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Validity of three time-dependent trial states for the Holstein Hamiltonian, namely, the D_2 , Merrifield and $\tilde{D}$ Ansätze has been examined in detail with regards to their deviations from the exact solution to the time-dependent Schrödinger equation. Linear absorption spectra are also calculated as an additional indicator of the Ansatz validity. It is found that the $\tilde{D}$ Ansatz is the most accurate trial state of the three, and all Ansätze fail to provide an adequate description of system dynamics in the weak-coupling regime.

1 Introduction

A quasiparticle induced by electron-phonon or exciton-phonon interactions is usually called a polaron. One of the most frequently used models for polaron is the Holstein molecular crystal model¹. Due to the elusiveness of an exact solution, various numerical approaches were developed in the past decades, including the exact diagonalization (ED)^{2–4}, quantum Monte Carlo (QMC) simulation^{5,6}, variational methods^{7–25}, density matrix renormalization group (DMRG)^{26–29}, and variational exact diagonalization (VED)^{30–35}. Most of these approaches were designed to probe the ground and low-lying excited states properties. Although the higher excited state properties can be obtained by ED, in practice however, memory limitations restrict it to small-sized lattices (typically, below 20 sites). QMC is capable of treating large systems of hundreds of sites, but it suffers from the well-known sign problem. DMRG has proved to be extremely accurate to solve the ground and low-lying excited states properties of 1D system and can deal with sufficiently large system sizes. However, calculations for the higher excited states are not known to be accurate, and so far there exist no efficient DMRG algorithms to tackle non-trivial problems in two or higher dimensions. A variational method attempts to describe a quantum system using an Ansatz with a number of variational parameters. As the variational parameters vary in the complex number space, the Ansatz scans over a subspace of the full Hilbert space. Ansätze which can describe the ground polaron state with sufficient accuracy have been constructed^{13,15}, and their time-dependent counterpart have been used to study the dynamics of polaron formation^{22–24}. VED is one of the most powerful approaches, capable to study the ground- and excited-state properties of the Holstein system in one, two

and higher dimensions^{32,34}. For much higher excited states, VED suffers from computational resource limitations in much the same way as ED, and is restricted to small-sized lattices. Ground-state properties calculated by aforementioned approximations have been compared for accuracy and consistency, and the consensus is that the results obtained for the ground and low-lying excited states in the Holstein systems are reliable. For the excited-state properties and the dynamics of polaron systems, however, none of these approaches provides a satisfactory resolution.

The advent of femtosecond laser spectroscopy^{36–42} made it possible to investigate quasiparticle dynamics at the time scale of optical phonons in molecular crystals. Theories to elucidate the polaron dynamics, such as the time-dependent variant of DMRG, i.e., t -DMRG^{43–46}, were then developed. Since high-lying excited states can not be adequately described by DMRG, t -DMRG is not able to accurately simulate the system dynamics from an arbitrary initial state. Usually the initial state in t -DMRG simulation is obtained by solving a self-consistent equation at the electron or exciton ground state⁴⁵. “Davydov soliton”^{9–11} was proposed in the 1970s to explain storage and transport of biological energy in protein. Kerr and Lomdahl²¹ gave a completely quantum-mechanical derivation of the equations of motion of the Davydov soliton in 1986. Equations of motion derived fully quantum-mechanically differ from their semi-classical counterparts^{11,20}, and give different predictions for observables such as optical spectra. The quantum-mechanical derivation provides a better description of the system than the semi-classical one. To simulate the time evolution of the Holstein polaron, two Davydov Ansätze, namely, the D_1 and D_2 Ansätze, were used following the Dirac-Frenkel variaton scheme^{22–24}. Bloch wave functions built from Davydov Ansätze, such as Toyozawa Ansatz^{7,8} (delocalized form of the D_2 Ansatz) and Global-Local (GL) Ansatz¹² (delocalized form of the $\tilde{D}$ Ansatz), had been utilized to study the ground-state properties of polaron sys-

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tems^{12,18}. Recently, the Merrifield Ansatz⁴⁷ was applied to study the polaron dynamics²⁵. The VED method was applied to the time-dependent case first by Ku and Trugman³⁵ to study the dynamics of Holstein polaron with a single phonon mode. They also discussed the electron-phonon correlation function and the spectral function, and derived a qualitative relation between the polaron formation time and the electron-phonon coupling strength. VED projects an initial quantum state onto a basis consisting of energy eigenstates, then the system dynamics is given by the time evolution of the relevant energy eigenstates. For small systems, ED or VED can also serve as a benchmark to check the accuracies of other numerical approaches. For large system sizes, however, independent checks need to be put in place for the approximate approaches (variational methods, DMRG, *t*-DMRG and VED) to estimate the deviation from the exact solutions to the Schrödinger equation.

The time-dependent variational methods^{21–25} are one of the most computationally efficient approaches to handle polaron dynamics, capable of treating large systems (e.g., 1000 sites). Although the applicability of a variational method is restricted to the subspace spanned by its Ansatz, one can employ various trial states to suit specific applications. Localized Davydov Ansätze, such as the $D_2/\tilde{D}$ Ansatz, are well-suited to simulate the ultra-fast relaxation process of a photo-excited state in a molecular lattice at zero temperature. When one or a few molecules on the lattice are excited by an ultra-short laser pulse, an exciton may be generated on those molecules, and there are no phonon displacements initially. This initial state, which is localized in space, can be approximated by a Davydov Ansatz. Deformation of the lattice is then induced by the exciton-lattice interaction. Using a time-dependent Davydov Ansatz, the dynamics of polaron formation can be investigated following the Dirac-Frenkel time-dependent variational method^{48,49}.

Questions on the validity of the Davydov Ansätze and their translationally invariant variants have been around for decades^{13,15,22–24}. In this contribution we study the validity of three Ansätze, the time-dependent D_2 , Merrifield and $\tilde{D}$ Ansätze for the Holstein model, and estimate deviations of the trial wave functions from those that strictly follow Schrödinger equation. We also derive time evolution equations of the $\tilde{D}$ Ansatz, and provide expressions for linear absorption spectra of the Holstein polaron system, which have not been reported before.

The rest of the paper is organized as follows. Methodology is presented in Section II, including the introduction of the Holstein Hamiltonian and the definition of the deviation vector which reflects the accuracy of the time-dependent trial states compared with the exact wave function obeying the Schrödinger equation. The amplitude of the deviation vector for the D_2 , Merrifield and $\tilde{D}$ Ansätze is also derived, and

compared with system energies with their ratio plotted as a function of the exciton hopping constant J and exciton-phonon coupling constant g in Section III. Linear absorption spectra are also calculated as an additional indicator of the Ansatz validity. Conclusions are drawn in Section IV.

2 Methodology

2.1 Holstein Hamiltonian with the D_2 , Merrifield and $\tilde{D}$ Ansätze

The Holstein molecular crystal model is employed to study the polaron dynamics in a one-dimensional aggregate of N molecules with periodic boundary condition. The Holstein Hamiltonian for the exciton-phonon system can be read^{1,50}

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ex-ph}} + \hat{H}_{\text{ph}} \quad (1)$$

with

$$\hat{H}_{\text{ex}} = -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}), \quad (2)$$

$$\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q, \quad (3)$$

$$\hat{H}_{\text{ex-ph}} = -g \sum_n \sum_q \omega_q \hat{a}_n^\dagger \hat{a}_n (\hat{b}_q e^{iqn} + \hat{b}_q^\dagger e^{-iqn}). \quad (4)$$

Here $\hat{H}_{\text{ex}}$ is the Hamiltonian for a single Frenkel exciton band in a rigid chain where $\hat{a}_n (\hat{a}_n^\dagger)$ is the annihilation (creation) operator for an exciton at the n th site, and J is the exciton transfer integral. $\hat{H}_{\text{ph}}$ is the phonon Hamiltonian where $\hat{b}_q (\hat{b}_q^\dagger)$ is the annihilation (creation) operator of a phonon with momentum q and frequency ω_q , and the Planck's constant for all calculations is set as $\hbar = 1$. $\hat{H}_{\text{ex-ph}}$ describes the linear, diagonal coupling between the exciton and phonons, with g the strength of exciton-phonon coupling. For simplicity, linear phonon dispersion is assumed in this paper

$$\omega_q = \omega_0 [1 + W(2|q|/\pi - 1)] \quad (5)$$

where W is a constant between 0 and 1, the band width of the phonon frequency is $2W\omega_0$, and $\omega_0 = 1$ is set in the formulary of this paper.

In this paper the D_2 , Merrifield and $\tilde{D}$ Ansätze are used as the trial states:

$$|\Psi_{D_2}(t)\rangle \equiv \sum_n \alpha_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \exp \left\{ \sum_q [\beta_q(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}}, \quad (6)$$

$$|\Psi_M(t)\rangle \equiv N^{-1/2} \exp[-i\phi(t)] \sum_n e^{iKn} \hat{a}_n^\dagger |0\rangle_{\text{ex}} \exp \left\{ \sum_q [e^{-iqn} \beta_q(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}}, \quad (7)$$

and

$$|\Psi_{\tilde{D}}(t)\rangle \equiv \sum_n \alpha_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \exp \left\{ \sum_{q \neq 0} \left\{ [\beta_q(t) + e^{-iqn} \gamma_q(t)] \hat{b}_q^\dagger - \text{H.c.} \right\} + [\lambda_0(t) \hat{b}_0^\dagger - \text{H.c.}] \right\} |0\rangle_{\text{ph}}. \quad (8)$$

Here $\alpha_n(t)$ are the variational parameters representing exciton amplitudes for the D_2 [Eq. (6)] and $\tilde{D}$ [Eq. (8)] Ansätze, and $\beta_q(t)$ in Eqs. (6) and (7) are the variational parameters representing phonon displacements for the D_2 and Merrifield Ansätze. While in the $\tilde{D}$ Ansatz, the phonon displacements are $\beta_{q \neq 0}(t)$ and $\gamma_{q \neq 0}(t)$ for $q \neq 0$, and $\lambda_0(t)$ for $q = 0$. With an additional set of parameters to describe the phonons, the $\tilde{D}$ Ansatz is expected to have better performance than the other two relatively simpler Ansätze.

In the Merrifield Ansatz, the exciton amplitudes are described by $N^{-1/2} \exp[-i\phi(t)] e^{iKn}$ (K is the total crystal momentum of the system), and there is only one variational parameter $\phi(t)$ for the exciton amplitudes. In this paper, we restrict our study for the Merrifield Ansatz in the $K = 0$ subspace.

2.2 Deviation Vector and System Energies

For a trial wave function $|\Psi(t)\rangle$ that does not strictly obey the Schrödinger equation, the deviation vector $|\delta(t)\rangle$ can be defined as

$$|\delta(t)\rangle \equiv i \frac{\partial}{\partial t} |\Psi(t)\rangle - \hat{H} |\Psi(t)\rangle. \quad (9)$$

To have a quantitative measure of the Ansatz deviation, one needs to calculate the amplitude of the deviation vector $|\delta(t)\rangle$ defined as $\Delta(t)$:

$$\Delta(t) \equiv \sqrt{\langle \delta(t) | \delta(t) \rangle}. \quad (10)$$

For the Holstein Hamiltonian $\hat{H}$ defined in Eqs. (1)-(4), explicit expressions of $\langle \delta(t) | \delta(t) \rangle$ for the D_2 and $\tilde{D}$ Ansätze are derived in Appendix A, and expressions of $\langle \delta(t) | \delta(t) \rangle$ for the Merrifield Ansatz ($K = 0$ case) are derived in Appendix B.

Substituting Eq. (33) into Eqs. (2), (3) and (4), one obtains the expectation values of various terms in the Holstein Hamiltonian:

$$E_{\text{ex}}(t) \equiv \langle \Psi_D(t) | \hat{H}_{\text{ex}} | \Psi_D(t) \rangle = -2J \sum_n \text{Re} [\alpha_n^*(t) S_{n,n+1}(t) \alpha_{n+1}(t)], \quad (11)$$

$$E_{\text{ph}}(t) \equiv \langle \Psi_D(t) | \hat{H}_{\text{ph}} | \Psi_D(t) \rangle = \sum_n \left[|\alpha_n(t)|^2 \sum_q \omega_q |\lambda_{n,q}(t)|^2 \right], \quad (12)$$

and

$$E_{\text{ex-ph}}(t) \equiv \langle \Psi_D(t) | \hat{H}_{\text{ex-ph}} | \Psi_D(t) \rangle = -2g \sum_n \left\{ |\alpha_n(t)|^2 \sum_q \omega_q \text{Re} [\lambda_{n,q}(t) e^{iqn}] \right\}. \quad (13)$$

Here $S_{n,n+1}(t)$ is the Debye-Waller factor of the Davydov Ansätze [cf. Eq. (42)]. For the D_2 Ansatz, the $K = 0$ Merrifield state, and the $\tilde{D}$ Ansatz, $\lambda_{n,q}(t)$ take the forms of Eqs. (35), (43) and (36), respectively.

Usually, in the parameters range of $g \in [0.1, 1]$ and $J \in [0, 1]$, $E_{\text{ex}}(t)$ of a localized polaron wave function is much smaller than $E_{\text{ph}}(t)$ and $E_{\text{ex-ph}}(t)$.

By comparing $\Delta(t)$ with system energies such as $E_{\text{ph}}(t)$ and $E_{\text{ex-ph}}(t)$, one can gauge the deviation of an Ansatz from the exact wave function that obeys the Schrödinger equation. From this perspective, the comparison between $\Delta(t)$ and the system energy components provide a good reference for the validity of the Ansatz.

2.3 Time Evolution Equations of the Ansätze

The time evolution of the photoexcited state of the one-dimensional molecular aggregate system follows the time-dependent Schrödinger equation. Despite the elusiveness of an exact solution, the time-dependent Schrödinger equation can be solved approximately using the Lagrangian formalism of the Dirac-Frenkel time-dependent variational method^{48,49}. This technique is a powerful tool to obtain approximate dynamics of many-body quantum systems. The Lagrangian L in this paper is formulated as follows

$$L = \langle \Psi(t) | \frac{i}{2} \frac{\overleftrightarrow{\partial}}{\partial t} - \hat{H} | \Psi(t) \rangle = \frac{i}{2} \left[\langle \Psi(t) | \frac{\overrightarrow{\partial}}{\partial t} | \Psi(t) \rangle - \langle \Psi(t) | \frac{\overleftarrow{\partial}}{\partial t} | \Psi(t) \rangle \right] - \langle \Psi(t) | \hat{H} | \Psi(t) \rangle \quad (14)$$

M equations of motion for all the variational parameters $u_m(t)$ ($m = 1, \dots, M$) and their time-derivatives $\dot{u}_m(t)$ can then be obtained from

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{u}_m^*} \right) - \frac{\partial L}{\partial u_m^*} = 0 \quad (15)$$

For the $\tilde{D}$ Ansatz, the variational parameters $u_m(t)$ consist

of $\alpha_n(t)$, $\lambda_0(t)$, $\beta_{q \neq 0}(t)$ and $\gamma_{q \neq 0}(t)$, and

$$\begin{aligned} & \langle \Psi_{\tilde{D}}(t) | \frac{\vec{\partial}}{\partial t} | \Psi_{\tilde{D}}(t) \rangle \\ &= \sum_n \left\{ \alpha_n^*(t) \dot{\alpha}_n(t) + i |\alpha_n(t)|^2 \text{Im} \left\{ \dot{\lambda}_0(t) \lambda_0^*(t) + \right. \right. \\ & \quad \left. \left. \sum_{q \neq 0} [\dot{\beta}_q(t) + e^{-iqn} \dot{\gamma}_q(t)] [\beta_q^*(t) + e^{iqn} \gamma_q^*(t)] \right\} \right\}, \end{aligned} \quad (16)$$

$$\begin{aligned} & \langle \Psi_{\tilde{D}}(t) | \frac{\overleftarrow{\partial}}{\partial t} | \Psi_{\tilde{D}}(t) \rangle \\ &= \sum_n \left\{ \dot{\alpha}_n^*(t) \alpha_n(t) + i |\alpha_n(t)|^2 \text{Im} \left\{ \lambda_0(t) \dot{\lambda}_0^*(t) + \right. \right. \\ & \quad \left. \left. \sum_{q \neq 0} [\beta_q(t) + e^{-iqn} \gamma_q(t)] [\dot{\beta}_q^*(t) + e^{iqn} \dot{\gamma}_q^*(t)] \right\} \right\}. \end{aligned} \quad (17)$$

From Eqs. (11)-(17), time evolution equations of the $\tilde{D}$ Ansatz can be derived:

$$\dot{\lambda}_0(t) = i\omega_0 [g - \lambda_0(t)], \quad (18)$$

$$\dot{\beta}_{q \neq 0}(t) = i \frac{\sum_n \alpha_n^*(t) \Theta_{n,q}(t) e^{-iqn} - \xi_q^*(t) b_q(t)}{1 - |\xi_q(t)|^2}, \quad (19)$$

$$\dot{\gamma}_{q \neq 0}(t) = i b_q(t) - \xi_q(t) \dot{\beta}_q(t), \quad (20)$$

and

$$\begin{aligned} \dot{\alpha}_n(t) &= iJ [S_{n,n+1}(t) \alpha_{n+1}(t) + S_{n,n-1}(t) \alpha_{n-1}(t)] \\ &+ i\alpha_n(t) \text{Re} \left\{ g\omega_0 \lambda_0^*(t) + \right. \\ & \quad \left. \sum_{q \neq 0} [\beta_q^*(t) + e^{iqn} \gamma_q^*(t)] \left\{ i[\dot{\beta}_q(t) + e^{-iqn} \dot{\gamma}_q(t)] \right. \right. \\ & \quad \left. \left. + 2g\omega_q e^{-iqn} - \omega_q [\beta_q(t) + e^{-iqn} \gamma_q(t)] \right\} \right\} \end{aligned} \quad (21)$$

where

$$\xi_q(t) \equiv \sum_n |\alpha_n(t)|^2 e^{iqn}, \quad (22)$$

$$\begin{aligned} \Theta_{n,q}(t) &\equiv \alpha_n(t) \omega_q \left\{ e^{-iqn} [g - \gamma_q(t)] - \beta_q(t) \right\} \\ &+ J\gamma_q(t) [S_{n,n+1}(t) \alpha_{n+1}(t) (e^{-iq} - 1) \\ &+ S_{n,n-1}(t) \alpha_{n-1}(t) (e^{iq} - 1)], \end{aligned} \quad (23)$$

and

$$b_q(t) \equiv \sum_n \alpha_n^*(t) \Theta_{n,q}(t). \quad (24)$$

With Eqs. (18)-(21), the time evolutions of the exciton and phonon are directly obtained by solving this set of differential equations.

Similar approaches can be done for the D_2 and Merrifield Ansätze, which lead to time evolution equations of the D_2 Ansatz:

$$\dot{\beta}_q(t) = i\omega_q \left[g \sum_n |\alpha_n(t)|^2 e^{-iqn} - \beta_q(t) \right], \quad (25)$$

$$\begin{aligned} \dot{\alpha}_n(t) &= i \left\{ J [\alpha_{n+1}(t) + \alpha_{n-1}(t)] + \alpha_n(t) \times \right. \\ & \quad \left. \text{Re} \sum_q [i\dot{\beta}_q(t) + 2g\omega_q e^{-iqn} - \omega_q \beta_q(t)] \beta_q^*(t) \right\}, \end{aligned} \quad (26)$$

and time evolution equations of the Merrifield Ansatz ($K = 0$ case):

$$\begin{aligned} \dot{\beta}_q(t) &= i \left\{ g\omega_q - \omega_q \beta_q(t) \right. \\ & \quad \left. + 2J \text{Re} [S_{0,1}(t) (e^{-iq} - 1)] \beta_q(t) \right\}, \end{aligned} \quad (27)$$

$$\begin{aligned} \dot{\phi}(t) &= -2J \text{Re} [S_{0,1}(t)] \\ &- \text{Re} \sum_q [i\dot{\beta}_q(t) + 2g\omega_q - \omega_q \beta_q(t)] \beta_q^*(t). \end{aligned} \quad (28)$$

where $S_{0,1}(t)$ is the Debye-Waller factor of the Merrifield Ansatz [cf. Eq. (49)].

3 Results and Discussions

3.1 Effects of g , J and W on the Relative Deviation of the Ansätze

The time-dependent variational parameters of the D_2 , Merrifield and $\tilde{D}$ Ansätze can be obtained by solving Eqs. (25)-(26), Eqs. (27)-(28), and Eqs. (18)-(21), respectively. With these variational parameters, one can calculate various properties such as components of the system energy [cf. Eqs. (11)-(13)] and the amplitude of deviation vector $\Delta(t)$ for the Ansätze [cf. Eqs. (41) and (48)].

Fig. 1 shows $\Delta(t)$ and system energies for four different parameter sets (g , J , W) using the D_2 Ansatz. For each calculation, the initial exciton state is one localized at the site $n = 0$ in a 1D molecular ring, i.e., $\alpha_n(0) = \delta_n$, and there is no phonon displacement over the entire ring, i.e., $\beta_q(0) = 0$. Since the Hamiltonian [Eq. (1)] is time-independent, the total

Fig. 1 $\Delta(t)$ (amplitude of the deviation vector $|\delta(t)\rangle$) and system energies of a 16-site one-dimensional Holstein system calculated from the D_2 Ansatz. (a) $g = 0.1$, $J = 0.3$, $W = 0.5$; (b) $g = 0.1$, $J = 0.1$, $W = 0.5$; (c) $g = 0.3$, $J = 0.1$, $W = 0.5$; (d) $g = 0.5$, $J = 0.1$, $W = 0.5$.

energy of the system E_{tot} is expected to be a constant during the time evolution, as shown in the figure. For a case of strong exciton-phonon coupling, $(g, J, W) = (0.5, 0.1, 0.5)$, as shown in Fig. 1d, $\Delta(t)$ is almost negligible compared with the major energy components (e.g., E_{ph} and $E_{\text{ex-ph}}$) of the system, indicating a high accuracy of the D_2 Ansatz in this case. However, as g decreases, the amplitude $\Delta(t)$ increases dramatically as shown in Figs. 1c, 1b and 1a. For the case $(g, J, W) = (0.3, 0.1, 0.5)$, the D_2 Ansatz can still capture nicely exciton-phonon dynamics as indicated by the small $\Delta(t)$ in Fig. 1c, but when g is reduced to 0.1, the D_2 Ansatz is no longer applicable due to a large value of $\Delta(t)$ compared to E_{ph} and $E_{\text{ex-ph}}$ (cf. Figs. 1a and 1b). Thus the D_2 Ansatz can be viewed as a valid trial state for the strong coupling regime.

Figs. 2 and 3 display $\Delta(t)$ and system energies calculated

Fig. 2 $\Delta(t)$ (amplitude of the deviation vector $|\delta(t)\rangle$) and system energies of a 16-site one-dimensional Holstein system calculated from the Merrifield Ansatz. (a) $g = 0.1$, $J = 0.3$, $W = 0.5$; (b) $g = 0.1$, $J = 0.1$, $W = 0.5$; (c) $g = 0.3$, $J = 0.1$, $W = 0.5$; (d) $g = 0.5$, $J = 0.1$, $W = 0.5$.

with the same sets of (g, J, W) parameters using the Merrifield and $\tilde{D}$ Ansatz, respectively. In the Merrifield Ansatz calculation, the initial state is a uniform exciton distribution over the entire molecular ring with no phonon displacement (cf. Fig. 2), while in the $\tilde{D}$ Ansatz calculation (Fig. 3), the initial state includes an electronic excitation localized at $n=0$. As expected, the total system energy E_{tot} keeps constant during the time evolution in all the cases presented in Figs. 2 and 3, as well as in Fig. 1.

From Figs. 1, 2 and 3, it is apparent that the Merrifield and $\tilde{D}$ Ansätze are more accurate than the D_2 Ansatz when the exciton-phonon coupling strength g is relatively small. And in the cases of large g (e.g., $g = 0.5$) and small J (e.g., $J = 0.1$), all three Ansätze provide solutions with almost identical accuracy. However, the information provided by these simple com-

Fig. 3 $\Delta(t)$ (amplitude of the deviation vector $|\delta(t)\rangle$) and system energies of a 16-site one-dimensional Holstein system calculated from the $\tilde{D}$ Ansatz. (a) $g = 0.1$, $J = 0.3$, $W = 0.5$; (b) $g = 0.1$, $J = 0.1$, $W = 0.5$; (c) $g = 0.3$, $J = 0.1$, $W = 0.5$; (d) $g = 0.5$, $J = 0.1$, $W = 0.5$.

parisons are far from sufficient to have a better understanding of the applicability of the Ansätze, thus we have carried out a detailed mapping of $\Delta(t)$ of these Ansätze over a large region of the (g, J, W) parameter space. For simplicity, we define the relative deviation of an Ansatz as

$$\sigma \equiv \frac{\max\{\Delta(t)\}}{\text{avg}\{E_{\text{ph}}(t)\}}, \quad t \in [0, t_{\text{max}}] \quad (29)$$

where t_{max} is the duration of simulated time evolution of these Ansätze. In this paper, the total time used is $t_{\text{max}} = 8(2\pi/\omega_0)$. Thus the smaller the relative deviation σ , the more accurate an Ansatz in describing the system dynamics. By mapping the (g, J, W) parameter space, σ as a function of g and J can be obtained for different values of W , providing a reliable way of finding applicable regimes of the Ansätze.

Fig. 4 Diagram of the relative deviation σ of the D_2 Ansatz versus the exciton-phonon coupling strength g and exciton transfer integral J for three values of phonon bandwidth W , (a) $W = 0.1$; (b) $W = 0.5$; (c) $W = 0.9$. The time evolution duration t_{max} to calculate σ [cf. Eq. (29)] is $8(2\pi/\omega_0)$.

Figs. 4a, 4b and 4c display σ for D_2 Ansatz with $W = 0.1$, $W = 0.5$ and $W = 0.9$, respectively. Similar plots of σ for the Merrifield and $\tilde{D}$ Ansätze can be found in Figs. 5 and 6, respectively. From Figs. 4, 5 and 6 one may conclude that the $\tilde{D}$ Ansatz is the best trial state for a relatively large parameters regime, and the D_2 performance is only limited to a relatively small region. Generally speaking, the relative deviation σ increases as g decreases or as J increases, indicating complicated relationships between exciton and phonons at weak coupling, which may require more sophistication in trial states in order to have a better description. For the cases with small g (e.g., $g \leq 0.1$) and large J (e.g., $J \geq 0.8$), all the Ansätze investigated in this paper have failed to deliver an adequate description of the system dynamics.

It is also revealed by Figs. 5 and 6, that the relative deviation

Fig. 5 Diagram of the relative deviation σ of the Merrifield Ansatz versus the exciton-phonon coupling strength g and exciton transfer integral J for three values of phonon bandwidth W , (a) $W = 0.1$; (b) $W = 0.5$; (c) $W = 0.9$. The time evolution duration $t_{\max}$ to calculate σ [cf. Eq. (29)] is $8(2\pi/\omega_0)$.

σ of the Merrifield trial state or the $\tilde{D}$ Ansatz is determined mostly by the exciton-phonon coupling strength g . For strong coupling ($g \geq 0.5$) cases, no matter what values J and W take, these two Ansätze deviate little from the exact solutions for the time-dependent Schrödinger equation of the Holstein system.

The initial state used in all the simulations for the D_2 Ansatz (Fig. 4) and $\tilde{D}$ Ansatz (Fig. 6) is an exciton localized on one site of the molecular ring. Interestingly, if the initial state of the $\tilde{D}$ Ansatz is the same as that of the Merrifield Ansatz, e.g., uniformly distributed exciton, the former Ansatz can provide results that are almost exactly the same as those from the latter. This case is usually true for the realistic scenarios with a large excitation wavelength and a small system size. One can also introduce a Gaussian distribution or other forms of initial states to approximate realistic situations. In these cases,

Fig. 6 Diagram of the relative deviation σ of the $\tilde{D}$ Ansatz versus the exciton-phonon coupling strength g and exciton transfer integral J for three values of phonon bandwidth W , (a) $W = 0.1$; (b) $W = 0.5$; (c) $W = 0.9$. The time evolution duration $t_{\max}$ to calculate σ [cf. Eq. (29)] is $8(2\pi/\omega_0)$.

the $\tilde{D}$ Ansatz can provide good results in describing a polaron system within a larger span of parameter regimes.

It should be pointed out that for the biologically interesting parameter regimes or the regimes that are important for organic semiconductors, both g and J are usually small⁵¹, the values of these two parameters usually range from 0.1 to 0.5. From the relative deviation σ as displayed in Fig. 4, it is obvious that the D_2 Ansatz is invalid in this region, and the Merrifield Ansatz is neither accurate enough in this region. For most cases, the $\tilde{D}$ Ansatz can provide a relatively accurate solution to the Schrödinger equation due to an additional set of variational parameters used to describe the phonons in the Holstein system. Although the $\tilde{D}$ Ansatz is not sufficiently accurate when $g \leq 0.2$, it still provides a qualitative description for the quantum dynamics of the Holstein system. In order to have

better description of the systems for small g and large J , more sophisticated Ansätze such as D_1 , Toyozawa, GL and delocalized D_1 Ansätze should be considered, however, the simpler Ansätze investigated in this paper can also provide insights in the fundamental understanding of interaction between excitation and lattice deformation that has dramatic impact in the optical and transport properties of materials. The simplicity of an Ansatz is overcome by choosing parameter regimes that are specifically dedicated to the Ansatz by looking into the relative deviation σ studied in this section. It is also possible for one to find materials described by important physical parameters, e.g., g , J and W that within the applicable regimes of the Ansätze used.

3.2 Optical Spectroscopy

Polaron dynamics is closely related to the optical spectroscopy. As the spectroscopy can provide valuable information on various correlation functions, optical spectra shall reveal quantum dynamics of the exciton-phonon system. In this study, the linear absorption spectra for the polaron dynamics calculated with different Ansätze have been studied to check the validity of these trial wavefunctions in various parameter regimes. The linear absorption spectrum $\tilde{F}(\omega)$ can be obtained by the Fourier transformation of the autocorrelation function $F(t)$:

$$\tilde{F}(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty F(t) e^{i\omega t} dt \quad (30)$$

In the exciton-phonon system the correlation function $F(t)$ is formulated as

$$F(t) = {}_{\text{ph}}\langle 0 | {}_{\text{ex}}\langle 0 | \hat{P} e^{-i\hat{H}t} \hat{P}^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \quad (31)$$

where $\hat{P}$ is the polarization operator

$$\hat{P} = \mu \sum_n (\hat{a}_n^\dagger | 0 \rangle_{\text{ex}} {}_{\text{ex}}\langle 0 | + | 0 \rangle_{\text{ex}} {}_{\text{ex}}\langle 0 | \hat{a}_n) \quad (32)$$

with μ the transition dipole matrix element for a single site.

In the time-dependent variational methods, once the variational parameters of the Ansätze are obtained by solving the time evolution equations, various physical quantities such as the autocorrelation function $F(t)$ can then be calculated. Exact expressions of $F(t)$ for the D_2 , Merrifield and $\tilde{D}$ Ansätze are given in Appendix C. The ability of the Ansätze in providing reliable dynamical information can also be gauged by the accuracy of optical spectra calculated from the trial states as analytical expressions for the absorption and fluorescence spectra were well-known if the transfer integral J and the phonon bandwidth W are negligible.

In this study, three representative parameter regimes, corresponding to weak exciton-phonon coupling, intermediate coupling and strong coupling, were selected to compare the absorption spectra of these Ansätze according to the $\Delta(t)$ studies. The parameters are chosen to keep $\sigma < 0.2$, and therefore

Fig. 7 Absorption spectra of the $\tilde{D}$ (a, b, c) and D_2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.1$. Three kinds of initial exciton distributions: single site excitation, Gaussian and uniform distributions are used for the initial states, and the exciton-phonon coupling strength ranges from 0.2 to 0.4, as indicated in the figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

ensuring a relatively accurate description of polaron dynamics by the Ansätze. According to the results on Δ , the $\tilde{D}$ Ansatz is found to have better performance compared to the other two, thus it is also expected for the $\tilde{D}$ Ansatz to generate better spectra.

Three different types of initial states, e.g., single site excitation, uniformly distributed excitation, and excitation with a Gaussian-type distribution spanned on 7 sites, have been applied in the study of optical spectra. Here only the $\tilde{D}$ and D_2 Ansätze are investigated as they differ by one set of variational parameters in describing the phonon behavior. Absorption spectra of Merrifield Ansatz has been studied in elsewhere⁴⁷, thus we will mention them briefly here. To facilitate comparisons, spectral maxima are normalized to 1.

Figs. 7, 8 and 9 demonstrate that the linear absorption spectra can be a very useful indicator of the Ansatz validity in the investigation of the dynamics of a polaron system. For example, in the D_2 Ansatz, the phonon displacement is only described by one set of variational parameters, leading to problems in its description of polaron correlations. When

Fig. 8 Absorption spectra of the $\tilde{D}$ (a, b, c) and D_2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.2$. Three kinds of initial exciton distributions: single site excitation, Gaussian and uniform distributions are used for the initial states, and the exciton-phonon coupling strength ranges from 0.2 to 0.4, as indicated in the figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

Fig. 9 Absorption spectra of the $\tilde{D}$ (a, b, c) and D_2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.3$. Three kinds of initial exciton distributions: single site excitation, Gaussian and uniform distributions are used for the initial states, and the exciton-phonon coupling strength ranges from 0.2 to 0.4, as indicated in the figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

the initial state was a δ -function at site $n = 0$, Figs. 7(a)-(c) reproduces correct spectral features. The lack of accuracy for the D_2 Ansatz is clearly reflected by its ability to capture vibronic spectra as shown in Figs. 7(d)-(f) when the initial electronic excitations adopt a uniform or gaussian distribution. The sensitivity of the spectral behavior that closely related to the accuracy of an Ansatz and the initial state is clearly revealed by comparing Fig. 7(a)-(c) with (d)-(f). In contrast, using the Huang-Rhys theory⁵² as a reference, the $\tilde{D}$ Ansatz can provide smooth and accurate absorption spectra with a tiny value of damping factor added to the Fourier transformation of the autocorrelation function. Moreover, the $\tilde{D}$ phonon sidebands obey a Poisson distribution that is well described by the Huang-Rhys theory. However, for the $\tilde{D}$ spectra with δ -function initial electronic excitations, additional side peaks appears besides the major phonon sidebands as shown in Figs. 7(a)-(c), 8(a)-(c) and 9(a)-(c). Such effect can be eliminated only when the value of J is close or equal to zero. In the DCPA⁵³ and DMFT⁵⁴ study of polaron system, no such effect can be found with finite value of J . Thus we suspect this kind

of lineshape is not physical due to the single site excitation in the all cases.

One can also observe the deterioration of the performance for both $\tilde{D}$ and D_2 Ansätze as J increases, which is in agreement with the trend of the σ results. However, it is also indicated from the figures that the $\tilde{D}$ state has much better performance compared to D_2 , a result in good agreement with the earlier conclusions. Such agreement is a crucial test of the sensitivity of the optical spectroscopy as an indicator of a sound trial state. More importantly, the trends obtained from the spectroscopy as well as the σ calculations provide rational criteria on further improving the performance of an Ansatz. The dramatic contrast between $\tilde{D}$ and D_2 spectra originates in their analytical expressions, where $\tilde{D}$ has superior description of phonons compared to D_2 . However, such improvement is limited by the coherent nature of the phonons parts as initiated from Davydov's original formulism. The static performance of the various polaron Ansatz has revealed limitations of the coherent phonon description in dealing with the situations with very weak exciton-phonon coupling ($g < 0.2$). Thus one

may apply the routines such as gradually increased basis size during the time evolution of a polaron, coupling of multiple phonon modes etc., to improve the performance of an Ansatz at the very weak exciton-phonon coupling regimes. Furthermore, construction of delocalized Bloch trial states with localized states is also a feasible approach.

4 Conclusions

Validity of three time-dependent trial states, namely, the D_2 , Merrifield and $\tilde{D}$ Ansätze has been examined in detail with regards to their deviation from the exact solutions to the time-dependent Schrödinger equation for the Holstein Hamiltonian. The amplitudes of the deviation vectors $\Delta(t)$ of these three Ansätze have been derived, and the relative deviation σ of the Ansätze is defined as the ratio between $\Delta(t)$ and the average phonon energy of the polaron system. By mapping the parameter space of the Ansätze and plotting the relative deviation vector σ as a function of J , g and W , the $\tilde{D}$ Ansatz is found to be a much more accurate trial state than the D_2 Ansatz. The $\tilde{D}$ Ansatz also exhibits superior performance in most parameter regimes compared to the Merrifield Ansatz, indicating the importance of accurate description of phonons in the system. In general, the relative deviation σ increases as g decreases or J increases [cf. Eqs. (41) and (48)]. For the cases with small g (e.g., $g \leq 0.1$) and large J (e.g., $J \geq 0.8$), all the Ansätze investigated in this paper have failed to adequately describe the system dynamics.

To support the validity study, linear absorption spectra have been calculated from the autocorrelation function directly linked to polaron dynamics providing a convenient comparison with experiment. The sensitivity of linear absorption spectra to the detailed dynamics of polaron formation and excited-state relaxation enables us to study the applicability of D_2 and $\tilde{D}$ Ansatz in the weak, intermediate and strong exciton-phonon coupling regimes. The superior performance of the $\tilde{D}$ Ansatz has been shown in all three regimes. The lineshapes of absorption spectra also suggest importance of initial exciton states, where δ -function, Gaussian and uniform initial exciton amplitude results similar spectra only when J is small.

Studies carried out in this work also provide valuable information on how to improve the trial states in a systematic manner. Issues associated with a robust description of phonon displacements and initially delocalized excitonic states can be resolved by formulating Ansätze that can describe both the delocalized and localized states in the molecular ring. The approach here can also extended to include other forms of exciton-phonon interactions such as the off-diagonal coupling. Work in this direction is in progress.

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A Deviation vector amplitudes of the D_2 and $\tilde{D}$ Ansätze

The D_2 and $\tilde{D}$ Ansätze can be written in the general form of the Davydov Ansätze

$$|\Psi_D(t)\rangle = \sum_n \alpha_n(t) \hat{a}_n^\dagger \hat{U}_n^\dagger(t) |0\rangle_{\text{ex}} |0\rangle_{\text{ph}} \quad (33)$$

where $\hat{U}_n^\dagger(t)$ is the Glauber coherent operator

$$\hat{U}_n^\dagger(t) \equiv \exp \left\{ \sum_q [\lambda_{n,q}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} \quad (34)$$

For the D_2 Ansatz [Eq. (6)]

$$\lambda_{n,q}(t) = \beta_q(t), \quad (35)$$

and for the $\tilde{D}$ Ansatz [Eq. (8)]

$$\lambda_{n,q}(t) = \beta_q(t) + e^{-iqn} \gamma_q(t). \quad (36)$$

With the Hamiltonian defined in Eqs. (1)-(4) and the formula for the time derivative of $\hat{U}_n^\dagger(t)$

$$\begin{aligned} \dot{\hat{U}}_n^\dagger(t) &= \sum_q \left\{ [\dot{\lambda}_{n,q}(t) \hat{b}_q^\dagger - \text{H.c.}] \right. \\ &\quad \left. - \frac{1}{2} [\dot{\lambda}_{n,q}(t) \lambda_{n,q}^*(t) - \text{c.c.}] \right\} \hat{U}_n^\dagger(t), \end{aligned} \quad (37)$$

substituting Eq. (33) into Eq. (9), one obtains

$$\begin{aligned} |\delta_D(t)\rangle &= \left\{ \sum_{n,q} [A_{n,q}(t) + B_{n,q}(t) \hat{b}_q^\dagger] \hat{U}_n^\dagger(t) \hat{a}_n^\dagger \right. \\ &\quad \left. + J \sum_n [\alpha_{n+1}(t) \hat{U}_{n+1}^\dagger(t) + \alpha_{n-1}(t) \hat{U}_{n-1}^\dagger(t)] \hat{a}_n^\dagger \right\} \\ &\quad |0\rangle_{\text{ex}} |0\rangle_{\text{ph}} \end{aligned} \quad (38)$$

where

$$\begin{aligned} A_{n,q}(t) &\equiv i\dot{\alpha}_n(t) \left\{ 1 - \text{Re} [\dot{\lambda}_{n,q}(t) \lambda_{n,q}^*(t)] \right\} \\ &\quad + \alpha_n(t) g \omega_q \lambda_{n,q}(t) e^{iqn}, \end{aligned} \quad (39)$$

and

$$B_{n,q}(t) \equiv \alpha_n(t) \left\{ i\dot{\lambda}_{n,q}(t) - \omega_q [\lambda_{n,q}(t) - g e^{-iqn}] \right\}. \quad (40)$$

From Eq. (38) one obtains

$$\begin{aligned}
 & \langle \delta_D(t) | \delta_D(t) \rangle \\
 &= \sum_{n,q,q'} \left\{ A_{n,q'}^*(t) A_{n,q}(t) + A_{n,q'}^*(t) B_{n,q}(t) \lambda_{n,q}^*(t) \right. \\
 & \quad \left. + B_{n,q'}^*(t) A_{n,q}(t) \lambda_{n,q'}(t) \right. \\
 & \quad \left. + B_{n,q'}^*(t) B_{n,q}(t) [\delta_{q,q'} + \lambda_{n,q}^*(t) \lambda_{n,q'}(t)] \right\} \\
 &+ 2J \text{Re} \sum_{n,q} \left\{ [A_{n,q}(t) + B_{n,q}(t)]^* \right. \\
 & \quad [S_{n,n+1}(t) \alpha_{n+1}(t) + S_{n,n-1}(t) \alpha_{n-1}(t)] \left. \right\} \\
 &+ J^2 \sum_n \left\{ |\alpha_{n+1}(t)|^2 + |\alpha_{n-1}(t)|^2 \right. \\
 & \quad \left. + 2\text{Re} [S_{n+1,n-1}(t) \alpha_{n+1}^*(t) \alpha_{n-1}(t)] \right\} \quad (41)
 \end{aligned}$$

where $\delta_{q,q'}$ is a delta-function and $S_{n,m}(t)$ is the Debye-Waller factor of the Davydov Ansätze

$$\begin{aligned}
 S_{n,m}(t) &= \exp \left\{ \sum_q \left\{ \lambda_{n,q}^*(t) \lambda_{m,q}(t) \right. \right. \\
 & \quad \left. \left. - \frac{1}{2} [|\lambda_{n,q}(t)|^2 + |\lambda_{m,q}(t)|^2] \right\} \right\}. \quad (42)
 \end{aligned}$$

B Deviation vector amplitude of the Merrifield Ansatz

The Merrifield Ansatz ($K=0$) [Eq. (7)] can also be written in the form of Eq. (33) with

$$\lambda_{n,q}(t) = e^{-iqn} \beta_q(t) \quad (43)$$

and

$$\alpha_n(t) = N^{-1/2} \exp[-i\phi(t)] \quad (44)$$

With Eqs. (1)-(4) and (37), substituting Eq. (7) into Eq. (9), one obtains the expression of $|\delta(t)\rangle$ for the Merrifield Ansatz ($K=0$):

$$\begin{aligned}
 |\delta_M(t)\rangle &= N^{-1/2} \exp[-i\phi(t)] \\
 & \sum_n \hat{a}_n^\dagger \left\{ [\theta(t) + \varpi_q(t) \hat{b}_q^\dagger] \hat{U}_n^\dagger(t) \right. \\
 & \quad \left. + J \hat{U}_{n+1}^\dagger(t) + J \hat{U}_{n-1}^\dagger(t) \right\} |0\rangle_{\text{ph}} |0\rangle_{\text{ex}} \quad (45)
 \end{aligned}$$

where

$$\begin{aligned}
 \theta(t) &= i\dot{\phi}(t) + g \sum_q \omega_q \beta_q^*(t) \\
 &- \text{Im} \sum_q [i\dot{\beta}_q(t) + 2g\omega_q - \omega_q \beta_q(t)] \beta_q^*(t), \quad (46)
 \end{aligned}$$

and

$$\varpi_q(t) = i\dot{\beta}_q(t) + g\omega_q - \omega_q \beta_q(t). \quad (47)$$

From Eq. (45) one obtains

$$\begin{aligned}
 & \langle \delta_M(t) | \delta_M(t) \rangle \\
 &= |\dot{\phi}(t)|^2 + 4J \text{Re} [S_{0,1}(t)] \text{Re} [\dot{\phi}(t)] \\
 &+ R(t) \left\{ R(t) + 2\text{Re} [\dot{\phi}(t)] + 4J \text{Re} [S_{0,1}(t)] \right\} \\
 &+ 2J^2 \left\{ 1 + \text{Re} [S_{0,2}(t)] \right\} \\
 &+ \sum_q \left\{ |\dot{\beta}_q(t)|^2 - 2\text{Im} [\dot{\beta}_q(t) v_q(t)] \right\} \\
 &+ 2 \sum_q \omega_q [g - \beta_q(t)] \left\{ \text{Re} [v_q(t)] - \text{Im} [\dot{\beta}_q(t)] \right\} \\
 &+ \sum_q \omega_q^2 [g - \beta_q(t)]^2 \quad (48)
 \end{aligned}$$

where $S_{0,n}(t)$ is the Debye-Waller factor of the Merrifield Ansatz

$$S_{0,n}(t) = \exp \left\{ \sum_q |\beta_q(t)|^2 (e^{-iqn} - 1) \right\}, \quad (49)$$

$$R(t) \equiv \text{Re} \sum_q [i\dot{\beta}_q(t) + 2g\omega_q - \omega_q \beta_q(t)] \beta_q^*(t), \quad (50)$$

and

$$v_q(t) \equiv 2J \text{Re} [S_{0,1}(t) (e^{-iq} - 1)] \beta_q(t). \quad (51)$$

C Linear absorption spectra by the D_2 , $\tilde{D}$ and Merrifield ($K=0$) Ansätze

Substituting Eq. (32) into Eq. (31), one can obtain

$$F(t) = \mu^2 \sum_n \sum_m \text{ph} \langle 0 |_{\text{ex}} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}$$

For the periodical Hamiltonian $\hat{H}$, one has

$$\begin{aligned}
 & \sum_m \text{ph} \langle 0 |_{\text{ex}} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \\
 &= \sum_m \text{ph} \langle 0 |_{\text{ex}} \langle 0 | \hat{a}_{m-n} e^{-i\hat{H}t} \hat{a}_{n-n}^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \\
 &= \sum_m \text{ph} \langle 0 |_{\text{ex}} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}
 \end{aligned}$$

Thus, one obtains

$$F(t) = \mu^2 N \sum_m \text{ph} \langle 0 |_{\text{ex}} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \quad (52)$$

wherein $e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}$ is the time evolution from the initial state $\hat{a}_0^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}$, and this time evolution can be approximated

by a localized Davydov trial state:

$$e^{-i\hat{H}t}\hat{a}_0^\dagger|0\rangle_{\text{ex}}|0\rangle_{\text{ph}} \approx \sum_n \alpha_n(t)\hat{a}_n^\dagger \exp\left\{\sum_q [\lambda_{n,q}(t)\hat{b}_q^\dagger - \text{H.c.}]\right\}|0\rangle_{\text{ex}}|0\rangle_{\text{ph}} \quad (53)$$

where the variational parameters $\alpha_n(t)$ and $\lambda_{n,q}(t)$ are initialized by

$$\alpha_n(0) = \delta_n \quad (54)$$

and

$$\lambda_{n,q}(0) = 0, \quad (55)$$

and then solved by the time evolution equations of the Ansatz.

Substitution of Eq. (53) into Eq. (52) obtains

$$F(t) = \mu^2 N \sum_m \alpha_m(t) {}_{\text{ph}}\langle 0 |_{\text{ex}} \langle 0 | \exp\left\{\sum_q [\lambda_{m,q}(t)\hat{b}_q^\dagger - \text{H.c.}]\right\} | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} = \mu^2 N \sum_m \alpha_m(t) \exp\left[-\frac{1}{2} \sum_q |\lambda_{m,q}(t)|^2\right] \quad (56)$$

where $\lambda_{n,q}(t)$ take the forms in Eq. (35) [D₂ Ansatz] or Eq. (36) [D Ansatz].

For the delocalized Ansätze, by substituting Eq. (32) into Eq. (31), one can obtain

$$F(t) = \mu^2 N^{1/2} \sum_m {}_{\text{ph}}\langle 0 |_{\text{ex}} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \sum_n N^{-1/2} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \quad (57)$$

wherein $e^{-i\hat{H}t} \sum_n N^{-1/2} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}$ is the time evolution from the initial state $\sum_n N^{-1/2} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}}$, and this time evolution can be approximated by a delocalized trial state, for example, by a Merrifield trial state:

$$e^{-i\hat{H}t} \sum_n N^{-1/2} \hat{a}_n^\dagger | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \approx N^{-1/2} \exp[-i\phi(t)] \sum_n \hat{a}_n^\dagger \exp\left\{\sum_q [e^{-iqn}\beta_q(t)\hat{b}_q^\dagger - \text{H.c.}]\right\} | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \quad (58)$$

where the variational parameters $\phi(t)$ and $\beta_q(t)$ are solved by the time evolution equations of the Merrifield Ansatz with the initial values

$$\phi(0) = 0 \quad (59)$$

and

$$\beta_q(0) = 0. \quad (60)$$

Then, by substituting Eq. (58) into Eq. (57), one obtains the expression of $F(t)$ by the Merrifield Ansatz:

$$F(t) = \mu^2 \exp[-i\phi(t)] \sum_m {}_{\text{ph}}\langle 0 |_{\text{ex}} \langle 0 | \exp\left\{\sum_q [e^{-iqm}\beta_q(t)\hat{b}_q^\dagger - \text{H.c.}]\right\} | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} = \mu^2 \exp[-i\phi(t)] \sum_m \exp\left[-\frac{1}{2} \sum_q |\beta_q(t)|^2\right] = \mu^2 N \exp[-i\phi(t)] \exp\left[-\frac{1}{2} \sum_q |\beta_q(t)|^2\right] \quad (61)$$

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