close to the three-body results. Clearly, the s-d shell plays a larger role in ^{6}Li in three-body models than in the shell models considered.[14] With three-body dynamics, the maximum of the shell orbitals (or the rms radial distances) order according to their approximate shell energies, and have a physical exponential tail at large radial distances. As an example, we show a comparison of the three-body prediction to that of Donnelly and Walecka[11] for the $p_{3/2}(p_{1/2})$ single-particle radial density in ^{6}Li (see Fig. 1).

Evidently, for those processes which are sensitive to structural details of the $A=6$ nuclei, a three-body model gives a more fundamental and physically meaningful description than conventional shell models.

Details and other results of our present calculation will be published elsewhere. This work is supported in part by the U. S. Department of Energy.

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Xα Approach for the Determination of Electronic and Geometric Structure of Polyacetylene and Other Chain Polymers

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The first self-consistent $X\alpha$ study of *trans*-polyacetylene, $(\mathrm{CH})_x$, is reported. This study is carried out by application of a new linear-combination-of-atomic-orbitals method which determines both the electronic structure and geometry of periodic chain polymers variationally from the $X\alpha$ total-energy functional. The present *trans*-$(\mathrm{CH})_x$ results compare favorably with experiment and indicate that the present method will be useful in the study of both the electronic and geometric properties of other quasi one-dimensional systems.

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Non-self-consistent local-density-functional (LDF) methods have recently been used[1,2] in informative studies of several quasi one-dimensional (1D) electroactive polymers. However, little if any attention has been given to the possibility of employing LDF-based techniques to predict simultaneously the ground-state geometry and electronic structure of these and other chainlike systems. For the quasi-1D semiconducting polymers such an *ab initio* ability would be especially useful since often important details of their intrachain geometry are not experimentally well known[3] because of difficulties in preparing single crystals of these materials. Very recently Dunlap and Mei[4] have shown that the fully self-consistent molecular LCAO-$X\alpha$ (LCAO denotes linear combination of atomic orbitals) method developed by Dunlap, Connolly, and Sabin[5] and Mintmire and Dunlap[6] can yield first-principles predictions of the geometry and force constants of the covalent dimers C_2 and Si_2 which are in excellent agreement with the results of full Hartree-Fock configuration-interaction (CI) calculations. In addition, the recent work of Becke[7] (where he solves the $X\alpha$ model using an accurate numerical scheme) shows that this LCAO-$X\alpha$ approach yields accurate total energies within the $X\alpha$ model. These results together with earlier demonstrations[5] that these LCAO-$X\alpha$ techniques can satisfactorily predict geometries for a range of molecules lead us to expect that the methods of Refs. 5 and 6, when generalized to the periodic chain polymers, may provide an important new way of studying these systems. In this Letter we discuss such a generalization and report results we have obtained from it for *trans*-polyacetylene, $(CH)_x$. These results are very encouraging when compared to experiment. That such a generalization should be possible has already been demonstrated by the work of Mintmire and co-workers[8] on model systems.

To describe our method we begin with the total-energy functional within the $X\alpha$ model[9] which (in Hartree atomic units) is

$$\langle E\rangle = -\tfrac{1}{2}\sum_{i,k} n_i(k)\int_\Omega d^3r\,\varphi_i^*(\vec{r};k)\nabla^2\varphi_i(\vec{r};k) + U_c - U_x, \qquad (1)$$

where Ω denotes integration over the unit cell and $n_i(k)$ is the occupation number of the one-electron wave function $\varphi_i(\vec{r};k)$ in the ith band with wave vector k. The Coulomb energy is $U_c = \frac{1}{2}[\rho - \rho_N|\rho - \rho_N]$, where

$$[\rho_a|\rho_b] = \int_\Omega d^3r_1 \int d^3r_2\,\rho_a(\vec{r}_1)\rho_b(\vec{r}_2)/r_{12},$$

and the interaction of a nuclear point charge with itself is taken to be zero in this notation. The charge density is $\rho = \sum_{i,k} n_i(k)|\varphi_i(\vec{r};k)|^2$ and ρ_N denotes the lattice of nuclear charges. Finally, the exchange energy is

$$U_x = 9\alpha[3/32\pi]^{1/3}\int_\Omega d^3r\,\rho^{4/3}(\vec{r}).$$

In our work we use a linear combination of atomic orbitals (LCAO) to construct the wave functions $\varphi_i(\vec{r};k)$ from a basis set of Bloch functions. These Bloch functions are generated from atom-centered s- and p-type Gaussian functions. Variational minimization of the total-energy expression yields the usual secular matrix which we then solve self-consistently with $\alpha = \frac{2}{3}$ to obtain the one-electron spectrum. Finally, the total energy per unit cell is evaluated directly from Eq. (1) with these self-consistent wave functions.

Two major problems[10] arise in any attempt to implement the above procedure. The first results from the fact that in an analytic basis the number of Coulomb matrix elements increases very rapidly as a function of basis-set size. The second is due to the long-range nature of the Coulomb interaction and the infinite extent of the chain. This leads to slow covergence in the lattice sums used in evaluating the Coulomb matrix elements. We have circumvented both of these problems by simultaneously treating the electronic and nuclear charges in an optimal fitting procedure. In more detail, we first introduce an approximate total Coulomb energy per unit cell

$$\tilde{U}_c = [\rho - \rho_N|\tilde{\rho} - \rho_N] - \tfrac{1}{2}[\tilde{\rho} - \rho_N|\tilde{\rho} - \rho_N],$$

where $\rho(\vec{r}) \simeq \tilde{\rho}(\vec{r}) = \sum_i f_i F_i(\vec{r})$ and the $F_i(\vec{r})$ are periodic fitting functions constructed from Gaussians. The exact U_c can then be shown to be a rigorous upper bound of $\tilde{U}_c$. The coefficients f_i defining $\tilde{\rho}$ are chosen optimally by finding the variational extremum of $\tilde{U}_c$ with respect to these coefficients while requiring that $\tilde{\rho}$ yield the same total charge per unit cell as ρ. This novel procedure, in addition to allowing an accurate evaluation of U_c, also allows a straightforward use of the multipole expansion techniques of Piela and Delhalle[11] to include all long-range multipole interaction contributions falling off slower than any desired level (currently octopole-octopole interactions). Thus the effects of neglecting long-range multipole terms which introduce errors in, e.g., the band energies[12] has been avoided. Also in our approach no constraints have been placed on the one-electron potential (such as muffin tins) in the self-consistent-field procedure. Finally, errors introduced by using our fitting techniques can be made as small as desired by increasing the size of the fitting-function basis. These methods enable us for the first time to calculate a well-defined total energy directly from Eq. (1) as well as solve the local-density-functional model self-consistently for systems as complicated as actual chain polymers.

We have chosen *trans*-$(CH)_x$ for initial application and testing of the above methods since $(CH)_x$ is a prototype system of great current interest[13] about which much is experimentally known. In implementing these $(CH)_x$ studies we have employed a $7s3p/3s$ basis set[14] and used ten evenly spaced wave vectors to describe the Brillouin zone. As a preliminary to this choice of basis set, calculations were preformed on the ethylene molecule (C_2H_4) using the molecular LCAO-$X\alpha$

method[5] on which our approach is partially based. For the $7s3p/3s$ basis set this molecular study yielded an equilibrium C-C bond distance of 1.35 Å which compares favorably with the experimentally determined[15] bond distance of 1.34 Å. For simplicity in these molecular calculations as well as in our $(\mathrm{CH})_x$ studies all bond angles were constrained to be 120° (as would be expected for sp^2 hybrid orbitals) and all the C-H bond distances were fixed at the generally accepted value of 1.08 Å.

The total energy per unit cell of *trans*-$(\mathrm{CH})_x$ was determined at eleven different geometries. These geometries encompass projected dimerization distances u (as defined by Su, Schrietter, and Heeger[16]; $u=0$ implies no dimerization) and unit cell lengths, L, ranging from 0 to 0.038 Å and 2.36 to 2.46 Å, respectively. Analysis of these results indicates a dimerized ground state ($E_T = -75.7349$ hartrees, which is -0.6817 hartree lower than the corresponding[17] separated atomic limit) that is stablized by 0.016 eV per CH unit[18] relative to the lowest-energy undimerized state ($E_T = -75.7337$ hartrees). We also find that the unit cell length of the dimerized ground state, L_0, differs insignificantly (~ 0.003 Å) from the unit cell length of the lowest-energy undimerized state.

Table I summarizes a number of our calculated equilibrium properties of *trans*-$(\mathrm{CH})_x$ and compares the results to experiment. We also include in this table the corresponding predictions of Karpfen and Petkov[12] obtained by employment of Hartree-Fock methods without CI. As can be seen from Table I our L_0 is in good agreement with the data and we do not expect this value to change more than a few percent in any larger-basis-set calculation. However, we are not as confident of the accuracy of our predicted value of the equilibrium dimerization coordinate $u_0 \sim 0.02$ Å (corresponding to long and short bonds of 1.434 and 1.377 Å, respectively) since we have found that the energy difference between our ground-state dimerized geometry and some appreciably more dimerized configurations up to $u \sim 0.03$ Å is only of the order of 25% of $E_{\mathrm{stab}} = 0.016$ eV/CH. In view of this result we think that even the present $7s3p/3s$ basis set may provide only an approximate answer to the value of u_0 actually implied by Eq. (1). This result also shows that it may not be profitable to pursue this question any further within the context of a single-chain calculation since because of these small energy differences interchain interactions may, e.g., play a prominent role in any final determination of u_0. However, extrapolating a comparison we have made between the present results and those obtained using a smaller basis set ($4s2p/3s$) indicates that u_0 will probably increase with a larger-basis-set calculation[20] because of a slightly better description of the bonding. This, coupled with the fact that the $4s2p/3s$ and $7s3p/3s$ results both show that the total energy increases rather rapidly for values of u_0 a little greater than 0.03 Å, gives us confidence that our present results restrict the actual value of u_0 implied by Eq. (1) to somewhere in the vicinity of ~ 0.02 to ~ 0.03 Å simply as a result of intrachain effects. This range of values of u_0 overlaps well with the corresponding experimentally suggested range,[20] $0.02\ \text{Å} \lesssim u_0 \lesssim 0.04$ Å. Interestingly, assuming that the u_0 of the actual system is, for whatever reason, somewhat larger than what we presently obtain can partially account for our underestimation (see Table I) of the experimental energy gap at the Fermi level. For example, we have shown that the present method yields an E_g of 1 eV if we suppose that $u_0 = 0.03$ Å. We would not expect our predicted E_g ever to agree much better with the data than this result since the $X\alpha$ method typically underestimates gaps by 30% to 50% when compared to experiment.[21] Note, though, that just because the $X\alpha$ method underestimates gaps does not imply that this method cannot yield a good deal of information about the excitation spectrum of the system. In fact, using our results corresponding to $u_0 = 0.03$ Å, we have calculated directly the complex (optical) susceptibility, $\chi''(\omega)$, em-

TABLE I. Comparison of present results to experimentally suggested values and corresponding predictions of the Hartree-Fock study of Ref. 12. The quantities L_0, u_0, and E_g are defined in the text. The energies E_1, E_2, and E_3 denote the positions of the three prominent peaks in the x-ray photoelectron spectroscopy data measured with respect to the highest occupied state (theory) or threshold (experiment).

	Ref. 12	Present work	Experiment
L_0 (Å)	2.48	2.44	2.46^{a}
u_0 (Å)	0.03	0.02	0.03 ± 0.1^{a}
E_1 (eV)	-7	-6	-6^{b}
E_2 (eV)	-14	-10	-10^{b}
E_3 (eV)	-22	-17	-17^{b}
E_g (eV)	5.7	0.6	$1.4\text{–}1.8^{a,c}$

[a] Ref. 19.

[b] Ref. 1.

[c] Ref. 16.

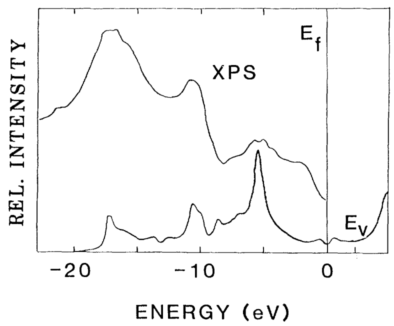

FIG. 1. Comparison of our valence band DOS (convoluted with a 0.3-eV-wide Lorentzian) to the x-ray photoelectron spectroscopy (XPS) results reported in Ref. 1. The energies E_F and E_V denote the Fermi and vacuum levels, respectively. Note: In XPS the cross section for *s* electrons is considerably larger than for *p* electrons and we do not try to account for this in our DOS.

ploying only our π bands, and find that the results with a slight broadening (~ 0.1 eV) and a small upward energy shift (~ 0.5 eV) agree very well with experiment.[22] Further details of these studies will be reported elsewhere.

Finally, in Fig. 1 we compare by aligning thresholds our equilibrium density of states (DOS) to the x-ray photoelectron spectrum of Brundle reported in Ref. 1. Excellent agreement may be seen in the positions of the peaks located at − 6, − 10, and − 17 eV. Based on these results, it certainly seems that the present method leads to the best overall description to date of the occupied valence bands of *trans*-$(\mathrm{CH})_x$.

Our work demonstrates for the first time the utility of a LCAO-$X\alpha$ approach in obtaining the ground-state geometry of a periodic chain polymer. The *trans*-$(\mathrm{CH})_x$ results reported above provide substantial evidence that the LCAO-$X\alpha$ method described here can be used to study informatively other related electroactive polymers, either extant or postulated. The present methods are not restricted to such polymers but can be used to investigate, e.g., piezoelectric polymers of current interest as well as various insulating covalent chain polymers such as polyethylene. Our approach when coupled with a pseudopotential should also be useful in studying realistic higher-dimension systems.

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[18] Our value of E_{stab} does not contradict the observed dimerization of the chain at room temperature ($kT = 0.026$ eV) and higher since for the present problem at such temperatures the thermal energy will effectively never be distributed in such a way as to cause significant effects on the average dimerization u_0. We have demonstrated this point explicitly within the Su-Schrieffer-Heeger model which for the parameters of Ref. 16 has an E_{stab} of 0.015 eV but, however, within a mean-field approach exhibits essentially no effects on u_0 at room temperature and has a Peierls transition temperature of $\sim (e^{\gamma}/2\pi k)E_g \sim 5\times10^3$ K.

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Slowing Down of Rubidium-Induced Nuclear Spin Relaxation of ^{129}Xe Gas in a Magnetic Field

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The longitudinal relaxation rate of ^{129}Xe nuclear spins slows down substantially in an external magnetic field of about 100 G. From an analysis of the magnetic slowing down and of the dependence of the zero-field relaxation rates on the third-body pressure, the authors have deduced the magnitudes of the spin-rotation and spin-exchange interactions in the Rb^{129}Xe molecule, as well as the formation and breakup rates of RbXe in N_2 gas and the dissociation constant of RbXe. The magnetic slowing down shows directly that binary collisions contribute no more than a few percent to the relaxation rates.

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The nature of the spin interactions in mixtures of ^{129}Xe or ^{131}Xe gas and Rb vapor has attracted much interest lately.[1-3] The production of large nuclear polarization in noble gases by optical pumping of a noble-gas–alkali-vapor mixture is simple and effective. Wall-dominated relaxation times of minutes to hours can be obtained. These systems have many potential uses as gyroscopes[1,2] or magnetometers, in the study of angular correlations of nuclear radiations from radioactive noble-gas nuclei, and in the search for nuclear electric dipole moments.[4] Thus, it is important to understand the properties of the van der Waals molecules, which mediate the spin exchange, in some detail. Recent experiments of Bhaskar, Happer, and McClelland[3] have shown that the absolute nuclear spin polarization of ^{129}Xe produced by optical pumping of the RbXe system is much too small to be consistent with the binary exchange cross sections reported in Ref. 2, and that the spin transfer must be completely dominated by interactions in RbXe van der Waals molecules. The estimate of interaction constants and of the molecular formation and breakup rates in Ref. 2 should therefore be revised. However, only ratios of interaction constants and no absolute magnitudes were measured in Ref. 3, and no information about molecular formation and breakup rates was obtained.

We have recently completed extensive studies of the slowing down of the ^{129}Xe spin relaxation rate in an external magnetic field[5] for cells with nearly the same composition as those of Ref. 2. These experiments show *directly* that the binary relaxation rates are no larger than a few percent of the molecular-induced relaxation rates. We have used magnetic decoupling data to infer the *magnitude* of the spin-rotation interaction $\gamma\vec{S}\cdot\vec{N}$ between rubidium electron spin $\vec{S}$ and the rotational angular momentum $\vec{N}$ of the RbXe molecule, and have also determined the formation and breakup rates of RbXe molecules in N_2 gas. The measured spin-rotation strength γN is the same, to within experimental uncertainties, as that inferred by Bouchiat and co-workers[6,7] from an analysis of the complementary phenomenon, the slowing down of the Xe-induced relaxation of Rb electron spins in a magnetic field.

The experimental procedures used in this work are much simpler than those used in Refs. 1 and 2. The basic apparatus used in our work and representative raw data are shown in Fig. 1. We used spherical Pyrex cells, containing 0.5 Torr of Xe (60% ^{129}Xe) at 20 °C, a small droplet of ^{87}Rb metal, and various amounts of N_2. The ^{129}Xe was spin polarized by pumping the cells with circularly polarized 7947-Å Rb resonance radiation ($5S_{1/2} \to 5P_{1/2}$). Representative pumping times, usually with a laser[3] but occasionally with a lamp, were about 10 min. In the probe phase of this experi-