Missing Bond-Charge Repulsion in the Extended Hubbard Model: Effects in Polyacetylene

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Translational invariance requires that the electron density operator is not diagonal in a Wannier representation. We show that this leads to important terms in the electron-electron interaction Hamiltonian, terms which involve the bond-charge density and which are not included in the widely studied extended Hubbard model. When these bond-charge interactions are included, we find that electron-electron repulsion tends to stiffen the lattice (for physically reasonable parameters) and to oppose dimerization in polyacetylene and in other charge-density-wave systems. A related decrease in the Peierls gap for fixed dimerization is also obtained. the extended Hubbard model.

Dimerization in a one-dimensional commensurability-two Peierls system, such as *trans*-polyacetylene, produces an inhomogeneous charge distribution (a charge-density wave) with amplitude proportional to the magnitude of the structural distortion. It would seem, therefore, that the Coulomb interaction between electrons would provide additional stiffness against distortion away from the uniform structure, and thereby tend to oppose the dimerization induced by the electron-phonon interaction. Similarly, since the electrons tend to screen the $2k_F$ potential caused by the dimerized lattice, the effect of electron-electron repulsion would be to reduce the single-particle gap (for fixed magnitude of dimerization).

Although the results of a number of model calculations have implied that weak interactions tend to enhance the dimerization,[1-4] these conclusions were based on models which omit direct repulsion between electrons in the "bonds" between sites. In this paper, we show that the repulsion between electrons in the bond leads to the effects argued physically above: For reason-

able choices of the parameters, the net effect of electron-electron interactions is to reduce the magnitude of the electron-phonon–induced dimerization, and to reduce the single-particle energy gap at fixed dimerization.

We assume a tight-binding model which consists of one electronic orbital (Wannier function) $\Phi_n(r)$ per site n (e.g., the carbon $2p_z$ orbital in the case of polyacetylene) and one ionic coordinate u_n per site; we consider in this paper only the half-filled band in which there is one electron per site (half an electron of each spin per site). We treat the lattice coordinates in the mean-field approximation in which the positions of the ions are chosen so as to minimize the adiabatic potential energy. Our model, which is similar in spirit to that used by Su, Schrieffer, and Heeger[5] (SSH) to study the properties of *trans*-polyacetylene, is described by the Hamiltonian where H_{SSH} is the SSH Hamiltonian which can be expressed in second-quantized form as

$$H = H_{SSH} + H_{int}, \qquad (1a)$$

$$H_{SSH} = -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n)][c^\dagger_{n+1,s}c_{n,s} + \text{H.c.}] + \tfrac{1}{2}K\sum_n(u_{n+1} - u_n)^2, \qquad (1b)$$

where $c^\dagger_{n,s}$ creates an electron with spin s on site n, and H_{int} is the electron-electron interaction, which can be written in its most general form as

$$H_{int} = \sum_{\substack{n,m,l,p \\ s,s'}} V(n,m,l,p)c^\dagger_{ns}c^\dagger_{ms'}c_{ls'}c_{ps} + \delta\mu\sum_{n,s}c^\dagger_{ns}c_{ns}, \qquad (1c)$$

where $V(n,m,l,p)$ is the appropriate matrix element of the electron-electron interaction potential, $V(r)$,

$$V(n,m,l,p) = \int dr\,dr'\,\rho_{np}(r)\rho_{ml}(r')V(r - r'). \qquad (2a)$$

In Eq. (2a), ρ_{np} denotes the matrix element of the electron-density operator, $\hat\rho(r)$, in the Wannier representation,

$$\rho_{np}(r) = \Phi^*_n(r)\Phi_p(r) = \langle n|\hat\rho(r)|p\rangle, \qquad (2b)$$

and $\delta\mu$ is an appropriate shift in the chemical potential so that the Fermi energy remains $E_F = 0$. Depending on the environment of the chain, $V(r)$ might be the bare Coulomb repulsion, $V(r) = e^2/\epsilon r$ (e.g., for an isolated polymer chain in a medium with dielectric constant ϵ), or it may be screened (e.g., by the collective motion of electrons on neighboring chains, as it is in conducting polymers). Since the orbitals $\Phi_n(r)$ are typically exponentially localized, $\rho_{np}(r)$, $\rho_{ml}(r)$, and hence $V(n,l,m,p)$ will fall off exponentially with the separations $|n - p|$ and $|m - l|$. On the other hand, the dependence of $V(n,l,m,p)$ on $|n - m|$ reflects the range of the interaction. In a single-band model, the Wannier functions can be chosen to be real, and hence $\rho_{np}(r) = \rho_{pn}(r)$.

In previous treatments of the electron-electron interactions, only terms involving the diagonal matrix elements

of $\hat\rho(r)$ were considered. A particularly well-studied example is the extended Hubbard model in which

$$H_{\text{int}} = U \sum_n \hat{Q}_\uparrow(n)\hat{Q}_\downarrow(n) + V \sum_{s,s'} \hat{Q}_s(n)\hat{Q}_{s'}(n+1),$$
(3)

where $U = 2V(0,0,0,0)$, $V = 2V(0,1,1,0)$, and $\hat{Q}_s$ is the density of electrons of spin s on site n (minus the average density),

$$\hat{Q}_s(n) = [c_{ns}^\dagger c_{ns} - \tfrac{1}{2}].$$
(4a)

In addition to neglecting off-diagonal terms, this model assumes short-ranged electron-electron interactions, perhaps due to metallic screening. However, even for δ-function interactions, $V(r) = V_0\delta(r)$, where the assumption of nearest-neighbor interactions is well justified, this model neglects terms proportional to the off-diagonal matrix elements of $\hat\rho(r)$ which are larger than (or at least as large as) those terms which are retained. Specifically, for reasonable forms of the Wannier function and $V(r) = V_0\delta(r)$, $U > X > V = W$ where X

$= 2V(0,1,1,1)$ and $W = 2V(0,1,0,1)$.

Thus, because $\hat\rho(r)$ is a function of the continuous spatial coordinate r (and not of a discrete lattice index n), we are led to include off-diagonal matrix elements of $\hat\rho(r)$. Indeed, the same large overlap between orbitals on nearest-neighbor sites that is responsible for the large value of t_0 (i.e., the bandwidth) is responsible for the importance of the off-diagonal matrix elements of $\hat\rho(r)$. For these fundamental reasons, we explicitly include interactions which come from nearest-neighbor off-diagonal matrix elements of $\hat\rho(r)$ and hence which depend on the "bond-charge density"

$$\hat{G}_s(n) = [c_{ns}^\dagger c_{n+1,s} + \text{H.c.}].$$
(4b)

Just as more distant-neighbor hopping matrix elements can be ignored in computing the band structure [since $\Phi_n(r)$ falls off exponentially with distance], terms proportional to further-neighbor matrix elements of $\hat\rho(r)$ can be ignored to a first approximation. The resulting translationally invariant model can be expressed as

$$H_{\text{int}} = \frac{1}{2}\sum_{n,m,s,s'} \tilde{V}(n-m)\hat{Q}_s(n)\hat{Q}_{s'}(m) + \frac{1}{4}\sum_{n,m,s,s'} \tilde{X}(n-m)\{\hat{Q}_s(n),\hat{G}_{s'}(m)\} + \frac{1}{2}\sum_{n,m,s,s'} \tilde{W}(n-m)\hat{G}_s(n)\hat{G}_{s'}(m),$$
(5)

where $\tilde{V}(n-m) = 2V(n,m,m,n)$, $\tilde{X}(n-m) = 2V(n,m,m+1,n)$, and $\tilde{W}(n-m) = 2V(n,m,m+1,n+1)$. In the spirit of the extended Hubbard model, and largely to help develop our physical intuition, we will consider the simplified version of this model in which we keep only nearest-neighbor interactions, and hence take $\tilde{V}(0) = U$, $\tilde{V}(1) = \tilde{V}(-1) = V$, $\tilde{X}(0) = X$, $\tilde{W}(0) = W$. All other matrix elements are assumed to be zero. While this simplified version of the model is not realistic for Coulomb interactions, it should be fairly accurate for short-range interactions. In this respect, it contrasts with the extended Hubbard model which is unlikely to be reliable for any range of interactions.

It is often convenient to consider the continuum version of the model discussed above. The resulting continuum Hamiltonian consists of a one-electron term [see Takayama, Lin-Liu, and Maki (TLM)[6]],

$$H_{\text{TLM}} = \int dx\, \Psi_s^\dagger(x)\left\{ -i\hbar v_F \frac{\partial}{\partial x}\sigma_z + \Delta(x)\sigma_x \right\}\Psi_s(x) + \int dx \left[\frac{\hbar v_F}{2g^2}\right]\left[\frac{\Delta(x)}{\hbar v_F}\right]^2$$
(6a)

and an electron-electron interaction term[7]

$$H_{\text{int}} = \sum_{ss'} \int dx\, \hbar v_F \{g_1 \Psi_{s2}^\dagger \Psi_{s'1}^\dagger \Psi_{s'1}\Psi_{s2} + g_2 \Psi_{s1}^\dagger \Psi_{s'2}^\dagger \Psi_{s'2}\Psi_{s1}$$
$$+ \tfrac{1}{2} g_3 [\Psi_{s1}^\dagger \Psi_{s'1}^\dagger \Psi_{s'2}\Psi_{s2} + \text{H.c.}] + \tfrac{1}{2} g_4 [\Psi_{s1}^\dagger \Psi_{s'1}^\dagger \Psi_{s'1}\Psi_{s1} + \Psi_{s2}^\dagger \Psi_{s'2}^\dagger \Psi_{s'2}\Psi_{s2}]\},$$
(6b)

where $\Psi_{s1}(x)$ creates a right-moving electron of spin s, $\Psi_{s2}(x)$ creates a left-moving electron, and σ_z and σ_x are Pauli matrices. If the continuum model is obtained by taking the continuum limit of the discrete model defined in Eqs. (1a)–(1c), then the parameters defining Eq. (6) become the following:

$$\hbar v_F = 2t_0 a, \quad g^2 = 2\alpha/Kt_0,$$
(7a,b)

where a is the lattice constant, and

$$g_1 = \frac{1}{t_0 N}\sum_{n,m,l,p}\left\{ V(n,m,l,p)\exp\left[\frac{i\pi(n+p-m-l)}{2}\right]\right\},$$
(8a)

$$g_2 = \frac{1}{t_0 N}\sum_{n,m,l,p}\left\{ V(n,m,l,p)\exp\left[\frac{i\pi(n-p-m+l)}{2}\right]\right\},$$
(8b)

$$g_3 = -\frac{1}{t_0 N}\sum_{n,m,l,p}\left\{ V(n,m,l,p)\exp\left[\frac{i\pi(n+p+m+l)}{2}\right]\right\},$$
(8c)

$$g_4 = \frac{1}{t_0 N}\sum_{n,m,l,p}\left\{ V(n,m,l,p)\exp\left[\frac{i\pi(n-p+m-l)}{2}\right]\right\},$$
(8d)

where g_1, g_2, and g_3 are the backward-scattering, forward-scattering, and umklapp-scattering matrix elements, respectively.

The advantages of the continuum model are that it is very general, that calculations are simpler than with the discrete model, and that the full effects of the arbitrary interactions between electrons at the Fermi surface are embodied in the values of the four interaction parameters, g_i. The disadvantage is that it is difficult to obtain physical insight into the relevant values of these coupling strengths. To obtain such an understanding, we have evaluated the expressions in Eq. (8) for the discrete model with nearest-neighbor interactions only. If one ignores the interaction between bond charges, then there are only two independent interactions since $g_1 = -g_3$ and $g_2 = g_4$ [this result is independent of the range of $V(r)$]. Thus, the quantities $g_1 + g_3$ and $g_2 - g_4$ measure the strength of the bond-charge repulsion. In terms of the interactions in the nearest-neighbor model, the relations in Eq. (8) can be written as follows:

$$g_1 = (U - 2V + 4W)/2t_0, \tag{9a}$$

$$g_2 = (U + 2V)/2t_0, \tag{9b}$$

$$g_3 = -(U - 2V - 4W)/2t_0, \tag{9c}$$

$$g_4 = (U + 2V)/2t_0, \tag{9d}$$

and hence

$$g_1 + g_3 = 2W/t_0, \tag{10a}$$

$$g_2 - g_4 = 0. \tag{10b}$$

Note that the interactions at the Fermi surface are in-

dependent of X, so that there is no cross coupling between the bond and site charge densities. This is a specific feature of the half-filled band where $k_F a = \pi/2$. For other fillings, $g_3 = g_4 = 0$, but g_1 and g_2 depend on X as well as U, V, and W.

The effect of weak interactions on the properties of the continuum model have been computed previously.[7] Having completed the discussion of the interaction Hamiltonian, we conclude this paper by repeating those calculations for the nearest-neighbor tight-binding model, so as to obtain insight into the physical meaning of the results. To zeroth order in H_{int}, the ground state is uniformly dimerized, $u = (-1)^n u_0$, where the magnitude of u_0 can be determined self-consistently (as in SSH) from the condition that the total ground-state energy is a minimum. For fixed dimerization, the system is a Peierls insulator with gap $2\Delta_0 = 8\alpha u_0$. The quantity $z = \Delta_0/2t_0$ is a convenient dimensionless measure of the dimerization.

The effect of interactions on the ground-state energy can be computed to first order by our taking the expectation value of H_{int} in the noninteracting ground state. We use Wick's theorem to factorize the expectation values of the products of four operators into products of the expectation values of $\hat{Q}_s(n)$ and $\hat{G}_s(n)$:

$$\langle H_{int} \rangle = \tfrac{1}{2} [3W - V] \sum_n |\langle \hat{G}_s(n) \rangle|^2 + (\text{const}), \tag{11}$$

where $\langle \hat{G}_s(n) \rangle$ is independent of s, $\langle \hat{Q}_s(n) \rangle = 0$, and where (const) refers to a term which is independent of the magnitude of the dimerization. $\langle \hat{G}_s(n) \rangle$ can be readily computed by use of the Hellman-Feynman theorem which implies that it can be determined from the derivative of the noninteracting electronic energy with respect to u_0:

$$\langle G_s(n) \rangle = -(2/\pi)\{1 + (1)^n [z/(1 - z^2)][K(1 - z^2) - E(1 - z^2)]\} \approx -(2/\pi)\{1 + (-1)^n z [\ln(4/z) - 1]\}, \tag{12}$$

where $K(1 - z^2)$ and $E(1 - z^2)$ are complete elliptic integrals of the first and second kinds, and the second equality is valid for small z. Thus, the first-order contribution to the effective potential for dimerization is the following:

$$\Delta E(z) = (2/\pi^2)[3W - V]z^2 \ln^2(4/ez). \tag{13}$$

For $3W > V$, ΔE is an increasing function of z (for $z \ll 1$); hence interactions oppose dimerization. As noted in the first paragraph, this occurs since the Coulomb repulsion between electrons provides additional stiffness against distortion away from the uniform structure and thereby opposes the dimerization induced by the electron-phonon interaction. The effect of interactions on the one-particle gap for fixed dimerization can also be computed in a straightforward manner. The result is

$$\Delta = \Delta_0\{1 - [(3W - V)/\pi t_0]\ln(4/ez)\}. \tag{14}$$

For $3W > V$, interactions tend to decrease the gap! This

is just the bond-charge screening effect noted in the introductory paragraph. Note that, more generally, the same conclusions hold provided $2g_1 + g_3 - g_2 > 0$. This condition, which in the absence of bond charge would require the (unphysical) condition that $V < 0$, is now seen to be satisfied for reasonable values of the bond-charge repulsion.

In conclusion, we have demonstrated that by proper inclusion of Coulomb interactions between electrons located not only on the same site (Hubbard model) and on neighboring sites (extended Hubbard model), but also on bonds between sites, there is an increase in the effective stiffness constant leading to a decrease in the magnitude of the dimerization as a function of the Coulomb potential strength. While earlier results based on models which neglected the bond-charge forces predict an initial increase in dimerization with increasing Coulomb strength, our analysis shows that this apparent increase

is the result of overlooking the interactions involving bond charge. By including this bond-charge interaction, we find that the dimerization monotonically decreases with increasing Coulomb strength, as is reasonable from a physical point of view.

On the basis of these results, corresponding changes are expected to occur in the physical properties of Hubbard-model systems when bond-charge interactions are included. For example, the tendency toward charge-density-wave formation is expected to be suppressed.

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