Semiclassical Formalism of Optical Absorption and Breathers in Polyacetylene

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A formalism for the optical absorption in a coupled electron-ion system is developed. The formalism assumes an initial trajectory with frequency much lower than electronic energy scales, and a short-memory condition, i.e., the excited-state trajectories diverge away from the initial trajectory within one period. The result shows nonadiabatic features such as level broadening, sidebands, and tails in nonclassical regimes. We apply the formalism to breather modes in polyacetylene and show that they can account for the intragap absorption tail and for the observed photoinduced absorption at 1.35 eV.

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The semiclassical description of many-body 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] A coupled electron-ion system is a natural application, since the heavier ions allow for "adiabatic dynamics,"[3,5] i.e., the ions obey classical dynamics while the electrons follow the ions instantaneously. The presence of an external electromagnetic field poses, however, new difficulties for this formalism by allowance of nonadiabatic effects. 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.

We note that the conventional Franck-Condon[10] 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 density of states.[11,12] Since such derivations are, in general, not feasible for many-body systems, we focus instead on deriving the leading semiclassical behavior. Furthermore, our direct evaluation of the absorption itself manifests the essential role of interference near classical turning points.

Consider a periodic initial state with frequency $\omega_B \ll \omega$, where the external field frequency ω is comparable to the gap in the electronic spectrum. The external field leads to excited states whose ion trajectories are assumed to deviate strongly from the initial trajectory within one period. We show that this "short memory" condition, together with adiabatic conditions (e.g., $\omega \gg \omega_B$), lead to a simple yet powerful expression for the real part of the conductivity $\mathrm{Re}\,\sigma(\omega)$. We apply the formalism to the polyacetylene model[5] and find that it describes the observed intragap absorption tail[13,14] and that nonlinear localized ion oscillators, i.e., breathers,[6] can account for the unusual photoinduced absorption data.[15-18]

A general Hamiltonian for an electron-ion system is

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

Here $q=(q_1,q_2,\ldots)$, $p=(p_1,p_2,\ldots)$, 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 $h(x;q)$ includes the electron kinetic energy, electron-electron interactions, and electron-ion interactions. The adiabatic limit corresponds to our solving $h(x;q)\psi(x;q)=E(q)\psi(x;q)$ considering q as a parameter. Within adiabatic dynamics[5,6] a trajectory $q=q_B(t)$ solves

$$M\ddot{q}(t)=-(\partial/\partial q)[V(q)+E_B(q)], \tag{2}$$

so that the initial-state wave function $\psi_B(x;q_B)$ has the eigenvalue $E_B(q_B)$. The excited states $\psi_e(x;q_B)$ with eigenvalues $E_e(q_B)$ define a complete set $\{\psi_B,\psi_e\}$ which evolves with time since $q_B=q_B(t)$.

To evaluate the optical absorption of ψ_B, we add to (1) $H_{\mathrm{ex}}(x)=(2i/\omega)J(x)\mathcal{E}_0\cos(\omega t)$, where $2\mathcal{E}_0\cos(\omega t)$ is an external electric field and $J(x)$ is the current operator. A simple guess is to use the static ion expression at any time on $q_B(t)$ and then average a period T_B,

$$\mathrm{Re}\,\sigma^{(0)}(\omega)=(\pi/\omega)\sum_e\int_0^{T_B}dt\,|\mu_e(t)|^2\delta(\hbar\omega-\Delta E_e(t))/T_B, \tag{3}$$

where $\Delta E_e(t)=E_e[q_B(t)]-E_B[q_B(t)]$ and $\mu_e(t)=\langle\psi_e(x;q_B(t))|J(x)|\psi_B(x;q_B(t))\rangle$. Equation (3) is similar to the Franck-Condon approximation,[10] except that the initial ion wave function is replaced by integration of q over its semiclassical range $\{q_B(t)\}$. Equation (3) yields absorption in the "classical" range of $\{\Delta E_e(t)\}$. For a periodic $\Delta E_e(t)$, Eq. (3) diverges at the turning points, i.e., at the upper ($\hbar\omega_{\max}$) and lower ($\hbar\omega_{\min}$) bounds of the classical regime.

For a proper derivation of $\mathrm{Re}\sigma(\omega)$ we need to solve Schrödinger's equation for $h(x;q)+H_{\mathrm{ex}}(x)$ whose solution can be expanded as

$$\psi(x,t;q)=c_B(t)\psi_B(x;q)+\textstyle\sum_e c_e(t)\psi_e(x;q),$$

with initial conditions $c_B(t_1)=1$ and $c_e(t_1)=0$. This yields coupled equations for $c_B(t)$ and $c_e(t)$ containing terms like $\langle\psi_B|\partial\psi_B/\partial t\rangle$, $\langle\psi_B|\partial\psi_e/\partial t\rangle$ which oscillate with the frequency ω_B of $q_B(t)$. These nonadiabatic corrections are exponentially small when $\hbar\omega_B \ll \Delta E_e$, $\Delta E_{e'}-\Delta E_e$ [i.e., Eq. (9) with ω replaced by ω_B]. Hence to first order in $\mathcal{E}_0$

$$c_e(t_2)=(\mathcal{E}_0/\hbar\omega)\int_{t_1}^{t_2} dt\,\mu_e(t)\exp\left\{-i\omega t-i\int_{t_1}^{t} E_B[q(t')]dt'/\hbar-i\int_{t}^{t_2} E_e[q(t')]dt'/\hbar\right\}. \tag{4}$$

Here t can be interpreted as the transition time to the excited state.

The energy dissipation $2\mathcal{E}_0^2\mathrm{Re}\sigma(\omega)$ equals the absorbed energy $\hbar\omega\int dx\,|\sum_e c_e(t_2)\psi_e(x;q_B)|^2$ per unit time. We assume first that the single periodic trajectory $q_B(t)$ is involved, which for $t_2-t_1\to\infty$ yields the fully adiabatic expression

$$\mathrm{Re}\sigma^{(1)}(\omega)=\sum_e\sum_{k=-\infty}^{\infty}\pi\delta(\omega-\omega_m+k\omega_B)\,|I_e(\omega)|^2/(\hbar\omega T_B^2), \tag{5}$$

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

$$I_e(\omega)=\int_0^{T_B} dt\,\mu_e(t)\exp\left[-i\omega t+i\int_0^{t}\Delta E_e(t')dt'/\hbar\right]. \tag{6}$$

The smooth envelope function $I_e(\omega)$ is modulated by the rather dense set of δ functions in (5), which represent long-time correlations between initial and final states. We expect these correlations to be seriously violated by nonadiabatic corrections and that coarse graining on a range of ω_B could be a better approximation. Hence

$$\mathrm{Re}\sigma(\omega)=\textstyle\sum_e |I_e(\omega)|^2/(2\hbar\omega T_B). \tag{7}$$

A systematic derivation of (7) is achieved by a functional-integral representation of the ion coordinates while we maintain the Schrödinger picture for the electrons. Thus we use Eq. (4) and a functional average on the trajectories $q(t)$. We define a propagator[9] $K_B(q_2,t_2;q_1,t_1)$ on the initial state with the Lagrangean $\frac{1}{2}M\dot{q}^2-E_B(q)-V(q)$ and similarly $K_e(q_2,t_2;q_1,t_1)$ for an excited state with $E_B(q)$ replaced by $E_e(q)$. After some algebra, the absorption becomes

$$\begin{aligned}\mathrm{Re}\sigma(\omega)=&\lim[2\hbar\omega(t_2-t_1)]^{-1}\int dq_1\int dq_3\,\phi_B^*(q_3)\phi_B(q_1)\int d\bar{q}\int d\bar{q}'\,\mu(\bar{q})\mu^*(\bar{q}')\\&\times\int_{t_1}^{t_2}dt\int_{t_1}^{t_2}dt'\exp[i\omega(t'-t)]K_B(\bar{q},t;q_1,t_1)K_e^*(\bar{q},t;\bar{q}',t')K_B^*(\bar{q}',t';q_3,t_1),\end{aligned} \tag{8}$$

where $t_2-t_1\to\infty$ and $\phi_B(q)$ is the initial ionic wave function.

The semiclassical limit of (8) is obtained by the stationary-phase (SP) condition,[1-4,7,9] i.e., by the requirement that the total phase in the integrand of (8) be extremal for variations in any of $\bar{q},\bar{q}',t,t'$. The SP condition shows that at both jump times from initial to excited state (t) or back from excited to initial state (t'), the time derivative $\dot{q}(t)$ is continuous while the energy change is $E_e(q)-E_B(q)=\hbar\omega$.

We next use two key assumptions: (a) $\phi_B(q)$ is localized near a periodic self-consistent trajectory q_B, valid for $\hbar\omega_B\ll\Delta E_e(t)$; (b) "short memory"—the excited-state dynamics [i.e., $E_e(q)$ in Eq. (2)] is very different from that of the initial state. The excited-state trajectory is constrained, however, at both ends t and t', by the SP matching to $q_B(t)$. Hence if $|t-t'|\gtrsim T_B$ the excited state will wander away and matching is not possible.

We conclude that $|t-t'|\lesssim T_B$ dominates in (8); this short time on the excited-state trajectory allows us to replace K_e^* by K_B^* up to a phase factor $\int_t^{t'}\Delta E_e(t'')dt''/\hbar$. Use of completeness relations and restriction of t and t' to be in the same period then leads to our central result, Eq. (7).

Equation (7) can be evaluated by standard SP methods[9] and shown to recover the short-memory condition. For $\omega_{\min}<\omega<\omega_{\max}$ (classical regime) there are two SP times per period τ_1,τ_2, for which $\Delta E_e(\tau_1)=\Delta E_e(\tau_2)=\hbar\omega$; the larger is $(\omega_{\max}-\omega_{\min})/\omega_B$, the smaller becomes $|\tau_1-\tau_2|$ for which interference (i.e., memory) between τ_1 and τ_2 is important. To achieve $|\tau_1-\tau_2|\lesssim$ actual memory time, we need an adiabatic-type large-amplitude condition $\omega_{\max}-\omega_{\min}\gtrsim\omega_B$. Near the turning points $\omega_{\min},\omega_{\max}$ the interference is essential and it eliminates the divergence of Eq. (3). Furthermore, Eq. (7) allows for absorption in the nonclassical regime $\omega<\omega_{\min}$ (or $\omega>\omega_{\max}$)

$$\mathrm{Re}\sigma(\omega)\sim\exp\left[-\frac{2}{3}\frac{(\omega_{\min}-\omega)^{3/2}}{d^{1/2}}\right] \tag{9}$$

$$(\omega<\omega_{\min}),$$

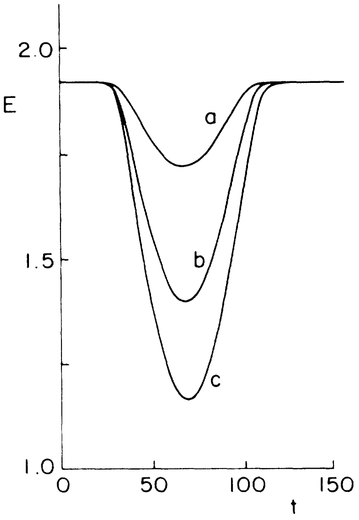

FIG. 1. The 43rd (lowest unoccupied) electron eigenvalue (or minus the 42nd eigenvalue) as a function of time for three different breather amplitudes. The 84-site ring has 84 electrons occupying the lower 42 states, bandwidth of 10, and gap of $2\Delta_0=3.92$. If we choose the time unit such that $\hbar\omega_B=2\pi\hbar/149=0.42$, the states shown are quantized with (a) $n=0$, (b) $n=1$, and (c) $n=2$.

where $d=[\partial^2\Delta E_e(t)/\partial t^2]/2\hbar$ is evaluated at the $\omega_{\min}$ turning point.

We proceed now to investigate this formalism for the ground state and breather excitations of a one-dimensional electron-phonon system, a model which has been applied extensively to polyacetylene.[6,7] The adiabatic ground state has a gap $2\Delta_0$ at the Fermi level; keeping the electron occupancy and quantizing Eq. (2) for ion oscillations leads to a series of bound states with energies $E_B(n)$, termed "breathers."[7] The ground state (*with* zero-point motion) corresponds to $n=0$, $n=1$ is the Raman-active "amplitude" phonon, and the $n>1$ states are localized bound states of n phonons.

Figure 1 shows the lowest unoccupied (or minus highest occupied) electron eigenvalue for three different breathers. Parameters were chosen so that the ratio $E_B(1)/2\Delta_0$ reproduces that of $(\mathrm{CH})_x$ where $2\Delta_0=1.7$ eV and $E_B(1)=0.18$ eV for the most strongly coupled Raman mode.[19] Our formalism is more accurate for large n, though even $n=0$ has $\omega_{\max}-\omega_{\min}\simeq\omega_B$ (Fig. 1). An excited electron-hole pair leads to soliton formation within one period,[5,6] justifying our short-memory assumption.

To demonstrate the features of Eq. (7), we show in Fig. (2) the absorption due to the state in Fig. 1(c) ($42\rightarrow43$ transition). The full line with $\hbar\omega_B=0.105$ corresponds to $n\simeq9$ and is close to the classical limit. The main peaks are near the classical turning points $\hbar\omega_{\min}=2.33$ and $\hbar\omega_{\max}=3.85$ with side branches spaced at $\hbar\omega_B$ intervals. The dashed line with $\hbar\omega_B=0.42$ corresponds to $n=2$ with strong quantum effects. The main intensity is near the mean transition energy $\hbar\omega_m=3.36$ with only few sidebands.

We consider next the total optical absorption involving all the states. The formalism for $\hbar\omega>2\Delta_0$ is less reliable since tunneling between levels in the excited state might be important. We are, however, mainly interested

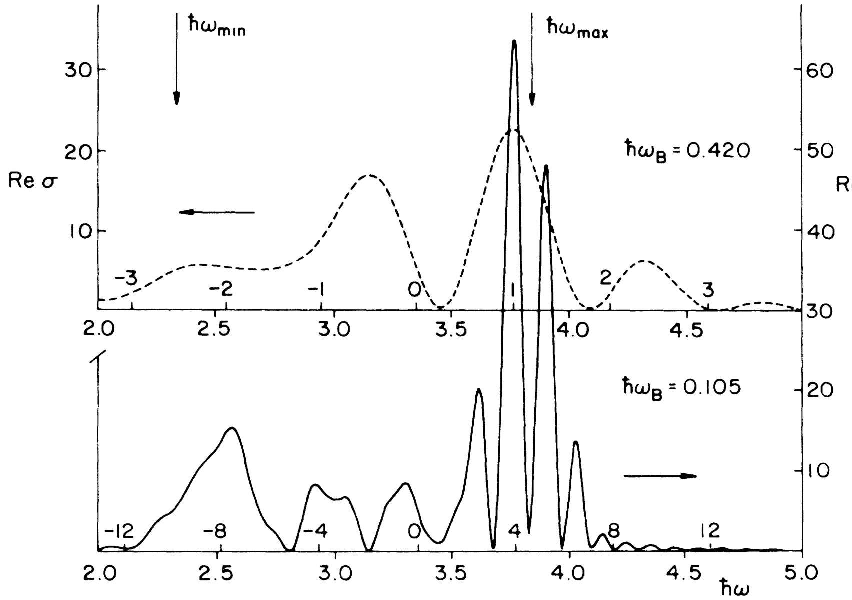

FIG. 2. Optical absorption Reσ of levels $42\rightarrow43$ in Fig. 1(c). Redefining the time unit in Fig. 1(c) allows for different quantum effects with $\hbar\omega_B=0.105$ (full curve) or $\hbar\omega_B=0.42$ (dashed curve). The distance from $\hbar\omega_m$ in units of $\hbar\omega_B$ is marked above axis. Reσ is in units of $e^2/(2Na\hbar)$, $N=84$, a the lattice constant.

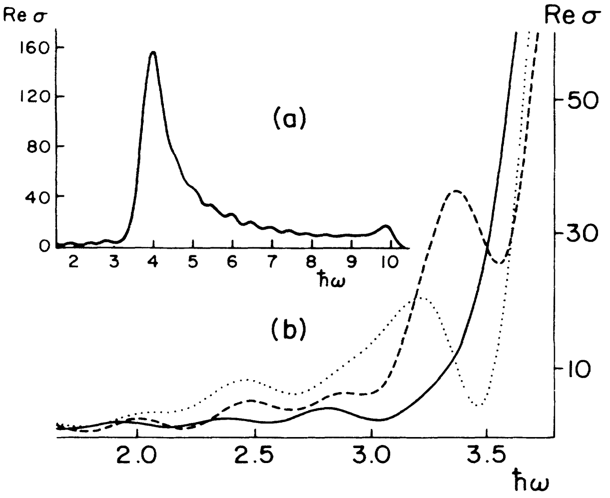

FIG. 3. Total optical absorption for (a) ground state ($n=0$); (b) near absorption edge for $n=0$ (full line), $n=1$ (dashed line), and $n=2$ (dotted line). Units of Reσ are as in Fig. 2; $\hbar\omega$ should be compared with the adiabatic gap $2\Delta_0=3.92$ which corresponds to 1.7 eV in $(CH)_x$.

in the intragap structure which involves a relatively isolated level. Figure 3(a) shows the ground-state absorption ($n=0$) with a pronounced tail below $2\Delta_0$. Experimental data[13,14] indeed show a pronounced tail in the range $\simeq 1.7-1.2$ eV consistent with Fig. 3(a). Other interpretations are a disorder-induced Urbach tail[12,14] or nonadiabatic tunneling into a soliton pair.[20]

Figure 3(b) shows the near-edge absorption of the ground state and that of the $n=1,2$ excited states. The latter states show a clear intragap peak with some weaker sidebands. Photoinduced absorption data[15-18] show a "high-energy" (HE) peak at 1.35 eV $=0.79\times 2\Delta_0$ while the $n=1$ and $n=2$ peaks are at $0.85\times 2\Delta_0$ and $0.81\times 2\Delta_0$, respectively; hence an $n=2$ breather can account for the data.

A few other features support the assignment of the HE peak as due to an $n=2$ breather. Photoinduced absorption polarized perpendicular to the chain[16] (which eliminates non-HE features) shows a significant tail down to $\simeq 1.1$ eV $=0.65\times 2\Delta_0$, consistent with the rather pronounced sideband of $n=2$ at 2.45 eV $=0.62\times 2\Delta_0$. Furthermore, the binding energy of an $n=2$ breather against decaying into two $n=1$ phonons is $\simeq 0.03\Delta_0 \simeq 300$ K. The HE peak has indeed a much shorter lifetime above $\simeq 200$ K.[15,17] The low-temperature lifetime is expected to be long since the breather has an A_g symmetry and cannot decay radiatively. Finally, third-order susceptibility data indicate the presence of one or more A_g states with energy below the optical gap.[21] While the binding of such an A_g state has been attributed to Coulomb correlations,[15] it may instead (or in addition) be due to ion dynamics which form an A_g breather state.

In conclusion, we have shown an efficient semiclassical method for evaluating optical absorption which can apply to a large variety of systems.[1-9] The method, applied to polyacetylene, accounts for unusual absorption data.

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