Dynamics of a one-dimensional Holstein polaron with Davydov Ansätze

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Following the Dirac-Frenkel time-dependent variational principle, dynamics of a one-dimensional Holstein polaron is probed by employing the Davydov D_2 Ansatz with two sets of variational parameters, one for each constituting particle in the exciton-phonon system, and a simplified variant of the Davydov D_1 Ansatz, also known as the $\tilde{D}$ Ansatz, with an additional set of phonon displacement parameters. A close examination of variational outputs from the two trial states reveals fine details of the polaron structure and intricacies of dynamic exciton-phonon interactions. Superradiance coherence sizes, speeds of exciton-induced phonon wave packets, linear optical absorption, and polaron energy compositions are also included in the study.

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I. INTRODUCTION

An electron in an insulating crystal induces a local lattice distortion around itself as it is excited by a photon. The electron together with the locally distorted lattice around it can be viewed as a quasiparticle which is also known as a polaron. Relaxation dynamics of photoexcited entities such as polarons in liquids and solids has recently received much interest thanks to the advent of the ultrafast laser spectroscopy[1–3]. It is now commonly accepted that dephasing and relaxation time scales in condensed matter are approximately picoseconds to tens of picoseconds. Emerging technological capabilities to control femtosecond pulse durations and down-to-one-hertz bandwidth resolutions provide novel probes on vibrational dynamics and excitation relaxation. For example, progress in femtosecond spectroscopic techniques has made it possible to observe a coherent phonon wave packet oscillating along an adiabatic potential surface associated with a self-trapped exciton in a crystal with strong exciton-phonon interactions[4].

Ultrafast events occur on femtosecond to picosecond timescales, and studies of ultrafast relaxation dynamics are a strategic research domain from both fundamental and technological points of view. It is the aim of an ultrafast optical experiment to provide information on the details of temporal evolution on a femtosecond scale, which, in turn, offers insights into fundamental processes governing the dynamics. Developments in ultrafast laser physics and technologies now allow studies of nonequilibrium carrier/exciton dynamics that is previously inaccessible to traditional linear optical spectroscopy. However, theoretical studies of polaron dynamics has not received much-deserved attention due to inherent difficulties in obtaining reliable solutions. Previously, a time-dependent form of the Merrifield-type polaron wave function with zero crystal momentum has been employed to yield an approximative solution to the Schrödinger equation that governs the ultrafast relaxation process of a one-dimensional molecular chain[5–8]. Results show that temporal changes of the exciton coherence size and related energy relaxation strongly depend on the exciton transfer integral, the exciton-phonon coupling strength, and the phonon bandwidth. The applicability of the Merrifield wave function, however, is restricted to the narrow-band regime where the electronic coupling between neighboring molecules is sufficiently weak leaving the electron-phonon coupling at a dominant role. In addition, in the presence of off-diagonal electron-phonon interactions, the Merrifield Ansatz is shown to fail[9].

Beyond the Merrifield Ansatz, there exist several trial wave functions of increasing sophistication to describe the polaron state in a translationally invariant manner such as the Toyozawa Ansatz[10], the Global-Local (GL) Ansatz formulated by Zhao and coworkers in the early 90s[11,12], and a delocalized form of the Davydov D_1 Ansatz that has been constructed very recently[13]. By using these Ansätze, we have previously investigated the ground state polaron energy band and the self-trapping phenomenon of a static Holstein polaron. Far superior results have been obtained compared with the Merrifield Ansatz[9,12,14]. Closely related to those polaron trial states are the Davydov Ansätze which originated from the theory of "Davydov soliton." Seeking to explain storage and transport of biological energy in protein structures, Davydov proposed in 1973 that quantum units of peptide vibrational energy might become "self-localized" through interactions with lattice phonons[15,16]. Following his suggestion, many related studies have been carried out on the "Davydov soliton," an essentially one-dimensional object that maintains dynamic integrity by balancing the effects of nonlinearity against those of dispersion. The original Davydov Ansätze include two forms of varying sophistication, namely, the D_1[17–23] and D_2 Ansätze, with the latter being a special case of the former.

In this work, we employ the Davydov D_2 Ansatz and a localized form factor of the GL Ansatz, previously known as the $\tilde{D}$ Ansatz, to study time evolution of the Holstein polaron following the Dirac-Frenkel time-dependent vari-

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