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Variational study of polaron dynamics with the Davydov Ansätze

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We derive explicit expressions for the amplitudes of the deviation vectors for the time-dependent Davydov D_1 , D_2 and $\tilde{D}$ Ansätze from the exact solution of the Schrödinger equation for the Holstein polaron.

By comparing the deviation amplitudes with the system energies, a systematic study is carried out on the validity of the Davydov Ansätze.

Keywords: polaron dynamics, Davydov Ansätze, deviation vector amplitude, relative deviation

1 Introduction

Exciton-phonon interactions in condensed phases are usually described by a quasiparticle called a polaron. One of the most frequently used models for polaron is the Holstein molecular crystal model [1]. Various numerical approaches, including the quantum Monte Carlo (QMC) methods [2,3], exact diagonalization (ED) [4] and its variants [5], density matrix renormalization group (DMRG) [6,7], and variational methods [8–12], have been employed in the past decades to explore the static and dynamic properties of a polaron. The most recent QMC development, the diagrammatic Monte Carlo method (DMC), is approximation-free and applicable to macroscopic systems. For small-sized systems, DMRG can also achieve extremely high accuracy for the ground and low-lying-excited properties. However, accuracies of DMRG fail for much-higher-excited states. Despite being less accurate than methods such as DMC, ED and DMRG, variational approaches are often surprisingly efficient and versatile, and can often reveal details accessible only by computationally much more expensive means.

Ansätze based on the “Davydov soliton”[8] theory are among the most often used trial wave functions in variational methods for Holstein polaron. The two original Davydov Ansätze are the D_1 Ansatz and D_2 Ansatz, with the latter being a simplified form of the former. They have been utilized for decades to simulate the time evolution of the Holstein polaron[11,12].

Femtosecond laser spectroscopy[13] makes it possible to investigate the quasiparticle

dynamics at the time scale of optical phonons in molecular crystals. It has also revived research interests in exploring the ultra-fast relaxation processes of photo-excited entities such as polarons in liquids and solids. When one or a few molecules of a lattice are excited by an ultra-short laser pulse, an exciton may be generated on those molecules, and there are no phonon displacements initially. Deformation of the lattice is then induced by the exciton-lattice interaction. This relaxation process from the localized initial exciton state can be simulated by the time evolution of a time-dependent Davydov Ansatz such as the D_1 , D_2 or $\tilde{D}$ Ansatz.

In this paper, we carried out a detailed and systematic study on the validity of the Davydov Ansätze in a one-dimensional Holstein system by computing the Ansätze deviation from the exact solutions of time-dependent Schrödinger equation and comparing the deviation amplitude with the system energies. With the information provided in this study, one can ascertain the validity and applicability of the Davydov Ansätze.

2 Methodology

2.1 The Hamiltonian and the Ansätze

In this paper we study a one-dimensional Holstein molecular crystal model of N sites with periodic boundary condition. The Holstein Hamiltonian for the exciton-phonon system reads as [1,14]

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

with

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

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

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

Here $\hat{a}_n^\dagger$ ($\hat{a}_n$) is the creation (annihilation) operator for an exciton at the n^{th} site, and J is the exciton transfer integral. $\hat{b}_q^\dagger$ ($\hat{b}_q$) is the creation (annihilation) operator of a phonon with momentum q and frequency ω_q , and the Planck's constant is set as $\hbar = 1$. $\hat{H}_{\text{ex-ph}}$ is the linear, diagonal exciton-phonon coupling Hamiltonian with g the coupling constant. For simplicity, linear phonon dispersion with $\omega_q = \omega_0[1 + W(2|q|/\pi - 1)]$ is assumed in this paper, where W is a constant between 0 and 1, and the band width of the phonon frequency is $2W\omega_0$, and $\omega_0 = 1$ is set in the formulary of this paper.

The time-dependent Davydov soliton Ansätze can be written in a general form as

$$|\Psi_{\Gamma}(t)\rangle = \sum_n \alpha_n(t) \hat{a}_n^\dagger \hat{U}_n^\dagger(t) |0\rangle_{\text{ex}} |0\rangle_{\text{ph}}, \quad (5)$$

where $\alpha_n(t)$ are the variational parameters representing exciton amplitudes, and $\hat{U}_n^\dagger(t)$ is the Glauber coherent operator

$$\hat{U}_n^\dagger(t) \equiv \exp \left\{ \sum_q [\lambda_{n,q}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\}. \quad (6)$$

For the D₁ Ansatz, $\lambda_{n,q}(t)$ are $N \times N$ independent variational parameters representing phonon displacements. The D₂ and $\tilde{\text{D}}$ Ansätze are two simplified cases of the D₁ Ansatz. In the D₂ Ansatz, $\lambda_{n,q}(t)$ are replaced by N independent variational parameters $\beta_q(t)$, i.e., $\lambda_{n,q}(t) = \beta_q(t)$. While in the $\tilde{\text{D}}$ Ansatz, $\lambda_{n,q}(t)$ are replaced by $2N - 1$ independent variational parameters $\lambda_0(t), \beta_{q \neq 0}(t)$ and $\gamma_{q \neq 0}(t)$, where $\lambda_{n,q=0}(t) = \lambda_0(t)$, and $\lambda_{n,q}(t) = \beta_q(t) + e^{-iqn} \gamma_q(t), q \neq 0$.

2.2 Deviation vector and its amplitude for the time-dependent Davydov Ansätze

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

$$|\delta(t)\rangle \equiv i \frac{\partial}{\partial t} |\Psi(t)\rangle - \hat{H} |\Psi(t)\rangle, \quad (7)$$

and the deviation amplitude $\Delta(t)$ is defined as

$$\Delta(t) = \sqrt{\langle \delta(t) | \delta(t) \rangle}. \quad (8)$$

For the Holstein Hamiltonian $\hat{H}$ defined in Eqs. (1)-(4), one can derive the explicit expression of $\langle \delta(t) | \delta(t) \rangle$ for the D₁ Ansatz:

$$\begin{aligned} \langle (\delta_{\text{D}_1}(t) | \delta_{\text{D}_1}(t) \rangle &= \sum_n \left| i \dot{\alpha}_n(t) + T_n(t) + \alpha_n(t) R_n(t) \right|^2 \\ &+ \sum_{\alpha_n(t) \neq 0} \sum_q \left| \alpha_n(t) \left[i \dot{\lambda}_{n,q}(t) + \frac{g}{\sqrt{N}} \omega_q e^{-iqn} - \omega_q \lambda_{n,q}(t) \right] \right. \\ &\left. + \Omega_{n,q}(t) \right|^2 + \Delta_{\text{D}}^2(t) - \sum_{\alpha_n(t) \neq 0} \sum_q \left| \Omega_{n,q}(t) \right|^2 \end{aligned} \quad (9)$$

with

$$R_n(t) \equiv \text{Re} \sum_q \left[i \dot{\lambda}_{n,q}(t) + \frac{2g}{\sqrt{N}} \omega_q e^{-iqn} - \omega_q \lambda_{n,q}(t) \right] \lambda_{n,q}^*(t), \quad (10)$$

where $T_n(t)$, $\Omega_{n,q}(t)$ and $\Delta_D^2(t)$ are three expressions which have no item of $\dot{\alpha}_n(t)$ or $\dot{\lambda}_{n,q}(t)$.

For the D_2 Ansatz, Eq. (9) can be further derived to

$$\begin{aligned} \langle \delta_{D_2}(t) | \delta_{D_2}(t) \rangle &= \sum_n \left| i\dot{\alpha}_n(t) + T_n(t) + \alpha_n(t)R_n(t) \right|^2 \\ &+ \sum_q \left| i\dot{\beta}_q(t) + \frac{g}{\sqrt{N}}\omega_q \sum_n |\alpha_n(t)|^2 e^{-iqn} - \omega_q \beta_q(t) \right|^2 \\ &+ \frac{g^2}{N} \sum_q \omega_q^2 \left[1 - \left| \sum_n |\alpha_n(t)|^2 e^{-iqn} \right|^2 \right]. \end{aligned} \quad (11)$$

And for the $\tilde{D}$ Ansatz, Eq. (9) can be further derived to

$$\begin{aligned} \langle \delta_{\tilde{D}}(t) | \delta_{\tilde{D}}(t) \rangle &= \sum_n \left| i\dot{\alpha}_n(t) + T_n(t) + \alpha_n(t)R_n(t) \right|^2 \\ &+ \left| i\dot{\lambda}_0(t) + \frac{g}{\sqrt{N}}\omega_0 - \omega_0 \lambda_0(t) \right|^2 \\ &+ \sum_{q \neq 0} \left| i\dot{\gamma}_q(t) + \xi_q(t)i\dot{\beta}_q(t) + y_q(t) \right|^2 \\ &+ \sum_{q \neq 0} \left[1 - |\xi_q(t)|^2 \right] \left| i\dot{\beta}_q(t) + \frac{d_q(t)}{1 - |\xi_q(t)|^2} \right|^2 \\ &+ \sum_{q \neq 0} \left\{ \sum_n \left| \Theta_{n,q}(t) \right|^2 - \left[|y_q(t)|^2 + \frac{|d_q(t)|^2}{1 - |\xi_q(t)|^2} \right] \right\} \\ &+ \Delta_D^2(t) - \sum_n \sum_q \left| \Omega_{n,q}(t) \right|^2, \end{aligned} \quad (12)$$

where $\xi_q(t)$, $\Theta_{n,q}(t)$, $y_q(t)$ and $d_q(t)$ are four expressions which have no item of $\dot{\alpha}_n(t)$, $\dot{\beta}_q(t)$, $\dot{\gamma}_q(t)$ or $\dot{\lambda}_0(t)$.

2.3 Comparison of $\Delta(t)$ with system energies

Substituting Eq. (5) into Eqs. (2)-(4), one obtains the expressions for the system energies by the Davydov Ansätze in the Holstein model:

$$\begin{aligned}
E_{\text{ex}}(t) &\equiv \langle \Psi_{\text{D}}(t) | \hat{H}_{\text{ex}} | \Psi_{\text{D}}(t) \rangle \\
&= -2J \text{Re} \sum_n \alpha_n^*(t) S_{n,n+1}(t) \alpha_{n+1}(t),
\end{aligned} \tag{13}$$

$$\begin{aligned}
E_{\text{ph}}(t) &\equiv \langle \Psi_{\text{D}}(t) | \hat{H}_{\text{ph}} | \Psi_{\text{D}}(t) \rangle \\
&= \sum_n \left[|\alpha_n(t)|^2 \sum_q \omega_q |\lambda_{n,q}(t)|^2 \right],
\end{aligned} \tag{14}$$

and

$$\begin{aligned}
E_{\text{ex-ph}}(t) &\equiv \langle \Psi_{\text{D}}(t) | \hat{H}_{\text{ex-ph}} | \Psi_{\text{D}}(t) \rangle \\
&= -\frac{2g}{\sqrt{N}} \sum_n \left[|\alpha_n(t)|^2 \text{Re} \sum_q \omega_q \lambda_{n,q}(t) e^{iqn} \right],
\end{aligned} \tag{15}$$

where $S_{n,m}(t)$ is the Debye-Waller factor.

Note that since the unit of $\Delta(t)$ is that of the energy, by comparing $\Delta(t)$ with the main component of the system energies such as $E_{\text{ph}}(t)$ and $E_{\text{ex-ph}}(t)$, one can observe whether the deviation of an Ansatz from obeying the Schrödinger equation is negligible or not, in the concerned case. From this perspective, the comparison between $\Delta(t)$ and energy components of the system provides a good reference for the validity of an Ansatz.

3 Results and discussions

3.1 Validity of the time-dependent $\mathbf{D}_1$, $\mathbf{D}_2$ and $\tilde{\mathbf{D}}$ Ansätze

The time evolution of the variational parameters of an Ansatz can be obtained by solving the corresponding equations of motion (EOM) which can be derived by the Dirac-Frankel time-dependent variational method [15,16]. Once the variational parameters are solved, various properties such as the components of the system energy [Eqs. (13)-(15)] and the deviation vector amplitude $\Delta(t)$ for a given Ansatz can be calculated.

To have a overview of the variation of $\Delta(t)$ of the Ansätze within a large region of the (g, J, W) parameter space, we define the relative deviation of a time-dependent Ansatz as:

$$\sigma \equiv \frac{\max\{\Delta(t)\}}{\text{avg}\{E_{\text{ph}}(t)\}}, \quad t \in [0, t_{\text{max}}] \tag{16}$$

where $t_{\max}$ is the maximum value of time t in the duration of each time evolution of the Ansätze. In this paper, the total time used is $t_{\max} = 8(2\pi/\omega_0)$. Thus the smaller the relative deviation σ , the more accurate an Ansatz is in describing the system. By scanning the parameter space, σ can be obtained as a function of g and J for different values of W .

Fig. 1(a)-1(f) show σ as a function of g and J for the D_2 , $\tilde{D}$ and D_1 Ansätze with $W = 0.1$ and $W = 0.5$. From Fig. 1 one may conclude that the D_1 Ansatz is the best trial state for a relatively large volume of the parameter space, and the D_2 performance is only limited to a very small region. Generally speaking, the relative deviation σ increases as g decreases or J increases, indicating complicated relationships between exciton and phonons at weak coupling or possible large polaron regions. For the cases with small g (eg., $g \leq 0.4$) and large J (eg., $J \geq 0.9$), all the Ansätze investigated in this paper have failed to describe the system. It is also revealed by Fig. 1 that the relative deviation σ of the $\tilde{D}$ and D_1 Ansätze are determined mostly by the exciton-phonon coupling strength g . For strong coupling ($g \geq 2.0$) cases, no matter what values J and W take, these two Ansätze deviate little from the exact solution to the time-dependent Schrödinger equation of the Holstein polaron system.

From Fig. 1 one can also notice that the difference between the accuracies of the $\tilde{D}$ and D_1 Ansätze is much smaller than the difference between the D_2 and D_1 Ansätze. In other words, the $\tilde{D}$ and D_1 Ansätze are close to each other.

3.2 Linear absorption spectroscopy

Polaron dynamics is closely related to the optical spectroscopy. In this study, linear absorption spectra for the polaron dynamics calculated with three Ansätze have been examined to check the validity of these trial wave functions in various parameter regimes. The linear absorption spectrum $\tilde{F}(\omega)$ can be obtained by the Fourier transformation of the autocorrelation function $F(t)$:

$$\tilde{F}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} F(t) e^{i\omega t} dt \quad (17)$$

where $F(t)$ can be calculated with the time-dependent Davydov Ansätze [17].

Figs. 2(a)-2(d) depict the linear absorption spectra calculated from the D_2 , $\tilde{D}$ and D_1 Ansätze for four different sets of (g, J, W) parameters. The spectrum calculated from an Ansatz should be a curve above the zero line if the Ansatz is accurate enough. In Fig. 2(a), however, the spectrum by the D_2 Ansatz shows negative values at some values of ω . This is also apparent in the spectra obtained with the $\tilde{D}$ Ansatz. The greater a resulting spectrum trails in the negative region, the worse is the accuracy of its underlying Ansatz. This result is consistent with the σ study. In Figs. 2(b)-2(d), both the D_1 and $\tilde{D}$ Ansätze yield precisely good spectra. While in Fig. 2(b), the spectrum by the D_2 Ansatz still has negative values. In Fig. 2(c), although the spectrum by the D_2 nearly has no negative values, but there are several peaks with no physical meaning, which are caused by the inaccuracy of the Ansatz.

As revealed by Figs. 2(a)-2(d), the magnitudes of the negative values of the spectra, hence the relative deviations of the Ansätze decrease when g increases or J decreases. And in all the four parameter regimes investigated and presented in Figs. 2(a)-2(d), the D_1 Ansatz yields spectra showing no negative values and with smoothest profiles, thereby establishing firmly, its superiority.

4 Conclusion

The validity of the time-dependent D_1 , D_2 , and $\tilde{D}$ Ansätze has been studied in detail with regards to their derivation from the exact solutions of time-dependent Schrödinger equation for the Holstein polaron. The amplitudes of the deviation vectors $\Delta(t)$ corresponding to these three Ansätze have been derived. 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 D_1 and $\tilde{D}$ Ansätze are found to have much better performance than the D_2 Ansatz, with the D_1 Ansatz being the most accurate. In general, the relative deviation σ increases as g decreases or J increases. For the cases with small g (e.g., $g \leq 0.4$) and large J (e.g., $J \geq 0.8$), all the three Ansätze have failed to describe the system. In addition, linear absorption spectra have been calculated from the time-dependent Ansätze. Spectral comparison lends further support to our validity study based on the relative deviation σ .

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Fig. 1 The relative deviation (σ) versus g and J for the D_2 (upper row), $\tilde{D}$ (middle row) and D_1 (bottom row) Ansätze.

Fig. 2 Linear absorption spectra for the D_2 , $\tilde{D}$ and D_1 Ansätze. (a) $g = 0.4$, $J = 0.3$, $W = 0.5$; (b) $g = 0.4$, $J = 0.1$, $W = 0.5$; (c) $g = 1.2$, $J = 0.1$, $W = 0.5$; (d) $g = 2.0$, $J = 0.1$, $W = 0.5$.

Fig. 1.

Fig. 2.