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Influence of electron-electron interaction on the vibrational frequency in one-dimensional dimerized conjugated systems

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We apply the correlated-basis-function approach to study the vibrational stretching mode in a one-dimensional dimerized conjugated system modeled as a Kronig-Penney square-well lattice. Polyacetylene is taken as prototypical example. Various potential parameters are considered in the one-dimensional energy-band calculations. We find that the one-electron theory is unable to afford simultaneously reasonable descriptions of the electronic and vibrational properties, which indicates the importance of electron-electron interaction in the vibrational modes (and lattice relaxation). Our parameters are selected according to the ionization potential value in polyacetylene. Electron-electron interaction is taken as a screened Coulomb potential. The correlated wave function is evaluated through the Chakravarty-Woo equation within the convolution approximation. We find that electron-electron interaction generally increases the stretching-mode frequency; however, in systems with very large spring constants, the vibrational frequency first decreases as the electron-electron interaction strength increases, then levels off and begins to increase.

I. INTRODUCTION

Electron-electron (*e-e*) interactions in one-dimensional (1D) systems have been studied extensively in recent years. Many contributions have been devoted to the effect of *e-e* interaction on dimerization and optical excitations.[1-5] However, understanding of the influence of *e-e* interaction on vibrational properties remains at an almost primitive stage in 1D conjugated systems. In fact, *e-e* interactions have been taken into account only at the Hartree-Fock level, but within this regime their effects are very small.[6]

The resonant Raman spectrum of polyacetylene, the prototypical 1D conjugated compound, indicates the presence of two prominent peaks; these have been attributed to the double-bond- and single-bond-stretching modes.[7,8] This assignment has been confirmed by Kürti and Kuzmany within a single-electron Hückel-type Longuet-Higgins-Salem model,[9] as well as by Zerbi and co-workers not only for polyacetylene but also for several other kinds of conjugated polymers.[10] The stretching mode, also denoted as the dimerization amplitude,[8] or $\mathfrak{A}$ mode,[10] has strong coupling with electron excitations. This coupling has been analyzed in the context of the vibronic structures of photoabsorption and photoluminescence processes in conjugated polymers and oligomers;[11] these phenomena are of importance, for instance, due to the recent development of optical devices such as light-emitting diodes.[12]

In this work, we exploit the Jastraw-Feenberg variational correlated-basis-function (CBF) theory to study the *e-e* interaction effect on stretching modes. CBF theory has been successfully applied in studying various correlated systems,[13] such as quantum liquids, nuclear matters, metal surfaces, and, more recently, 1D conjugated systems with respect to dimerization,[1] optical transition,[5] and soliton creation.[14] There are several advantages in using the CBF method: (i) there occurs no finite-size effect, since we are explicitly dealing with an infinite system; (ii) the *e-e* interaction can be expressed in the form of a complete potential, rather than in that of a truncated expansion; and (iii) explicit (through variation) many-body wave functions in terms of one-electron densities and two-body correlation functions can be obtained.

We briefly describe the CBF methodology in Sec. II. In Sec. III, we present some results for polyacetylene on the one-electron energy bands within the 1D Kronig-Penney model; the main results obtained when *e-e* interactions are included are presented and discussed in Sec. IV.

II. MODEL HAMILTONIAN AND CORRELATED-BASIS-FUNCTION THEORY

The Hamiltonian for a 1D system is expressed as

$$\begin{aligned} H &= H_0 + \tfrac{1}{2}\sum_{i,j} V(x_i,x_j) + \tfrac{1}{2}K\sum_j (R_{j+1}-R_j-a)^2 , \\ H_0 &= \sum_i \left[-\frac{\hbar^2}{2m}\nabla_i^2 + \sum_j V_0(x_i-R_j) \right] , \end{aligned} \tag{1}$$

where $V_0(x_i-R_j)$ is the potential produced by site R_j on an electron at position x_i and $V(x_i,x_j)$ is the electron-electron interaction potential. The last term in Eq. (1) describes the elastic energy term due to dimerization, K being the spring constant. The one-electron Hamiltonian can be solved rigorously for model potentials to obtain the complete basis ϕ_k:

$$H_0\phi_k(x)=\epsilon_k\phi_k(x) \ . \tag{2}$$

The many-body ground-state wave function of (1) is written down in the Jastraw variational form:

$$\Psi(1,2,\ldots,N)=D[\phi_k]\exp\left[\sum_{ij}u(x_i,x_j)\right] . \tag{3}$$

$D[\phi_j]$ is the many-body wave function of H_0 (a Slater determinant), and $u(x_i,x_j)$, called the correlation factor, is a variational function which comes from the *e*-*e* interactions. The total energy of the ground state is obtained as

$$\begin{aligned}E&=\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}\\&=\sum_{\text{occ}}\epsilon_k+\tfrac{1}{2}\int d1\int d2[P(1)-n_0]V(1,2)[P(2)-n_0]+\tfrac{1}{2}\int d1\int d2P(1)P(2)V(1,2)[g(1,2)-1]\\&\quad+\frac{\hbar^2}{8m}\int d1\int d2P(1,2)(\nabla_1u_{12})^2+\frac{\hbar^2}{8m}\int d1\int d2\int d3P(1,2,3)(\nabla_1u_{12})(\nabla_1u_{13})+\tfrac{1}{2}K\sum_j(R_{j+1}-R_j-a)^2 ,\end{aligned} \tag{4}$$

where n_0 is the averaged density of electrons and $P(1,2,\ldots,n)$ is the *n*-particle distribution function

$$P(1,2,\ldots,n)=\frac{n!}{(N-n)!}\frac{\int|\Psi(1,2,\ldots,N)|^2d(n+1)\cdots dN}{\int|\Psi(1,2,\ldots,N)|^2d1\cdots dN} . \tag{5}$$

$P(1)$ is the one-electron density distribution; $P(1,2)$ is equal to $P(1)P(2)g(1,2)$, where $g(1,2)$ is the electron correlation function describing two-body correlation. Three- or multiple-body correlation functions are usually much less important than the two-body correlation, so that the convolution approximation[15] is applied. The iterative equations for $P(1)$ and $P(1,2)$ are established in the framework of the Chakravarty-Woo approach:[16]

$$P(1|\lambda)=P(1/0)\exp\left\{\int_0^\lambda d\lambda'\int d2\,u_{12}\frac{P(1,2|\lambda')}{P(1|\lambda')}+\tfrac{1}{2}\int_0^\lambda d\lambda'\int d2\int d3\left[\frac{P(1,2,3|\lambda')}{P(1|\lambda')}-P(2,3|\lambda')\right]\right\} , \tag{6}$$

$$\begin{aligned}P(1,2|\lambda)=P(1,2,|\lambda)\exp\Bigg\{&\lambda u_{12}+\int_0^\lambda d\lambda'\int d3(u_{13}+u_{23})\frac{P(1,2,3,|\lambda')}{P(1,2,|\lambda')}\\&+\tfrac{1}{2}\int_0^\lambda d\lambda'\int d3\int d4u_{34}\frac{[P(1,2,3,4|\lambda')-P(1,2,|\lambda')P(3,4,|\lambda')]}{P(1,2|\lambda')}\Bigg\} .\end{aligned} \tag{7}$$

In this expression, λ is a parameter that characterizes the *e*-*e* interaction strength; for $\lambda=0$, we deal with an electron distribution which is the same as in the Hartree-Fock approximation, with many-body wave function $D[\phi_k]$, while for $\lambda=1$, we obtain the full interaction that is eventually needed. The λ parameter is used in the iteration process, starting with $\lambda=0$ and going all the way to $\lambda=1$. The convolution approximation is used to make Eqs. (6) and (7) closed. The Hartree-Fock distribution functions are obtained easily:

$$P(1|0)=\sum_{k,s}|\phi_{k,s}(x_1)|^2 , \tag{8}$$

$$g(1,2|0)=1-\sum_s\frac{\left|\sum_k\phi^*_{k,s}(x_1)\phi_{k,s}(x_2)\right|^2}{P(1|0)P(2|0)} . \tag{9}$$

The iteration results are inserted into Eq. (4) to calculate the total energy which is required for the optimization process.

III. ONE-DIMENSIONAL SQUARE-WELL POTENTIAL

Since the π-electron bandwidth of a 1D conjugated system is usually large, the non-nearest hopping integrals, which are omitted in Hückel-type calculations, are not negligible. Therefore, in this work, where we focus on trans-polyacetylene, we model the one-electron states as in an infinitely long Kronig-Penney square-well lattice. The rigorous solution of this problem has been previously worked out for dimerized systems.[1,5] In order to deal with reasonable parameters to describe the square well (i.e., the height V_0 of the well and its width b), in Table I we present the results obtained for ionization potentials (IP's) and valence-band widths for different sets of parameters. The 1D lattice constant (undimerized) is set at 1.22 Å (which is characteristic of polyacetylene). Since the IP value and the bandwidth are not sensitive to dimerization amplitude u_0, we set u_0 at 0.03 Å. Note that the experimental IP value for polyacetylene is around 4.6 eV,[17] and the valence π-electron bandwidth is on the order of 6 eV

TABLE I. Square-well parameters (height V_0, in eV, and width b, in Å) and the resulting ionization potentials IP, in eV) and hopping integrals t_0 (taken as half the valence-band width, in eV); the dimerization amplitude u_0 is set at 0.03 Å.

V_0,b	30,0.3	30,0.35	30,0.4	40,0.25	40,0.3	50,0.2	50,0.21	50,0.22	70,0.13	70,0.14	70,0.15	100,0.1
IP	2.97	4.54	6.06	4.37	6.6	4.4	5.0	5.6	3.46	4.44	5.32	4.8
t_0	3.0	2.96	2.93	2.94	2.88	2.92	2.9	2.88	2.93	2.91	2.90	2.91

(corresponding to a nearest-neighbor hopping integral of 3 eV). In Table I, we observe that bandwidths are rather insensitive to our choice of V_0 and b parameters; these are therefore chosen on the basis of the IP value, and we select the $V_0 = 50$ eV and $b = 0.2$ Å values.

It must be borne in mind that the equilibrium dimerization amplitude u_0 depends on the actual choice of the spring constant K. Therefore, in Table II, we investigate the influence of the K value on u_0, IP, the band gap (E_g), and the stretching-mode frequency (ω), on the basis of the selected square-well parameters. For $K = 21$ eV/Å^2, we reproduce the one-electron properties of the Su-Schrieffer-Heeger (SSH) model[18] in terms of the dimeriza-

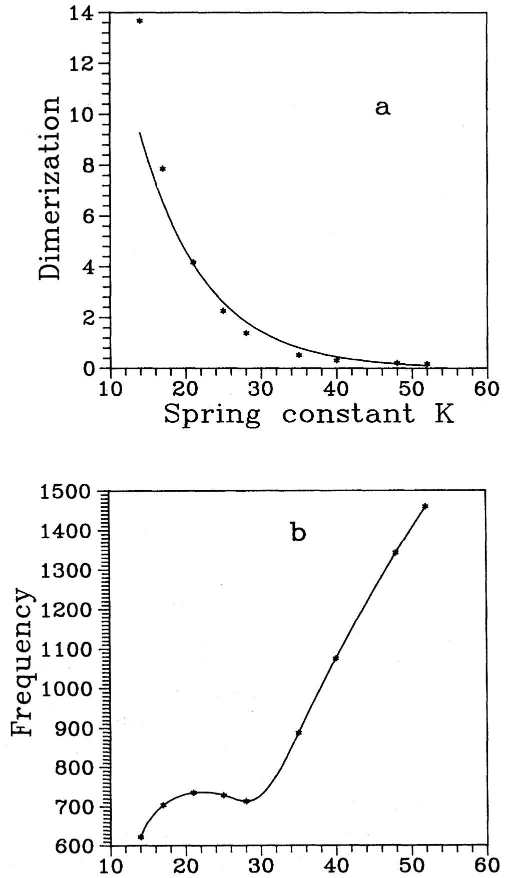

FIG. 1. Evolution of (a) optimized dimerization u_0 (in 10^{-2} Å) and (b) stretching-mode frequency ω (in cm^{-1}) as a function of spring constant K (in eV/Å^2) within one-electron theory for a Kronig-Penney square well ($V_0 = 50$ and $b = 0.2$). The solid line in (a) is an exponential fit: $u_0 = 0.47 \exp(-0.116\,\mathrm{K})$.

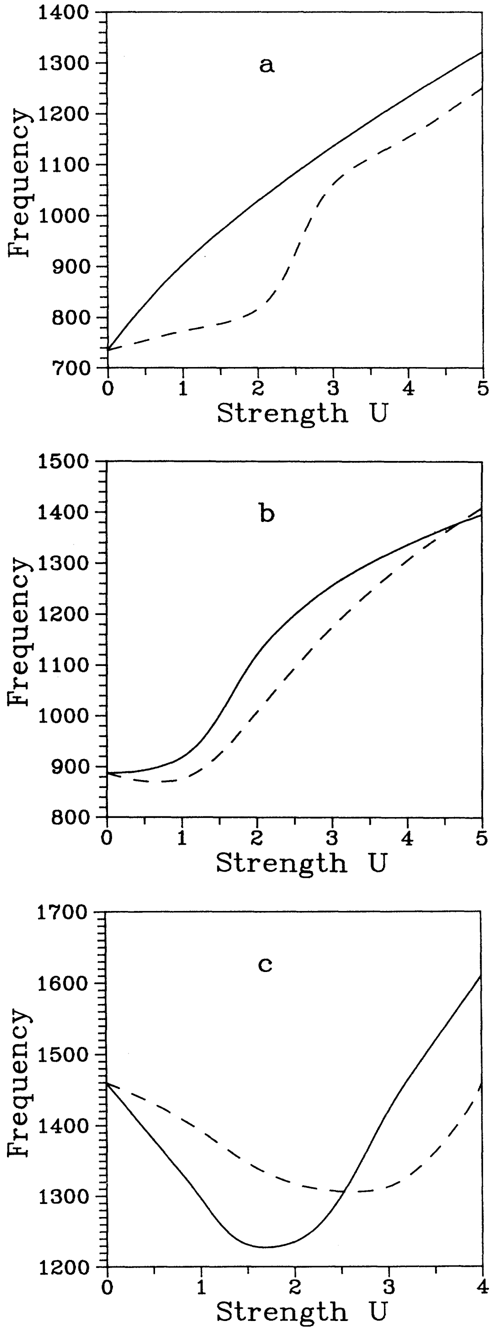

FIG. 2. The dependence of the stretching-mode frequency ω (in cm^{-1}) on the e-e interaction strength $\{U,\beta\}$ (solid line for $\beta = 1$ and dashed line for $\beta = 2$) for three typical spring constants: $K =$ (a) 21, (b) 35, and (c) 52 eV/Å^2. The interaction strength U is given in units of t_0.

TABLE II. Optimized results for dimerization u_0 (in Å), ionization potential IP (in eV), optical gap E_g (in eV), and amplitude-mode frequency ω (in cm^{-1}) in one-electron theory for different spring constants K (in eV/Å^2). The square potential is characterized by $V_0=50$ and $b=0.2$.

K	14	17	21	25	28	35	40	48	52
u_0	0.1367	0.079	0.042	0.023	0.014	0.005	0.003	0.0021	0.0018
IP	6.32	5.38	4.77	4.45	4.3	4.15	4.11	4.09	4.09
E_g	4.93	2.79	1.47	0.79	0.49	0.18	0.11	0.074	0.063
ω	622	704	735	728	713	887	1075	1342	1459

TABLE III. CBF variational results for dimerization u (in Å), stretching frequency ω (in cm^{-1}), and optimized correlation parameters η and ν as functions of interaction strengths U (in units of t_0) and β (dimensionless). The K spring constant is set at 21 eV/Å^2.

U	0	1	2	3	4	5	1	2	3	4	5
β		1	1	1	1	1	2	2	2	2	2
u	0.0416	0.0547	0.0621	0.0655	0.0695	0.0715	0.0462	0.0505	0.0538	0.0556	0.0569
ω	735	904	1028	1135	1232	1322	773	816	1060	1153	1251
η		0.245	0.30	0.345	0.3825	0.41	0.215	0.3225	0.409	0.44	0.4975
ν		0.525	0.55	0.575	0.575	0.575	0.345	0.355	0.34	0.365	0.39

TABLE IV. CBF variational results for dimerization u (in Å), stretching frequency ω (in cm^{-1}), and optimized correlation parameters η and ν as functions of interaction strengths U (in units of t_0) and β (dimensionless). The K spring constant is set at $K=35$ eV/Å^2.

U	0	1	2	3	4	5	1	2	3	4	5
β		1	1	1	1	1	2	2	2	2	2
u	0.0052	0.0123	0.0205	0.0273	0.033	0.038	0.0081	0.0131	0.018	0.022	0.0259
ω	887	918	1120	1256	1336	1396	876	1007	1174	1305	1409
η		0.22	0.295	0.3425	0.3725	0.415	0.1925	0.2925	0.3665	0.4375	0.4975
ν		0.575	0.575	0.575	0.575	0.575	0.36	0.365	0.375	0.375	0.38

TABLE V. CBF variational results for dimerization u (in Å), stretching frequency ω (in cm^{-1}), and optimized correlation parameters η and ν as functions of interaction strengths U (in units of t_0) and β (dimensionless). The K spring constant is set at $K=52$ eV/Å^2.

U	0	0.5	1	1.5	2	3	4	0.5	1	1.5	2	3	4
β		1	1	1	1	1	1	2	2	2	2	2	2
u	0.0018	0.0024	0.0034	0.005	0.0073	0.0126	0.0174	0.002	0.0025	0.0031	0.0041	0.0069	0.0106
ω	1459	1380	1297	1231	1236	1420	1610	1430	1392	1347	1317	1313	1459
η		0.16	0.21	0.2475	0.28	0.375	0.3675	0.1225	0.185	0.2325	0.27	0.335	0.3975
ν		0.58	0.585	0.585	0.585	0.585	0.585	0.36	0.365	0.375	0.38	0.39	0.395

tion amplitude and energy gap. However, the calculated stretching-mode frequency (735 cm^{-1}) is too small when compared to experiment ($\sim 1460\ \mathrm{cm}^{-1}$).[19] One could use a larger K value[19] and, at the same time, increase the electron-phonon coupling constant α (i.e., change the square-well shape in our case) in order to fit the dimerization amplitude, optical gap, and vibrational frequency. However, within our 1D Kronig-Penney approach, the resulting ionization potential (which is arbitrary in the SSH model) is then obtained to be much too large. This illustrates the fact that in the absence of explicit *e-e* interactions, it is not possible to describe adequately both electronic and vibrational properties.

The dependence of dimerization u_0 and stretching-mode frequency ω on K are plotted in Fig. 1. When increasing K, elastic energy is gained but the optimized dimerization, which results from electron-phonon coupling, is reduced exponentially. It is interesting to note that the evolution of ω as a function of K is not monotonic. In the next section, we investigate *e-e* interaction effects for a range of K values covering the parameters used in the literature.[1–5]

IV. RESULTS AND DISCUSSION

To include electron-electron interactions, we adopt a screened form for the potential:

$$V(x_i,x_j)=\frac{U}{\left[1+\frac{(x_i-x_j)^2}{a^2}\right]^{1/2}}\exp\left[-\frac{\beta|x_i-x_j|}{a}\right], \tag{10}$$

where a is the 1D lattice spacing, U is the *e-e* interaction strength, and β is the screening factor. This potential comprises all the diagonal and nondiagonal elements when expanded within a Wannier basis; for long-range interactions (small β), U is close to the Hubbard term, while for short-range interactions (large β), the U value becomes effectively smaller. The correlation factor $u(x_i,x_j)$ [see Eq. (3)] is taken variationally from

$$u(x_i,x_j)=-\eta[V(x_i,x_j)]^{\nu}, \tag{11}$$

where η and ν are the parameters to be optimized. Then the total energy in Eq. (4) contains three variational parameters (i.e., η, ν, and dimerization u_0) for each *e-e* interaction $\{U,\beta\}$. The stretching-mode frequency is calculated through the corresponding adiabatic potential.

We take the Kronig-Penney square well to be $V_0=50$ eV, $b=0.2$ Å. Three typical spring constants are chosen: $K=21$, 35, and 52 eV/Å^2. The *e-e* interaction strength U is varied from 0 to $5t_0$ (t_0 is the half-width of the π valence band), and β is set to 1 or 2. The variational results are presented in Tables III, IV, and V, and the dependence of frequency ω on U is plotted in Fig. 2.

From Tables III–V, one observes that the variational parameter ν, the exponent of the correlation factor, is much more sensitive to the screening factor β than to U. For a two-body system, the Wentzel-Kramers-Brillouin (WKB) method provides a value of 0.5 for ν. Our variational results are close to this value. Within the parameters used in this work, *e-e* interaction increases the dimerization. However, in the case of $K=21$ eV/Å^2 and $\beta=2$, there is almost no influence of interaction strength U on the dimerization. We note that the iteration process [Eqs. (8) and (9)] is extremely slow for large values of U (U larger than $4t_0$).

As to the influence of *e-e* interaction on vibrations, we limit our attention to moderate U values, which are relevant for most conjugated polymers. The most important result is that *e-e* interaction generally enhances the vibrational frequency. However, for large K values, the frequency first starts decreasing up to U values around $2-3t_0$ and then increases (see Fig. 2). Since the 1D model considered in this work constitutes a simple approximation, the obvious course is not to make a thorough comparison between the experimental results and the different theoretical parametrizations used here. The main feature of this contribution is to point out the importance of taking into account *e-e* interaction in 1D lattice vibration problems, and to illustrate the stretching frequency evolution as a function of the *e-e* interaction strength.

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