for the $\bar{q},\bar{q}'$ integrals is then

$$p_B(t) = p_e(t), \quad p_B(t') = p_e(t') , \tag{32}$$

while for the t,t' integrals SP yields

$$\hbar\omega = H_e(t) - H_B(t), \quad \hbar\omega = H_e(t') - H_B(t') . \tag{33}$$

Substituting Eqs. (25) and (26) yields

$$\hbar\omega = \tilde{E}_e(q,\dot{q}) - \tilde{E}_B(q,\dot{q}) - \frac{\hbar^2}{2M}\left[\left[\mathrm{Im}\left\langle \psi_e(x;q) \left| \frac{\partial}{\partial q}\psi_e(x;q)\right.\right\rangle\right]^2 - \left[\mathrm{Im}\left\langle \psi_B(x;q) \left| \frac{\partial}{\partial q}\psi_B(x;q)\right.\right\rangle\right]^2\right] \tag{34}$$

at both transitions times t and t'. The last term in (34) modifies Eq. (11) by $\sim(\hbar\omega_B)^2$ terms. When the nonadiabatic terms in Eq. (8) are absent (e.g., real eigenfunctions) the more intuitive result

$$\hbar\omega = E_e(q(t)) - E_B(q(t)) \tag{35}$$

is obtained.

The trajectory $q(t)$ jumps from the initial potential $E_B(q)$ to the excited one $E_e(q)$ at time t and jumps back at time t'. Equation (32) shows that at the jump times $p(t)$ is continuous, while Eq. (33) shows that the energy jumps by $\hbar\omega$. For a given initial trajectory $q_i(t)$ [with the dynamics following $E_B(q_i)$] we need to watch the time evolution of an excited state and find a time $t=\tau$ for which Eq. (34) is satisfied. Since both $q(t)$ and $p(t)$ are continuous at this jump time, they provide initial conditions for the excited-state trajectory. The latter's dynamics follows the potential $E_e(q)$ and is therefore uniquely determined. The same considerations apply also at the return jump. If $q_f(t)$ is a final trajectory [obeying $E_B(t)$], then the excited-state trajectory and the jump time $t' = \tau' > \tau$ must also satisfy Eq. (34).

Applying the SP condition to Eq. (24) yields the classical equation of motion Eq. (13) for the trajectory $q_B(t)$. Since $\phi_B^{(n)}(q)$ propagates via Eq. (24), the AD condition implies that $\phi_B^{(n)}(q)$ is localized near the trajectory $q_B(t)$.

At this stage we employ our short-memory condition, i.e., the excited-state dynamics are very different from those of the initial state. Near the transition point, the excited-state trajectory then deviates rapidly (within one period) from the trajectory $q_B(t)$. Thus the excited-state trajectory is constrained on both of its ends—it has to match both $q_i(t) \simeq q_B(t)$ at $t=\tau$ and $q_f(t) \simeq q_B(t)$ at $t=\tau'$. If $\tau' - \tau \gg T_B$ the excited state will wander away and the matching conditions cannot be satisfied. In a Schrödinger picture the $\tau' - \tau \gg T_B$ situation would correspond to ion wave functions whose overlap is negligible.

We conclude that the t' integral is limited to one period from t. Since there are two jumps per period at (τ_1,τ_2), this allows for either $\tau = \tau' = \tau_1$ or $\tau = \tau' = \tau_2$ and also for $\tau = \tau_1$, $\tau' = \tau_2$ when $\tau_2 - \tau_1 \ll T_B$. For the short interval $\{t,t'\}$ we can therefore replace the dynamics of the excited state by those of the initial state in the trajectory $q_B(t)$, i.e.,

$$K_e^*(\bar{q}t;\bar{q}'t') \simeq K_B^*(\bar{q}t;\bar{q}'t') \times \exp\left[i\int_{t'}^{t} \Delta\tilde{E}_e(t'')dt''/\hbar\right] . \tag{36}$$

Replacing $\mu_e(\bar{q}) \simeq \mu_e(q_B(t))$, $\mu_e(\bar{q}') \simeq \mu_e(q_B(t'))$ we can exactly integrate all of q_1, q_3, $\bar{q}$, and $\bar{q}'$ by using closure [Eq. (30)] and the property $K_B(q_1,t_1;q_3,t_1) = \delta(q_1 - q_3)$ with the result

$$\mathrm{Re}\sigma(\omega) = \lim_{t_2 - t_1 \rightarrow \infty} [2\hbar\omega(t_2 - t_1)]^{-1} \sum_e \int_{t_1}^{t_2} dt \int dt' \mu_e(t)\mu_e^*(t') \exp\left[-i\omega(t-t') - i\int_t^{t'} \Delta\tilde{E}_e(t'')dt''/\hbar\right] . \tag{37}$$

The semiclassical result generally involves a sum of many trajectories with varying energies.[15,16] Yet, in our case, the single trajectory $q_B(t)$ dominates in Eq. (31) (up to a shift in time), which justifies Eq. (36). The sum on all trajectories in Eq. (31) is in fact maintained and can be done exactly once Eq. (36) is used.

The limits on the t' integral correspond to the memory time $t' - t = T_M$ over which the excited-state trajectory tracks the initial one. We wish, however, to be in a situation where minimal information on the excited state is required so that the precise value or even the precise definition of T_M is not essential. This situation is achieved when the t' integral is not sensitive to its precise limits and when it decays rapidly when $|t-t'|\gtrsim T_M$. This is indeed the case when the phase in Eq. (33) is large and the rapid oscillations of the exponential lead to a negligible integral. We thus require

$$\omega(\tau_2-\tau_1)-\int_{\tau_1}^{\tau_2}\Delta\tilde{E}_e(t')dt'/\hbar >> 1 \ , \qquad |\tau_2-\tau_1|\gtrsim T_M \ . \tag{38}$$

The SP points (τ_1,τ_2) where Eq. (34) is satisfied are of particular relevance in Eq. (38). Expanding $\Delta E_e(t)=\hbar\omega_{\min}+\frac{1}{2}d_2t^2$ near a turning point with $d_2\simeq\hbar(\omega_{\max}-\omega_{\min})\omega_B^2$ shows that (38) is equivalent to our assumption on a large-amplitude oscillation,

$$(\omega_{\max}-\omega_{\min})/\omega_B >> (T_B/T_M)^3\gtrsim 1 \ . \tag{39}$$

Hence, for longer T_M the constraint (39) is less stringent and the interference between SP times τ_1,τ_2 is meaningful for longer separations $|\tau_1-\tau_2|$.

Returning to Eq. (37), the t integral can be written as a sum of $(t_2-t_1)/T_B$ integrals as in Eq. (18). The limits T_B of the t integration can be chosen to be far away from the SP points τ_1,τ_2. The potentially important transition sequences are $t=t'=\tau_1$; $t=t'=\tau_2$; $t=\tau_1$, $t'=\tau_2$; and $t=\tau_2$, $t'=\tau_1$. All these transitions are accounted for if the t' is over the same period as the t integral. This yields our central result

$$\mathrm{Re}\sigma(\omega)=\sum_e |I_e(\omega)|^2/(2\hbar\omega T_B) \ , \tag{40}$$

as suggested in Sec. III. $I_e(\omega)$ is defined in Eq. (19) with the provision that the limits $(0,T_B)$ are chosen to be far from the SP points (τ_1,τ_2).

Equation (40) was derived in Sec. III by first assuming infinite time correlation between initial and excited trajectories and then applying coarse graining to Eq. (20) on a scale of ω_B. In this section we have shown the precise meaning of this coarse graining—it means a short time correlation between initial and final trajectories. Precise information on this memory, or correlation time, is not needed if a large-amplitude condition is satisfied.

V. ANALYSIS

In this section we analyze the function $I_e(\omega)$ and obtain some general features of $\mathrm{Re}\sigma(\omega)$. We first evaluate $I_e(\omega)$ by SP methods, which emphasize classical aspects, and then examine $I_e(\omega)$ by Fourier transforms, which show how the classical shape is modulated by quantum features.

Consider $\omega\lesssim\omega_m$, a range that includes the turning point at $\omega_{\min}$. (Similar results hold for $\omega\gtrsim\omega_m$.) We also assume for simplicity a symmetric trajectory, i.e., $q_B(\tau_{\min}+t)=q_B(\tau_{\min}-t)$ where $\tau_{\min}$ is the turning point time, $\Delta E_e(\tau_{\min})=\hbar\omega_{\min}$. There are three regimes with distinct behavior. The first regime is $\omega>\omega_{\min}$ and $\omega-\omega_{\min}$ sufficiently large so that the interference between the two SP points (τ_1,τ_2) [Eq. (34)] is negligible; this is the case of a large phase difference [Eq. (38)]. Thus we expand the phase in Eq. (19) to second order in $t-\tau_1$ [neglecting the slow variation of $\mu(t)$], use $\Delta E(t)=\Delta E(\tau_1)\pm d_1(t-\tau_1)$ where $d_1=|\partial\Delta E(t)/\partial t|$ at $t=\tau_1$ or at $t=\tau_2$ and the integral

$$\int_{-\infty}^{\infty} dt\,\exp[id_1(t-\tau_1)^2/2\hbar]=(2\pi i\hbar/d_1)^{1/2} \ . \tag{41}$$

The integral limits were extended to $\pm\infty$, since in the present regime the integral is dominated by each SP point individually. Summing the equal contribution of τ_1 and τ_2 yields

$$\mathrm{Re}\sigma(\omega)=2\pi|\mu(\tau_1)|^2/(\omega T_B d_1) \ . \tag{42}$$

This is precisely the simple guess of Eq. (15), i.e., the time average of the static form of $\mathrm{Re}\sigma(\omega)$. Equation (15) is thus justified when ω is sufficiently far from a turning point.

The second regime is for small $\omega-\omega_{\min}>0$, i.e., $\tau_1,\tau_2\rightarrow\tau_{\min}$ and $d_1\rightarrow 0$. The procedure for evaluating an integral with two interfering SP points is well known.[10] The region near $\tau_{\min}$ can be transformed to a variable z by

$$-\hbar\omega t+\int_0^t\Delta\tilde{E}_e(t')dt'=\tfrac{1}{3}z^3-\beta z+\gamma \ . \tag{43}$$

The z integral is dominated by its SP points at $z=\pm\sqrt{\beta}$ and can therefore be extended to the limits $\pm\infty$,

$$I_e(\omega)=\int_{-\infty}^{\infty} k(z)\exp[i(\tfrac{1}{3}z^3-\beta z+\gamma)/\hbar]dz \ . \tag{44}$$

The parameters β and γ are identified by equating (43) at SP points $t=\tau_1$ $(z=-\sqrt{\beta})$ and $t=\tau_2$ $(z=\sqrt{\beta})$. Hence

$$\beta=\left[\tfrac{3}{4}\left[\hbar\omega(\tau_2-\tau_1)-\int_{\tau_1}^{\tau_2}\Delta E(t')dt'\right]\right]^{2/3} \ . \tag{45}$$

The function $k(z)=\mu_e(t)dt/dz$ can be expanded as $k(z)=\sum_{m=0}^{\infty}p_m(z^2-\beta)^m$ without odd terms $\sim z(z^2-\beta)^m$ due to the assumed symmetry. This sum defines an asymptotic expansion whose leading $\hbar\rightarrow 0$ term is $m=0$. To identify $p_0=\mu_e(\tau_1)(dt/dz)_{\tau_1}$, evaluate $\partial^2/\partial z^2$ of Eq. (43), which results in $p_0=\mu_e(\tau_1)(2\sqrt{\beta}/d_1)^{1/2}$. The integral in (44) yields then the Airy function[23] $\mathrm{Ai}(-\beta\hbar^{-2/3})$ with the final result

$$\mathrm{Re}\sigma(\omega)=4\pi^2|\mu(\tau_1)|^2(\beta\hbar^{-2/3})^{1/2} \times|\mathrm{Ai}(-\beta\hbar^{-2/3})|^2/(\omega T_B d_1) \ . \tag{46}$$

This expression has several remarkable features. As $\omega\rightarrow\omega_{\min}$ we obtain $\beta\rightarrow\hbar(\omega-\omega_{\min})(2/d_2)^{1/3}$ where $d_2=\partial^2\Delta E_e(t)/\partial t^2$ at $t=\tau_{\min}$ and

$$\mathrm{Re}\sigma(\omega\rightarrow\omega_{\min})=2\pi^2|\mu(\tau_{\min})|^2(2\hbar/d_2)^{2/3}|\mathrm{Ai}((2\hbar/d_2)^{1/3}(\omega_{\min}-\omega))|^2/(\hbar\omega T_B) \ . \tag{47}$$

Since $\mathrm{Ai}(0)=0.35$ is finite, $\mathrm{Re}\sigma(\omega)$ does *not* diverge at $\omega=\omega_{\min}$ and the spurious divergence of the simple guess, Eq. (15), is eliminated. This crucial result is due to proper treatment of the transition-time concept and allowing for interference between transition times near a turning point.

Equation (46) also provides a precise meaning to the crossover into the first regime where interference is negligible. When $\beta\hbar^{-2/3} \gg 1$ the $|\mathrm{Ai}(\;)|^2$ function approaches a rapidly oscillating $\sin^2$ function; replacing the latter by $\frac{1}{2}$ yields the previous result, Eq. (42). The form (47) shows that it is essentially the curvature d_2 that determines the range of significant interference. Using the rough estimate $d_2 \simeq \hbar(\omega_{\max}-\omega_{\min})\omega_B^2$, the range where nonclassical interference is significant is

$$|\omega-\omega_{\min}| \lesssim \omega_B[(\omega_{\max}-\omega_{\min})/\omega_B]^{1/3} \; . \tag{48}$$

In view of the large-amplitude condition, Eq. (39), this range is somewhat larger than ω_B.

The third and final regime of ω is $\omega < \omega_{\min}$, the classically forbidden regime. Since $\mathrm{Re}\sigma(\omega)$, as found below, falls rapidly to zero with $\omega_{\min}-\omega$, it is sufficient to use the expansion near $\tau_{\min}$ and evaluate

$$I(\omega)=\mu(\tau_{\min})\int_{-\infty}^{\infty} dt \exp[-i(\omega-\omega_{\min})t + d_2(t-\tau_{\min})^3/6\hbar] \; . \tag{49}$$

The result is precisely Eq. (47), where now the argument of the Ai function is positive. When this argument is large the result is[27] exponentially small

$$\mathrm{Re}\sigma(\omega) \sim \exp[-\tfrac{2}{3}(2\hbar/d_2)^{1/2}(\omega_{\min}-\omega)^{3/2}] \; . \tag{50}$$

The range $\omega_{\min}-\omega$ over which this nonclassical tail is significant can again be estimated by Eq. (48).

Equation (50) is also significant for estimating nonadiabatic corrections to the initial adiabatic wave function. Equation (6) shows that even for $\mathscr{E}_0=0$ there are terms with frequency $\sim\omega_B$ which may excite the initial state $\psi_B(x;q)$. These nonadiabatic effects are now seen to be negligible; they act as a field with $\omega \simeq \omega_B$, but since $\omega_B \ll \omega_{\min}$, the transition probability from Eq. (50) is

$$\sim \exp[-\omega_{\min}^{3/2}(\omega_{\max}-\omega_{\min})^{-1/2}/\omega_B] \ll 1 \; . \tag{51}$$

We proceed now to examine $I_e(\omega)$ by a different method which emphasizes quantum effects. Since $\int_0^t [\Delta E_e(t')-\hbar\omega_m]dt'$ is periodic, we can define the Fourier expansion

$$\mu_e(t)\exp\left[i\int_0^t [\Delta E_e(t')-\hbar\omega_m]dt'/\hbar\right] = \sum_k g(k)\exp(ik\omega_B t) \; . \tag{52}$$

Substituting in Eq. (19) yields

$$I_e(\omega)=i\sum_k g(k)\frac{\exp[-2\pi i(\omega-\omega_m)/\omega_B]-1}{\omega-\omega_m-k\omega_B} \; . \tag{53}$$

A given $g(k)$ has a maximal contribution at $\omega=\omega_m+k\omega_B$ and additional sidebands spaced by $\sim\omega_B$. This structure appears in $\mathrm{Re}\sigma(\omega)$ when only a few terms $g(k)$ in Eq. (52) are significant, which is the case for low-amplitude oscillations, i.e., $(\omega_{\max}-\omega_{\min})/\omega_B \gtrsim 1$ but not too large. While this is a marginal case for the condition equation (39), this feature indicates quantum effects expected for $\mathrm{Re}\sigma(\omega)$. In fact, the Airy function with negative argument [Eq. (46)] also exhibits such oscillations. Equation (53) indicates that these oscillations persist into the nonclassical regime.

We conclude that the smooth "zeroth-order" guess of Eq. (15) is modified by (a) $\mathrm{Re}\sigma(\omega)$ at a turning point does not diverge, though it may have local maxima; (b) nonclassical regimes have exponentially decaying, but finite contribution; (c) The whole structure is modulated on a scale ω_B. These are not the sharp δ functions of Eq. (20) but rather gentle modulations whose lowest-frequency component is ω_B.

VI. APPLICATION TO POLYACETYLENE

In this section we demonstrate our formalism for the optical absorption from breathers[6] in *trans*-$(\mathrm{CH})_x$. A more detailed presentation of these breathers and their optical absorption is presented elsewhere.[18,28]

trans-$(\mathrm{CH})_x$ is described by the electron-phonon tight-binding Hamiltonian[5]

$$\mathscr{H}=-\sum_n [t_0+\beta(u_n-u_{n+1})](C_{n+1,s}^\dagger C_{n,s}+\mathrm{H.c.}) + \tfrac{1}{2}K\sum_n (u_{n+1}-u_n)^2+\tfrac{1}{2}M\sum_n \dot{u}_n^2 \; , \tag{54}$$

where $C_{n,s}^\dagger$ creates an electron with spin s at site n and u_n is the ion displacement at site n; t_0 is the transfer integral, β is the electron-phonon coupling, K is the ion spring constant, and M is the ion mass. The AD proceeds[5,29] by first solving the electron eigenvectors $\hat{f}_\alpha=\sum_n f_\alpha(n)C_n$ for a fixed-lattice configuration u_n [the analog of Eq. (3)]

$$\epsilon_\alpha f_\alpha(n)=-[t_0+\beta(u_n-u_{n+1})]f_\alpha(n+1) + [-t_0+\beta(u_n-u_{n-1})]f_\alpha(n-1) \; . \tag{55}$$

The second step is the time evolution of $u_n(t)$ [the analog of Eq. (13)],

$$M\ddot{u}_n=-K(2u_n-u_{n+1}-u_{n-1})-\frac{\partial}{\partial u_n}\sum_{\alpha,s}{}' \epsilon_\alpha \; , \tag{56}$$

where $\sum'$ denotes summation on occupied states and ϵ_α are functions of the instantaneous $u_n(t)$ via Eq. (55). The advanced coordinates $u_n(t)$ are then used to find new eigenfunctions in (55), which in turn modify the nonlinear forces in (52), thus repeating this two-step procedure. Note that (55) has charge-conjugation symmetry[5] and for each level at ϵ_α there is a level at $-\epsilon_\alpha$. Also, since (55) defines a real symmetric matrix, the eigenfunctions $f_\alpha(n)$ are real and the correction of Eq. (8) is absent.

The ground state of (54) with one electron per site corresponds to a dimerized lattice $u_n=(-1)^n\bar{u}$. The electron eigenvalues have a gap $2\Delta_0$ in their spectrum, all states with $\epsilon_\alpha \leq -\Delta_0$ are doubly occupied, while all states with $\epsilon_\alpha \geq \Delta_0$ are empty.

Breather states[6,28] are periodic nonlinear oscillations which satisfy Eqs. (55) and (56) with the same occupancy as the ground state, i.e., the lower (upper) halves of the states are doubly occupied (empty). A low-amplitude expansion for the continuum version of (54) (valid when $\Delta_0/t_0 \ll 1$) yields, for the staggered displacement $4(-1)^n \beta u_n(t) = \Delta_0[1+\delta(x,t)]$, which varies slowly with $x = na$,

$$\delta(x,t) = \tilde{\varepsilon}\sqrt{6}\,\mathrm{sech}(x\tilde{\varepsilon}\sqrt{12}/\xi_0)\cos[(1-\tfrac{1}{2}\tilde{\varepsilon}^2)\omega_R t] + \tfrac{3}{2}\tilde{\varepsilon}^2 \mathrm{sech}^2(x\tilde{\varepsilon}\sqrt{12}/\xi_0) \times \{\tfrac{1}{3}\cos[2(1-\tfrac{1}{2}\tilde{\varepsilon}^2)\omega_R t] - 1\} \ . \tag{57}$$

Here a is the lattice constant, $\xi_0 = 2t_0 a/\Delta_0$ is the coherence length, $\omega_R = 4\beta(\pi t_0 M)^{-1/2}$ is a renormalized phonon frequency, and $\tilde{\varepsilon}$ is a continuous variable.

We have numerically solved Eqs. (55) and (56) with (57) as an initial condition and the dimensionless coupling $\lambda = 2\beta^2/(\pi t_0 K) = 0.34$; for $t_0 = 2.5$ this yields $2\Delta_0 = 3.92$. Figure 2 shows the time evolution of the dimerization pattern, exhibiting a persistent, localized large-amplitude oscillation. The breather state is also associated with large oscillations in the highest-occupied and lowest-unoccupied electron eigenvalues. As shown in Fig. 3, these states become "intragap" states with energies well below the ground-state gap Δ_0 $(=1.96)$ during most of the period. The other eigenvalues are above Δ_0 and are weakly affected.

Breathers can be quantized semiclassically,[6,28] such that $\tilde{\varepsilon}$ and the breather energy E'_B depend on an integer quantum number $n \geq 0$,

$$E'_B(n) = \hbar\omega_R(n+\tfrac{1}{2})\left[1 - \frac{\pi^2}{72}\left(\frac{\hbar\omega_R}{\Delta_0}\right)^2 (n+\tfrac{1}{2})^2\right] \ . \tag{58}$$

$E'_B(0)$ is the zero-point motion energy of the ground state, while the excitation energy to the nth state is

$$E_B(n) = E'_B(n) - E'_B(0) \ . \tag{59}$$

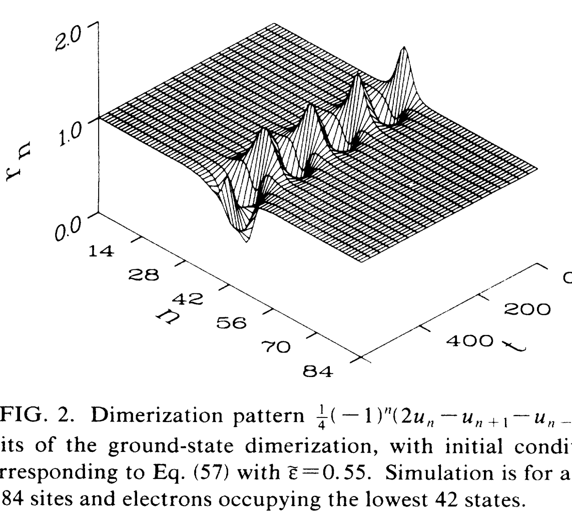

FIG. 2. Dimerization pattern $\frac{1}{4}(-1)^n(2u_n - u_{n+1} - u_{n-1})$ in units of the ground-state dimerization, with initial conditions corresponding to Eq. (57) with $\tilde{\varepsilon} = 0.55$. Simulation is for a ring of 84 sites and electrons occupying the lowest 42 states.

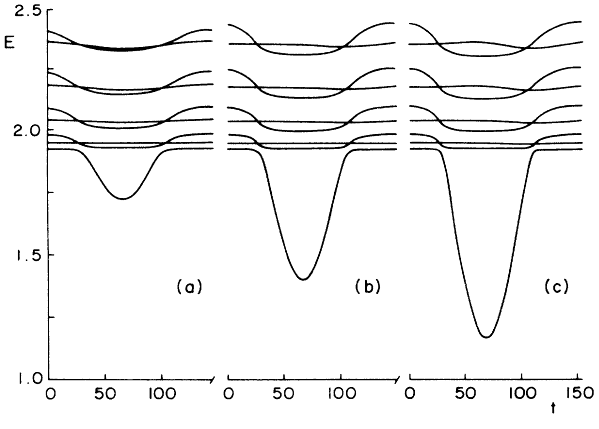

FIG. 3. Lowest-unoccupied electron eigenvalues in one period for three different breathers with quantized amplitudes (Table I): (a) $n = 0$, (b) $n = 1$, (c) $n = 2$. Note the large oscillations of the 43rd intragap eigenvalue. The energy unit corresponds to $t_0 = 2.5$ [Eq. (54)] or $\Delta_0 = 1.96$.

$E_B(1)$ is then the lowest vibration state, i.e., the Raman active mode of oscillations in the dimerization amplitude. As seen from (58), the $n > 1$ states correspond to a bound state of n phonons.

trans-$(\mathrm{CH})_x$ exhibits also nonlinear soliton solutions which can be produced by an electron-hole photoexcitation.[5] Solitons are topologically distinct from the ground state, since they interpolate between the two degenerate ground states of *trans*-$(\mathrm{CH})_x$; hence solitons are produced in pairs. An electron-hole pair with energy $2\Delta_0$ can decay to a pair of moving solitons with energy $\sim 1.4\Delta_0$, while the rest of the energy forms a breather.[6]

The expansion in (58) is not valid for large n. We expect, however, that when $E_B(n)$ exceeds the energy of two static solitons $(\sim 1.2\Delta_0)$ a breather becomes unstable. Thus the number of breather bound states is $\simeq \Delta_0/\hbar\omega_R$.

We have chosen the time unit such that the ratio $E_B(1)/2\Delta_0$ reproduced that of *trans*-$(\mathrm{CH})_x$ where $2\Delta_0 = 1.7$ eV and $E_B(1) = 0.18$ eV for the most strongly coupled Raman mode;[26] with this choice $\hbar\omega_B = 2\pi\hbar/149 = 0.420$ in Fig. 2. Table I shows quantized values of $\tilde{\varepsilon}$ that correspond to $n = 0,1,2$. Using these $\tilde{\varepsilon}$ values, Fig. 3 shows the upper intragap eigenvalue $\epsilon_i(t)$ for one period. The intragap transition energy is $\Delta E_e(t) = 2\epsilon_i(t)$, since the lower intragap level is $-\epsilon_i(t)$. The parameters ω_m, $\omega_{\min}$, and $\omega_{\max}$ corresponding to this $\Delta E_e(t)$ are also given in Table I.

We apply now Eq. (40) to evaluate the optical absorption between the intragap states. The adiabatic assumption on the initial state is well justified $\hbar\omega_B/2\Delta_0 \simeq 0.1$ (Table I). We also need, however, that the excited (upper intragap) state be well separated from other excited states. This is not the case near the upper part of $\epsilon_i(t)$ in Fig. 3, where extended states are closely spaced in a long chain. Most of $\epsilon_i(t)$ is, however, well separated from the extended states, and results for the interesting range $\hbar\omega < 2\Delta_0 - \hbar\omega_B \simeq 1.6$ should be reliable. As for the

TABLE I. Quantized values of $\tilde{\epsilon}$ for generating breather solutions [Eq. (57)]. The excitation energy is E_B [Eq. (59)] and the numerically observed frequency on an 84-site ring is ω_B. The transition energy between the intragap states ($42 \rightarrow 43$ transition) has a mean $\hbar\omega_m$, maximum $\hbar\omega_{\max}$, and minimum $\hbar\omega_{\min}$.

n	$\tilde{\epsilon}$	$E_B/2\Delta_0$	$\hbar\omega_B$	$\hbar\omega_m$	$\hbar\omega_{\min}$	$\hbar\omega_{\max}$
0	0.10	0	0.431	3.725	3.442	3.846
1	0.31	0.107	0.425	3.519	2.798	3.846
2	0.55	0.198	0.420	3.356	2.332	3.848

large-amplitude condition, the $n=0$ case is marginal, while $n=1,2$ satisfy it with $(\omega_{\max}-\omega_{\min})/\omega_B=2.5$ and 3.6, respectively. We also show results for a case with ω_B smaller by a factor of 4, for which the large-amplitude condition is even better satisfied.

To examine the short-memory condition we note that an electron-hole excitation within the intragap states is similar to the same excitation in a uniform ground state; the latter produces a soliton pair within one period,[5,6] which confirms the short-memory assumption.

We have evaluated $\text{Re}\sigma(\omega)$ by using the current operator[28]

$$J=-ie[t_0+\beta(u_n-u_{n+1})](C_n^\dagger C_{n+1}-C_{n+1}^\dagger C_n) \tag{60}$$

and the procedure of Eq. (53). Figures 4, 5, and 6 show our results for the intragap transition of Figs. 3(a), 3(b), and 3(c), respectively. Figure 4 corresponds to $\tilde{\epsilon}=0.1$, which for $\Delta_0=1.96$ and $\hbar\omega_B=0.431$ is the $n=0$ ground state (allowing for zero-point motion). By redefining the time unit we can use the same levels $\epsilon_i(t)$ and matrix elements $\mu_c(t)$ for a different $\hbar\omega_B$. Figure 4 thus shows $\text{Re}\sigma(\omega)$ for $\hbar\omega_B=0.108$ (lower line) which corresponds to $n \simeq 2$ and for $\hbar\omega_B=0.431$ (upper line), the $n=0$ case. The first case is closer to the classical limit and shows increased intensities near the classical turning points (marked by arrows) modulated by structure on the scale of $\hbar\omega_B$. The second case (upper curve) demonstrates more quantum features. The main intensity is near the mean energy $\hbar\omega_m$ and the few sidebands show that the expansion Eq. (53) is dominated by a few terms.

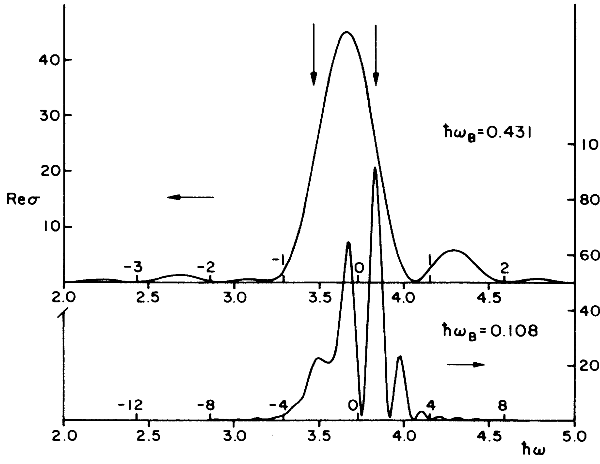

FIG. 4. Optical absorption $\text{Re}\sigma$ corresponding to the $42 \rightarrow 43$ levels of Fig. 3(a). Redefining the time unit in Fig. 3(a) allows for different quantum effects: $\hbar\omega_B$ for the lower line is smaller by a factor of 4 from that of the upper line. The arrows show the limits of the classical range $\hbar\omega_{\min}$ and $\hbar\omega_{\max}$, while the quantum scale, i.e., the distance from $\hbar\omega_m$ in units of $\hbar\omega_B$, is marked above the axis. $\text{Re}\sigma$ is in units of $e^2(2Na\hbar)$, $N=84$.

The fully adiabatic, i.e., static-lattice situation, has a gap at $2\Delta_0=3.92$. It is remarkable then that the zero-point motion can generate a considerable intensity at lower energies. This contribution is peaked within $\hbar\omega_B$ from $2\Delta_0$ and will therefore appear as a tail to the total absorption,[28] consistent with data on *trans*-$(\text{CH})_x$.[20,21]

Figures 5 and 6 show the $\tilde{\epsilon}=0.31$ and $\tilde{\epsilon}=0.55$ cases, respectively. The lower curves show increased classical nature with modulated maxima near the turning points. The upper curves develop more sidebands as $\tilde{\epsilon}$ increases, but an effect of the turning points is not yet apparent. The main intensity is still near $\hbar\omega_m$, which is now below $2\Delta_0-\hbar\omega_B$, and will therefore result in an isolated peak in the total absorption.[28] We have suggested[6,28] that the $n=2$ breather can in fact be photogenerated and its optical absorption accounts for photoinduced absorption data.[23–26]

VII. CONCLUSIONS

We have developed a formalism which for given adiabatic and short-memory conditions yields a simple yet powerful expression for the optical absorption. In particular, our result handles classical turning points for which a "simple" adiabatic approach like Eq. (15) gives an incorrect diverging result.

We note that even if the short-memory condition is satisfied there may be additional interesting contributions by following the excited-state trajectory for longer times.

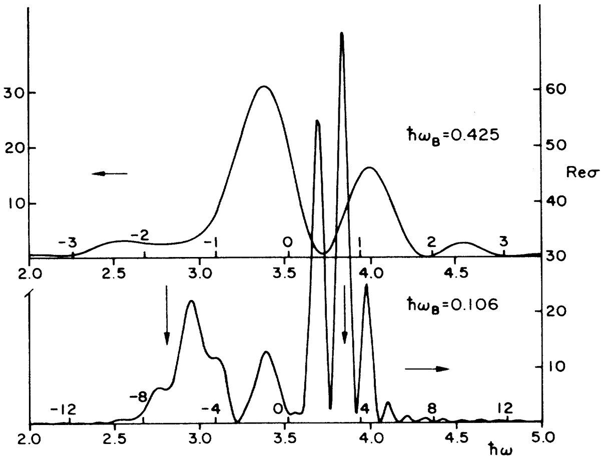

FIG. 5. Same as Fig. 4 for the $n=1$ breather [Fig. 3(b)].

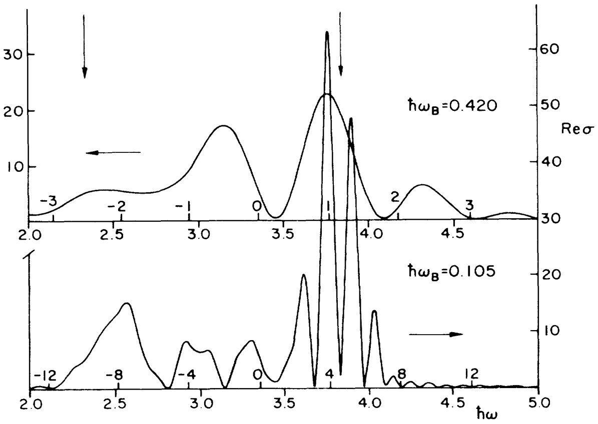

FIG. 6. Same as Fig. 4 for the $n=2$ breather [Fig. 3(c)].

In particular, a photoexcited electron-hole pair in *trans*-$(\mathrm{CH})_x$ with $\hbar\omega < 2\Delta_0$ can tunnel into a soliton pair leading to absorption down to $\hbar\omega \simeq 4\Delta_0/\pi$.[30–32] The overlap of the ionic final wave function with the initial one is very small in this case and we expect this contribution to be much smaller than our results.

We have focused on a periodic initial trajectory. For other types of trajectories, Eq. (40) and (19) should be used with the time integral around a turning point. The precise limits of the integral are not important when the condition (38) is valid. When the probing frequency $\hbar\omega$ is far from a turning point the simple approach of Eq. (15) is justified.

As a side benefit of our derivation we gained insight into the adiabatic approximation in the absence of an external electric field. We have seen that nonadiabatic terms act like an external field with a low frequency ω_B, of the order of a phonon frequency. The rate of decay of an adiabatic wave function is then exponentially small [Eq. (51)]. We have also found a velocity-dependent nonadiabatic correction to the electron eigenvalues, Eq. (8). This correction may be important for (complex) current-carrying eigenfunctions.

We have applied our formalism to a case of current interest, *trans*-$(\mathrm{CH})_x$. Our results account for unusual photoinduced absorption[22–26] data as well as for a pronounced intragap tail of the ground-state absorption.[19–21] Further details on this application and its comparison with experimental data are published elsewhere.[28]

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