retical approach, where, by using the pseudopotential scheme, oscillations near the core region are taken out and the profiles are underestimated for large q and overestimated for small q.

In conclusion, except for a small directionally independent difference which can be reduced by approximating correlation effects, this is the first time that the calculated and observed Compton profiles of beryllium are in excellent agreement. This calculation can serve as a model for other systems both to assess the accuracy of one-electron schemes and to estimate the effects of electron correlation.

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Elementary Excitations of a Linearly Conjugated Diatomic Polymer

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The low-lying particlelike excitations of a model linearly conjugated diatomic polymer, $\{A=B\}_x$, are found to be pairs of either spin-0 or spin-$\frac{1}{2}$ solitons with irrational charge values. The charge values and excitation energies are calculated as functions of the difference of the energy levels of the atomic p orbitals of the two atomic constitutents of the unit cell. The phonon spectrum of the uniform polymer is also calculated.

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We have extended the soliton model of polyacetylene[1-4] to study theoretically the ground state, phonon spectrum, and possible soliton excitations of a linearly conjugated *diatomic* polymer, $\{A=B\}_x$, as a function of the difference $(2\alpha=E_A-E_B)$ of the energy levels of the atomic p orbitals

of the two atomic constituents (A and B) of the unit cell. An example of such a polymer is polycarbonitrile, $+CH=N+_x$, or one of its several derivatives.[5] We find that the lowest-lying particlelike excitations of the dimerized polymer are pairs of either spin-0 or spin-$\frac{1}{2}$ solitons with *irrational* charge values.

Our model polymer is defined by the Hamiltonian

$$H = H_L + \alpha\sum_{j,\sigma} a_{j,\sigma}^{\dagger}a_{j,\sigma} - \sum_{j,\sigma}(t_{j+1,j}a_{j,\sigma}^{\dagger}b_{j+1,\sigma} + \text{H.c.}) - \alpha\sum_{l,\sigma} b_{l,\sigma}^{\dagger}b_{l,\sigma} - \sum_{l,\sigma}(t_{l+1,l}b_{l,\sigma}^{\dagger}a_{l+1,\sigma} + \text{H.c.}) \quad (1)$$

describing a diatomic linear chain of $N/2$ ($N\to\infty$) atoms of type A (odd sites, labeled by j) and $N/2$ atoms of type B (even sites, labeled by l), in which

$$H_L = \tfrac{1}{2}M_1\sum_j \dot{u}_j^2 + \tfrac{1}{2}M_2\sum_l \dot{y}_l^2 + (K/2)\sum_j (y_{j+1}-u_j)^2 + (K/2)\sum_l (u_{l+1}-y_l)^2 \quad (2)$$

denotes the lattice energy and

$$t_{j+1,j} = t_0 - \gamma(y_{j+1}-u_j), \qquad t_{l+1,l} = t_0 - \gamma(u_{l+1}-y_l) \quad (3)$$

the hopping integrals for the transfer of a π electron between neighboring sites. In (1) $a_{j,\sigma}^{\dagger}$, $a_{j,\sigma}$ and $b_{j,\sigma}^{\dagger}$, $b_{j,\sigma}$ are fermion creation and destruction operators for a π electron with spin σ at the A and B atomic sites, respectively. In (2) and (3) u_j and y_l denote, respectively, the displacements of the jth A atom and the lth B atom from their respective equilibrium positions in a uniformly spaced diatomic chain of lattice constant $2a$. K denotes a harmonic spring constant, M_1 and M_2 the masses of the A and B atoms, respectively, t_0 the hopping integral characteristic of the uniformly spaced chain, and γ the derivative of $t_{j+1,j}$ with respect to the intersite separation. The electronic energy is measured relative to the total atomic orbital energy $(N/2)(E_A+E_B)$ and it is assumed that there is one π electron per atom.

We discuss first the ground-state properties and the phonon spectrum. In general, when we treat the atomic displacements as a classical field, the ground state of (1) is an insulator possessing a spontaneous (Peierls) dimerization with a ground-state displacement field $y_j = -u_l = \pm w/2$ (all j and l) where w is a constant. The spectrum of π states is $\Pi_k = \pm E_k = \pm[\alpha^2+\Delta^2\sin(ka) + \epsilon_k^2]^{1/2}$ with $-(\pi/2a) \le k < (\pi/2a)$, where $\epsilon_k = 2t_0\cos(ka)$ and $\Delta = 2\gamma w$. The lower (valence) band is completely filled while the upper (conduction) band is empty. The energy gap at the zone edges is $E_g = 2(\alpha^2+\Delta^2)^{1/2}$. The constant w, or equivalently, the dimerization contribution Δ to the gap, minimizes the total ground-state energy

$$E = (N/2)(K/4\gamma^2)\Delta^2 - \sum_{k,\sigma}{}' E_k,$$

i.e., Δ is determined as the solution of

$$1 = (4\gamma^2/KN)\sum_{k,\sigma}{}' \sin^2(ka)E_k^{-1}, \quad (4)$$

where the primes on the summation symbols indicate summation over occupied states. Since the atomic level $E_A \neq E_B$ a "charge transfer" $2e^*$ between the A and B atoms is a characteristic property of the ground state. With the definition that $2e^*$ is the ground-state expectation value of $|e|\sum_{\sigma}(b_{l,\sigma}^{\dagger}b_{l,\sigma} - a_{l+1,\sigma}^{\dagger}a_{l+1,\sigma})$, we find

$$e^*/e = (\alpha/N)\sum_{k,\sigma}{}' E_k^{-1},$$

where $|e|$ denotes the magnitude of the charge, e, on an electron. When we take into account the adiabatic polarization of the π electrons to second order in γ, the phonon dispersion, $\Omega(q)$, is given by $\det\|\hat{D}(q) - \Omega^2(q)\hat{I}\| = 0$, where

$$D_{ij} = (M_iM_j)^{-1/2}\{\delta_{ij}[2K - 8\gamma^2\chi_1(q)] + (1-\delta_{ij})[2K\cos(qa) - 8\gamma^2\chi_2(q)]\}. \quad (5)$$

In Eq. (5) the π-electron contributions are obtained from

$$\chi_i(q) = N^{-1}\sum_{k,\sigma} s_i(k,k+q)F(k,k+q)/(E_{k+q}+E_k), \quad (6)$$

where

$$F(k,k') = 1 + (\alpha^2+\epsilon_k\epsilon_{k'} - \Delta^2 z_k z_{k'})/(E_kE_{k'}),$$

$z_k = \sin(ka)$, and

$$s_1(k,k') = z_k^2 + z_{k'}^2, \quad s_2(k,k') = 2z_kz_{k'}.$$

With the employment of the representative values $t_0 = 3$ eV, $K = 68.6$ eV Å^{-2}, and $\gamma = 8$ eV Å^{-1}, which yield a Peierls gap $2\Delta_0 = 1.4$ eV for the case $\alpha = 0$, we have numerically calculated Δ, e^*, and the phonon spectrum as a function of α/Δ_0. The results are shown in Figs. 1 and 2, where in

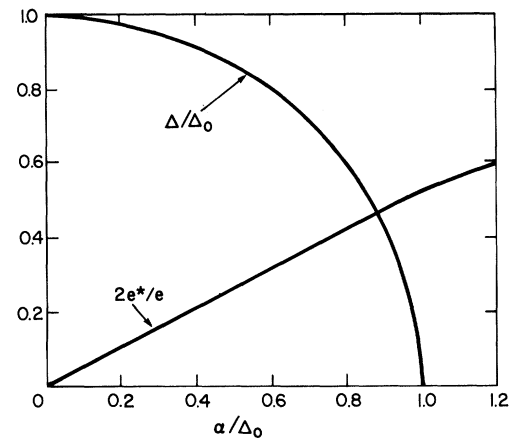

FIG. 1. The dimerization gap Δ and charge transfer $2e^*$ as functions of α/Δ_0.

Fig. 2 we have employed values of M_1 and M_2 appropriate for $\{CH=N\}_x$. The results show that a spontaneous lattice dimerization occurs only for $0 \leq \alpha \lesssim \Delta_0$, and that the functional form of Δ closely follows $\Delta = (\Delta_0^2 - \alpha^2)^{1/2}$. The latter form is in fact the solution of (4) in the limit of weak intrinsic electron-phonon coupling, i.e., $(\Delta_0/2t_0) \ll 1$. Figure 2 shows that the optical branch of the phonon spectrum, $\Omega_+(q)$, develops a giant Kohn anomaly in the critical region $|\alpha - \Delta_0| \sim 0$, although, interestingly, there is always a gap ($\simeq 2\alpha$) in the electronic π states. This is a consequence of the property that the restoring force for long-wavelength optical displacements is, for $\alpha < \Delta_0$, purely electronic in origin and proportional to the square of the amplitude of the off-diagonal charge density: Evaluation of (5) and (6) in the limit $(\Delta_0/2t_0) \ll 1$ yields $M_0\Omega_+^2(0) = (8\gamma^2/\pi t_0)(\Delta/\Delta_0)^2$, where $M_0 = M_1M_2/(M_1+M_2)$ is the optical mass. The critical behavior of $\Omega_+(0)$ as a function of α/Δ_0 is sketched in the inset in Fig. 2.

We now consider the possible soliton excitations of the polymer. These may be investigated with the use of the continuum methods employed by Brazovskii[3] and by Takayama, Lin-Liu, and Maki[4] for the polyacetylene problem. As the relevant analytical derivations are lengthy we shall restrict the analysis in this Letter to a statement of the fundamental system of equations and discussion of the salient results. In the continuum limit of the Hamiltonian (1), which provides an accurate description of the inhomogeneous polymer for $\Delta_0/2t_0 \ll 1$, we find that the one-electron eigenstates ϵ_n and the local dimerization gap $\Delta(x)$ are determined by the simultaneous

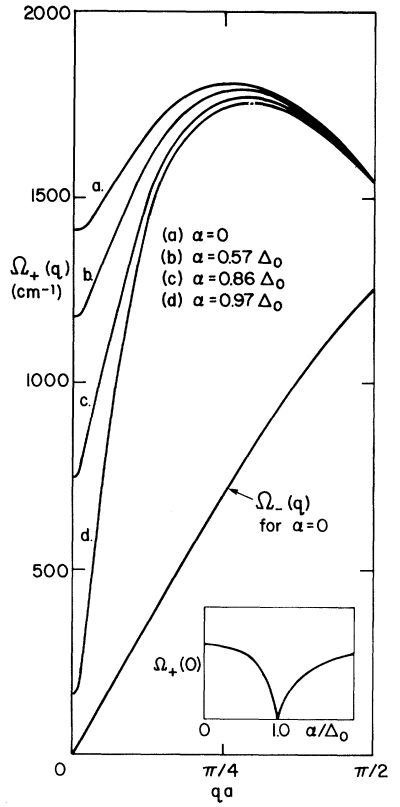

FIG. 2. The phonon spectrum as a function of α. The acoustic branch is only weakly dependent on α.

equations ($\hbar = 1$)

$$(\epsilon_n - \alpha)A_n(x) = [-iv_F\nabla_x + i\Delta(x)]B_n(x), \quad (7a)$$

$$(\epsilon_n + \alpha)B_n(x) = [-iv_F\nabla_x - i\Delta(x)]A_n(x), \quad (7b)$$

$$\Delta(x) = -(4\gamma^2 ai/K)\sum_{n,\sigma}{}'[A_n^*(x)B_n(x) - \text{c.c.}], \quad (7c)$$

where the eigenvector corresponding to ϵ_n is the spinor $\Psi(x) = (A_n(x), B_n(x))$, normalized according to $\int dx\, \Psi_n^*(x)\Psi_n(x) = 1$, $v_F = 2t_0a$, and $L = Na \to \infty$. The total energy of the polymer is

$$E = \sum_{n,\sigma}{}'\epsilon_n + (K/4\gamma^2)\int_{-L/2}^{L/2}(dx/2a)\Delta^2(x), \quad (8)$$

while the local mean charge density is $\rho(x) = e\sum_{n,\sigma}{}'\Psi_n^*(x)\Psi_n(x)$. These equations apply for the case of a static inhomogeneity. The ground-state solutions of Eqs. (7) are plane waves with $\epsilon_n = \pm E_k = \pm(\alpha^2 + \Delta^2 + v_F^2k^2)^{1/2}$ and $\Delta = \pm(\Delta_0^2 - \alpha^2)^{1/2}$ for $\alpha < \Delta_0$ and $\Delta = 0$ for $\alpha > \Delta_0$. (Here, and in the following paragraph, the wave vector k is measured relative to the zone edge $\pi/2a$.)

For $\Delta < \Delta_0$, we find that Eqs. (7) possess the exact solitary-wave solutions $\Delta(x) = \pm\Delta\tanh(x/\xi)$

with $\zeta = v_F/\Delta$. The first of these, which we designate A, is associated with an eigenspectrum consisting of a single bound state $\epsilon_0 = \alpha$ (lying precisely at the atomic level A) with wave function $A_0(x) = (2\zeta)^{-1/2}\,\mathrm{sech}(x/\zeta)$, $B_0(x) = 0$, and a spectrum of plane wave states $\epsilon_n = \pm E_k$ ($k \neq 0$) that are phase shifted in the region of the soliton distortion. The second solution, which we designate B, is associated with a similar spectrum of phase-shifted plane-wave states and a single bound state $\epsilon_0 = -\alpha$ (lying precisely at the atomic level B) with wave function $A_0(x) = 0$, $B_0(x) = (2\zeta)^{-1/2}\,\mathrm{sech}(x/\zeta)$. The interesting aspect of these solutions is that they lead to local deficiencies in the continuum states which differ from unity by an *irrational* fraction f. The bound state $\epsilon_0 = -\alpha$, which lies closer to the filled valence band than the empty conduction band, removes $\frac{1}{2}(1+f)$ of a state per spin from the former band and $\frac{1}{2}(1-f)$ of a state per spin from the latter band. For the bound state $\epsilon_0 = \alpha$, the deficiencies are interchanged.[6] Two consequences immediately follow. First the soliton excitations must always occur in the form of pairs of (widely separated) A and B solitons which remove precisely two electrons from the filled valence band. Second, independently of the occupation of the bound states, the solitons will always carry a net irrational charge. If we denote the occupation of the state $\epsilon_0 = \alpha$ by v_+ and that of the state $\epsilon_0 = -\alpha$ by $v_- = 2 - v_+$ the possible charge and spin values of the solitons are $Q = \pm e(v_- - 1 - f)$ and $s = \pm\frac{1}{2}v_-(2 - v_-)$, respectively. An analysis of the phase-shifted continuum states yields $f = 1 - (2/\pi)\tan^{-1}(\Delta/\alpha)$. Moreover, the energy required to excite an AB soliton pair, $2E_s(v_+, v_-)$, may be computed from Eq. (8) with the result

$$2E_s(v_+, v_-) = (4/\pi)[\Delta - \alpha\tan^{-1}(\Delta/\alpha)] + \alpha(2 + v_+ - v_-).$$

We note that $2E_s(0,2)$ and $2E_s(1,1)$ are always less than the electron-hole pair threshold $2(\alpha^2 + \Delta^2)^{1/2} = 2\Delta_0$. The formation of the soliton pairs is schematically depicted in Fig. 3(a).

We may conclude, therefore, that the lowest-lying charged excitations of the dimerized polymer are pairs of spin-0 solitons with charge $Q_0 = \pm e(2/\pi)\tan^{-1}(\Delta/\alpha)$ and excitation energy $2E_s(0,2) = (4/\pi)[\Delta - \alpha\tan^{-1}(\Delta/\alpha)]$, while the lowest-lying magnetic excitations are pairs of spin-$\frac{1}{2}$ solitons with charge $Q_1 = \mp e(2/\pi)\tan^{-1}(\alpha/\Delta)$ and excitation energy $2E_s(1,1) = 2E_s(0,2) + 2\alpha$. In Fig. 3(b), these charges and excitation energies

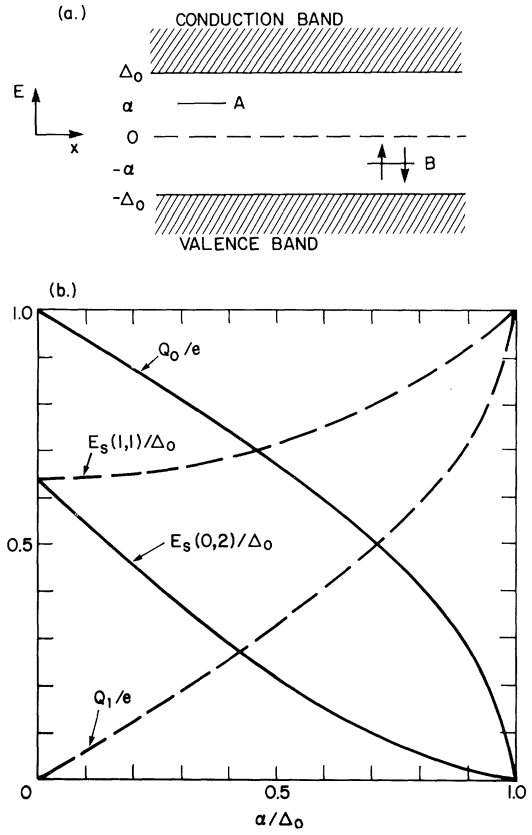

FIG. 3. (a) Formation of the (lowest-lying) AB soliton pair (schematic), and (b) the charges and excitation energies of the spin-0 and spin-$\frac{1}{2}$ solitons (see text).

are plotted as a function of α/Δ_0. We note that as $\alpha \to \Delta_0$, both Q_0 and $E_s(0,2) \to 0$, while $Q_1 \to \pm e$ and $E_s(1,1) \to \alpha$, corresponding to the excitation of an electron-hole pair.

Finally, we note that since $E_s(2,2) = E_s(1,1) < \Delta_0$, the addition of a pair of electrons to the dimerized polymer at $T = 0$ will lead to the spontaneous creation of an AB pair of spinless solitons with charge $Q_A = (1+f)e$ on the A soliton and charge $Q_B = (1-f)e$ on the B soliton. In the hypothetically doped polymer such solitons would lead to separate intragap absorptions at $\hbar\omega = \Delta_0 - \alpha$ and $\hbar\omega = \Delta_0 + \alpha$ and the difference in their charges might also lead to separate vibrational bands in the infrared.

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Gravitation, Phase Transitions, and the Big Bang

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Introduced here is a model of the early universe based on the possibility of a first-order phase transition involving gravity, and arrived at by a consideration of instabilities in the semiclassical theory. The evolution of the system is very different from the standard Friedmann-Robertson-Walker big-bang scenario, indicating the potential importance of semiclassical finite-temperature gravitational effects. Baryosynthesis and monopole production in this scenario are also outlined.

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The rapproachement between particle physics and cosmology cannot be complete until quantum gravity is fully understood, when it will be possible to trace quantitatively the big bang to times $\sim t_{\text{Planck}}$ ($= 5.4\times10^{-44}$ s). Developments in particle theory, however, have motivated a consideration of periods shortly thereafter. Not only might one explain such fundamental quantities as the observed baryon-to-photon ratio,[1] but the early universe may have undergone phase transitions during which its dynamics may have differed greatly from that of the adiabatic Robertson-Walker model.[2] Thus the early universe can serve as a laboratory in which to test our models of particle interactions at high energies. In particular, the resolution of various problems of cosmology may be tied to understanding the peculiarities of gravity as a field theory.

The model I present, based on treatment of classical gravity as a remnant of a phase transition, is somewhat speculative and preliminary, but illustrates several important aspects of such an approach: (1) The attempt to couple quantum mechanics and general relativity is strongly tied to thermodynamics. Resulting effects will be important in the early universe, and need further investigation. (2) Quantum, or semiclassical, gravitational effects may be relevant at temperatures below the Planck temperature.

Specifically this model indicates that after such a transition the temperature of space may have always been lower than the critical temperature for restoration of grand unified gauge symmetries. At the same time it may be possible to generate the observed baryon excess while suppressing monopole production. I here briefly outline these results, leaving more detailed discussions to a future paper.

Although they present some problems, first-order transitions may play a crucial role in early-universe dynamics, perhaps resolving several paradoxes of the standard Friedman-Robertson-Walker adiabatic model. Indeed, given the possibility that baryon number may not be conserved, all the observed matter and entropy of the present universe may have been generated in such a transition.[2] Thus the big-bang explosion itself may have been the result of a first-order phase transition. In an earlier article[3] I suggested that it may be feasible to connect such a possibility to the nature of classical gravity. The gravitational Lagrangian with its dimensional coupling $K = (16\pi G)^{-1} \sim O(m_{\text{Planck}}{}^{2})$ has the form of a nonrenormalizable low-energy effective interaction in an expansion in inverse powers of a large mass scale at which some heavy degree of freedom is frozen out. In this sense it resembles the Fermi weak effective Lagrangian.

