Hamiltonian defined in Eq. (1) is time-independent, the total energy of the system is expected to be a constant during the time evolution. At $t = 0$, an exciton is assumed localized at one site and there are no phonons on the entire ring. As shown in Fig. 11, the phonon energy $E_{\rm ph}$ rises from zero and oscillates as time goes on. In the meantime, the interaction energy between the exciton and phonons, $E_{\rm ex-ph}$, oscillates with almost the same amplitude but an opposite sign. And the total energy $E_{\rm tot}$ of the system stays as a constant at all times. As shown in Figs. 11a and 11b, the D_2 Ansatz and Merrifield Ansatz agree with each other when J is small and S is large. However, when J is large (e.g., $J = 1.0$) and S is small (e.g., $S = 0.5$), these two Ansätze no longer agree. For this case, the Merrifield Ansatz, which is translationally invariant (a Bloch wave function) but with a built-in small-polaron correlation, is not suitable to describe the dynamics. As shown in Figs. 11c and 11d, the total system energy $E_{\rm tot}$ vanishes during the time evolution of the $\tilde{\rm D}$ Ansatz. While in the Merrifield Ansatz, $E_{\rm tot}$ remains at a constant value -2 that is equal to the initial value of $E_{\rm ex}$. This is because in the Merrifield Ansatz, the exciton amplitude is assumed to distribute uniformly over all the sites of the system, thus according to Eq. (2), $E_{\rm ex}$ has a negative value when J is not negligible. However, for an initial state in which the exciton is localized at one site, according to Eq. (2), $E_{\rm ex}$ should be zero at $t = 0$ as shown in Figs. 11c and 11d for the $\tilde{\rm D}$ Ansatz. This shows that the $\tilde{\rm D}$ Ansatz is a more flexible trial state than the Merrifield Ansatz.

Lastly, we give a brief discussion on the validity of the Davydov Ansätze. A Davydov Ansatz is an approximative solution to the Schrödinger equation with the Holstein Hamiltonian. For a trial wave function $|D(t)\rangle$ that does not strictly obey the Schrödinger equation, the deviation vector $|\delta(t)\rangle$ can be written as

$$|\delta(t)\rangle \equiv i\hbar\frac{\partial}{\partial t}|D(t)\rangle - \hat{H}|D(t)\rangle \tag{32}$$

Here $\hat{H}$ is the Holstein Hamiltonian Eq. (1). For the Davydov D_1 Ansatz, the explicit form of $|\delta(t)\rangle$[17] was given by Škrinjar *et al.* in 1988. It was also proven that $|\delta(t)\rangle$ is orthogonal to $|D_1(t)\rangle$. However, such orthogonality relations are insufficient to conclude that the deviation vector $|\delta(t)\rangle$ is negligible, and the trial state is a good approximation to the true solution of Schrödinger equation. To have a quantitative measure of the Schrödinger-equation deviation, one needs to calculate the amplitude of the deviation vector $|\delta(t)\rangle$, which is defined as $\Delta(t)$:

$$\Delta(t) \equiv \sqrt{\langle\delta(t)|\delta(t)\rangle} \tag{33}$$

An explicit expression for $\Delta(t)$ as the D_2 Ansatz is substituted into the Schrödinger equation is derived in Appendix F.

Note that the dimension of $\Delta(t)$ is that of the energy. Therefore, one can gauge whether the trial state is a good approximative solution by comparing $\Delta(t)$ with the system energies. Two examples of such comparisons for the D_2 Ansatz are shown in Figs. 12a and 12b. The control parameters in Figs. 12a and 12b are the same as those in Figs. 11a and 11b, respectively. For both two cases, the main system energies are $E_{\rm ph}$ and $E_{\rm ex-ph}$, and $\Delta(t)$ is found to be negligible to either $E_{\rm ph}$ or $E_{\rm ex-ph}$. We conclude that the D_2 Ansatz yields quantitatively accurate solutions to the Schrödinger equation for these two cases.

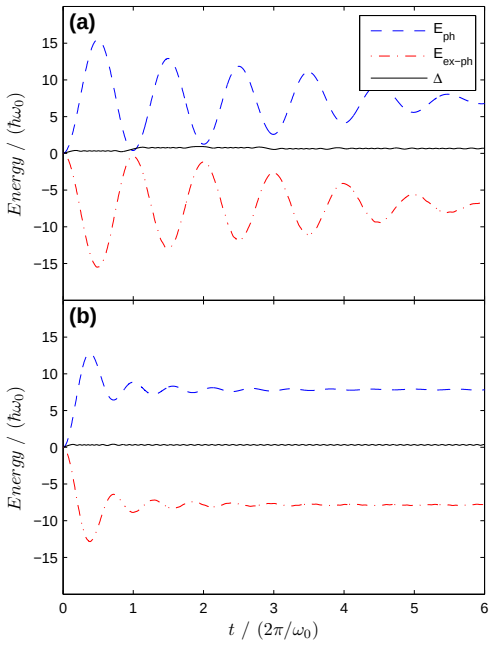

FIG. 12: Amplitude of the deviation vector $|\delta(t)\rangle$ calculated from the D_2 Ansatz. The results are compared with the system energies. (a) $J = 0.1$, $W = 0.1$, $S = 4.0$; (b) $J = 0.1$, $W = 0.8$, $S = 4.0$.

IV. CONCLUSION

In this paper we simulate polaronic dynamics in a one-dimensional molecular chain following the Dirac-Frenkel time-dependent variational approach. After the optical excitation, the coupled exciton-phonon system will undergo a relaxation process from the initial photo-induced nonequilibrium. Based on the Holstein Hamiltonian, we examined time evolution of the exciton amplitude, the reduced exciton density matrix, the exciton coherence size, linear optical absorption, and induced phonon displacements for two types of variational wave functions, namely, the Davydov D_2 Ansatz, and a simplified variant of Davydov D_1 Ansatz, also known as the $\tilde{\rm D}$ Ansatz. It is shown that following the equations of motion derived from the time-dependent variation, the exciton amplitude will transfer from the site of creation to neighboring sites, and as J increases, the velocity of exciton propagation will increase as well. Exciton-induced phonon deformations can be found to form at the locations where the