Conformation and electronic structure of polyethylene: A density-functional approach

M. S. Miao, P. E. Van Camp, and V. E. Van Doren
Department of Physics, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

J. J. Ladik
Institute for Theoretical Chemistry, Friedrich-Alexander University Erlangen-Nürnberg, D-8520 Erlangen, Germany

J. W. Mintmire
Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342
(Received 21 February 1996)

Two different local-density approximations, the Gáspár-Kohn-Sham and the Perdew-Zunger approximations, of the density-functional method have been used to calculate structural and electronic properties of polyethylene systems with several different dihedral angles. For each system, the CC bond lengths and the CCC and HCH bond angles are optimized simultaneously. All the parameters appear to be strongly coupled with torsional freedom and vary with the change in dihedral angle in a pattern similar to that of the total energy. The total energy has an absolute minimum for the planar zigzag conformation but a distinct local minimum for the quasi-stable helical conformation. Another minimum occurs in the energy curve close to this gauche minimum. The calculated valence and conduction bands are discussed and compared with other theoretical calculations and experiment. [S0163-1829(96)02239-4]

INTRODUCTION

Polyethylene—perhaps the simplest primary structure of any polymer, (CH₂)ₙ—is at the same time one of the most technologically and commercially important as well as one of the most experimentally well-characterized polymeric materials known. Because of these characteristics, polyethylene is frequently used as a standard test case for new developments of theoretical techniques and methods before investigating more complicated structures. Crystals of polyethylene are also easily synthesized with a high degree of purity, allowing the experimental determination of very precise structure parameters.¹-⁵ The mechanical and elastic properties of this material have been an ongoing subject for both theoretical and experimental study for several decades.⁶ Furthermore, angle-resolved photoemission experiments on linear alkanes, CH₃(CH₂)₃₃CH₃,⁷,⁸ have been used to derive the valence-band structure of polyethylene. Thus, not only the results of the theoretical calculations of the geometrical structure but also of the electronic structure can be compared with experiment.

Previous theoretical studies range from semiempirical to first-principles methods. Most previous electronic structure calculations on polyethylene, and on polymers, in general, have ranged from semiempirical calculations⁹-¹⁵ to ab initio calculations¹⁶-¹⁹ including correlation effects from many-body perturbation theory.²⁰ Unlike the case in solid-state and molecular physics, density-functional approaches have not been widely used for polymers, with a mere handful of local-density functional (LDF) calculations applied to polyethylene.²¹-²³ Most of the electronic structure calculations on polyethylene have been carried out for the planar zigzag conformation with a dihedral angle of 180°, or for structures with dihedral angles close to the planar carbon backbone conformation. Helical conformations of macro-molecules have been widely known especially for some biopolymers such as proteins or DNA. The problem is the same as that of a small molecule in which the total energy will vary with dihedral angle. By changing the dihedral angle between neighboring CCC planes helical structures are introduced, in contrast to the translational symmetry present in the planar zigzag conformation. Such structures require the use of dramatically larger unit cells for band-structure calculations unless helical symmetry is directly incorporated into the electronic structure calculation. This was first proposed for semiempirical methods¹² and later for an ab initio approach.²⁴ Karpfen and Beyer¹⁷ performed Hartree-Fock (HF) calculations on polyethylene, calculating the total energy for a range of helical angles. No such comprehensive study of the total energy as a function of backbone dihedral angle has been made using LDF methods, although Springborg and Lev²¹ report a study of a calculated LDF energy over a very limited range of dihedral angles close to 180° with the results severely disagreeing with previously reported ab initio results.

The work presented herein describes the results of a systematic evaluation as a function of conformation, in particular as a function of dihedral angle, of the electronic structure and total energy of polyethylene within a local-density-functional approach using a contracted Gaussian orbital-type basis set. One of the authors has recently extended a first-principles local-density-functional approach, developed originally to treat the electronic properties of chain polymers with translational periodicity,²⁵,²⁶ to calculate the total energies and electronic structures of chain polymers with helical symmetry. This method calculates the total energy and the electronic structure using local Gaussian-type orbitals within a one-dimensional band-structure approach. A preliminary study of polyethylene was presented in an earlier paper as a test of the algorithms used.²⁷ In contrast to the previous pa-
per where all internal coordinates but the backbone dihedral angle were held fixed, the current work includes optimization of both the backbone and the substituent conformation. We find that the total energy, the carbon-carbon bond length, and the carbon backbone bond angle exhibit similar features as a function of backbone dihedral angle. Each shows an absolute minimum at the planar zigzag angle of 180°, a local minimum around the gauche conformation of 60°, and a local maximum for the rotational energy barrier height at about 120°. Furthermore, a satellite structure appears in these curves for a backbone dihedral angle of about 80°, close to the gauche minimum. The quasistable gauche minimum will be discussed because it corresponds to a commonly observed stable conformation in many polymers, especially biopolymers such as proteins and DNA.

THEORY

In this work, we use the local-density-functional approach based on a linear combination of Gaussian-type orbital originally developed for molecular systems,28,29 and extended to two-dimensionally periodic systems30 and chain polymers,25–27 to calculate the total energies and electronic structures of helical chain polymers. We present below a brief overview of this approach, with special attention paid to those aspects of this scheme that are specific to helical polymer systems. Full details of the approach are reported elsewhere.27

Let us begin by defining the systems that we shall consider. Borrowing concepts from solid-state band-structure theory, we can define a helical chain polymer as a nuclear lattice constructed from a finite basis of atoms and a screw operation $S(h, \phi)$. For mathematical convenience, we define the screw operation in terms of a translation $h$ units down the $z$ axis in conjunction with a right-handed rotation $\phi$ about the $z$ axis. That is,

$$S(a, \phi)r = \begin{pmatrix} x \cos \phi - y \sin \phi \\ x \sin \phi + y \cos \phi \\ z + h \end{pmatrix},$$

with the screw operation henceforth denoted as $S$, with arguments $h$ and $\phi$ implicitly understood. Because the symmetry group generated by the screw operation $S$ is isomorphic with the one-dimensional translation group, Bloch’s theory can be generalized so that the one-electron wave functions will transform under $S$ according to

$$S^\kappa \psi_i(r; \kappa) = e^{i\kappa r} \psi_i(r; \kappa).$$

(3)

The quantity $\kappa$ is a dimensionless quantity which is conventionally restricted to a range of $-\pi < \kappa < \pi$, a central Brillouin zone. For the case $\phi=0$ (i.e., $S$ a pure translation), $\kappa$ corresponds to a normalized quasimomentum; i.e., $\kappa = kh$, where $k$ is the traditional wave vector from Bloch’s theorem in a solid-state band-structure theory, and $h$ is the primitive lattice translation.

The one-electron wave functions $\psi_i$ are constructed from a linear combination of Bloch functions $\phi_j$, which are in turn constructed from a linear combination of nuclear-centered Gaussian-type orbitals $\chi_j(r)$ (in this case, products of Gaussians and the real solid spherical harmonics),

$$\psi_i(r; \kappa) = \sum_j c_{ji}(\kappa) \phi_j(r; \kappa),$$

$$\phi_j(r; \kappa) = \sum_m e^{-i\kappa m} \chi_j(r).$$

(4)

The one-electron-density matrix is then given by

$$\rho(r;r') = \sum \frac{1}{2\pi} \int_{-\pi}^{\pi} d\kappa \ n_i(\kappa) \psi^*_j(r'; \kappa) \psi_j(r; \kappa)$$

$$= \sum_{ij} \sum_m P_{ij}^m \chi_i^{m+} \chi_j^{m'}(r).$$

(6)

where $n_i(\kappa)$ are the occupation numbers of the one-electron states, $\chi_j^m$ denotes $S^m \chi_j(r)$, and $P_{ij}^m$ are the coefficients of the real lattice expansion of the density matrix given by

$$P_{ij}^m = 0 \frac{1}{2\pi} \int_{-\pi}^{\pi} d\kappa \ n_i(\kappa) \phi_j^*(k) \phi_i(k) e^{i\kappa m}.$$  

(7)

The total energy for the polymer system is given in atomic units by

$$E = \sum_{ij} \sum_m \sum_{m'} \frac{1}{2} \left( \chi_i^m | \nabla^2 \chi_j^{0} \right) + \sum_{ij} \epsilon_{xc} [\rho(r)] \left( \chi_j^{0} \right)$$

$$+ \sum_{ij} \sum_{m} \sum_{m'} \frac{Z_n Z_n'}{R_{n-R_{n'}}} P_{ij}^m \chi_i^m \chi_j^{m'}$$

$$- 2 \sum_{n} \sum_{m} \chi_i^{m} \left( \frac{Z_n}{R_{n-R_{n'}}} \right) \chi_j^0 \chi_j^{m}.$$  

(8)

where $Z_n$ and $R_n$ denote the nuclear charges and coordinates within a single unit cell, $R_{n-n'}$ denotes the nuclear coordinates in unit cell $m$ ($R_{n-n}=S^n R_n$), and $[\rho_1|\rho_2]$ denotes an electrostatic interaction integral

$$[\rho_1|\rho_2] = \int d^3r_1 \int d^3r_2 \frac{\rho_1(r_1)\rho_2(r_2)}{r_{12}}.$$  

(9)

Rather than solve for the total energy directly as expressed in Eq. (8), we follow the suggestion of earlier workers to fit the exchange-correlation potential and the charge density (in the Coulomb potential) to a linear combination of Gaussian-type functions. The methods used are essentially a straightforward extension of fitting methods developed for molecular calculations. For the exchange-correlation functional, two local-density approximations were used: the Gáspar-Kohn-Sham (GKS) exchange approximation (or the Hartree-Fock-Slater model),31,32 and the Kohn-Sham exchange functional together with the Perdew-Zunger33 (PZ) analytic fit to the numerical electron-gas correlation results of Ceperley and Alder.34

The Gaussian orbital and auxiliary basis sets used were optimized for LDF calculations by Godbout et al.35 Using Huzinaga’s notation,36 the hydrogen atoms had a (4111#) contraction pattern, and the carbon atoms had a
TABLE I. Optimized geometries and torsional potential using the GKS and PZ local-density approximations. In addition to the CC bond length, CCC bond angle, and HCH bond angle, the torsional potential and Mulliken population on carbon are tabulated.

<table>
<thead>
<tr>
<th>Dihedral angle (degrees)</th>
<th>Optimized geometries</th>
<th>Relative energy (kcal/mol)</th>
<th>Carbon population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC (Å)</td>
<td>CCC (degrees)</td>
<td>HCH (degrees)</td>
</tr>
<tr>
<td>GKS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>1.534</td>
<td>112.970</td>
<td>109.989</td>
</tr>
<tr>
<td>150</td>
<td>1.543</td>
<td>113.454</td>
<td>109.969</td>
</tr>
<tr>
<td>145</td>
<td>1.547</td>
<td>113.732</td>
<td>109.921</td>
</tr>
<tr>
<td>120</td>
<td>1.557</td>
<td>114.550</td>
<td>109.833</td>
</tr>
<tr>
<td>90</td>
<td>1.544</td>
<td>111.642</td>
<td>110.312</td>
</tr>
<tr>
<td>80</td>
<td>1.542</td>
<td>112.707</td>
<td>110.114</td>
</tr>
<tr>
<td>70</td>
<td>1.542</td>
<td>113.281</td>
<td>110.193</td>
</tr>
<tr>
<td>60</td>
<td>1.541</td>
<td>113.079</td>
<td>110.118</td>
</tr>
<tr>
<td>50</td>
<td>1.548</td>
<td>113.739</td>
<td>109.931</td>
</tr>
<tr>
<td>45</td>
<td>1.550</td>
<td>115.825</td>
<td>109.672</td>
</tr>
<tr>
<td>PZ</td>
<td>180</td>
<td>1.515</td>
<td>112.984</td>
</tr>
<tr>
<td>150</td>
<td>1.523</td>
<td>113.569</td>
<td>109.624</td>
</tr>
<tr>
<td>145</td>
<td>1.527</td>
<td>113.889</td>
<td>109.572</td>
</tr>
<tr>
<td>120</td>
<td>1.536</td>
<td>114.975</td>
<td>109.509</td>
</tr>
<tr>
<td>90</td>
<td>1.524</td>
<td>111.968</td>
<td>109.914</td>
</tr>
<tr>
<td>80</td>
<td>1.522</td>
<td>112.402</td>
<td>109.854</td>
</tr>
<tr>
<td>70</td>
<td>1.522</td>
<td>113.411</td>
<td>109.804</td>
</tr>
<tr>
<td>60</td>
<td>1.521</td>
<td>113.405</td>
<td>109.784</td>
</tr>
<tr>
<td>50</td>
<td>1.527</td>
<td>114.183</td>
<td>109.547</td>
</tr>
<tr>
<td>45</td>
<td>1.529</td>
<td>116.139</td>
<td>109.426</td>
</tr>
</tbody>
</table>

(7111/4111/1*) contraction pattern. Auxiliary fitting functions consisting of four s functions and four sets of s, p, and d functions chosen to share the same exponents, denoted as a (4,4,4,4) auxiliary basis, were used on the carbon atoms, while a (3,1;3,1) auxiliary basis was used for the hydrogen atoms.

RESULTS

Based on the formalism described above, the total energy and electronic band structure has been calculated for the polyethylene system over a range of carbon backbone dihedral angles. Only dihedral angles larger than 40° have been considered because of the large steric repulsion present for conformations with larger helical twist. At each dihedral angle we minimized the total energy with respect to the carbon-carbon bond length, the carbon backbone bond angle, and the hydrogen-carbon-hydrogen bond angle. We included the carbon-hydrogen bond distance in a preliminary set of optimizations and found that the optimum choice of this internal coordinate is relatively insensitive to the choice of backbone dihedral angle. Thus we have fixed the carbon-hydrogen bond distance at the average value of 1.10 Å. In Table I, we list the optimized values for these internal coordinates at each given carbon backbone dihedral angle examined for both the GKS and PZ local-density functionals. We also tabulate the calculated torsional potential for the polyethylene helix, where the torsional potential is defined as the total energy per CH$_2$ unit relative to the energy of the all-

trans conformation. The calculated CC bond lengths of 1.534 and 1.515 Å for GKS and PZ, respectively, are in good agreement with the experimentally suggested values of 1.53 Å from x-ray-scattering results,1–4 and 1.58 Å from neutron scattering.5 Our theoretical results can also be compared with two other first-principles results: 1.56 Å obtained from an ab initio HF calculation by Karpfen,16 and 1.52 Å obtained from the LDF calculation of Springborg and Lev.23 This latter LDF calculation used an LDA scheme with a linear combination of muffin-tin orbitals (LMTO) basis set. The calculated carbon backbone bond angles of 113.0° for both the GKS and PZ results are both in excellent agreement with the experimentally suggested range1–5 of 108–112° and with the HF result16 of 112.3°. For the HCH bond angle the calculated values of 110.0° (GKS) and 109.7° (PZ) agree well with an experimental range1–5 of 107–109° and the HF result16 of 107.4°.

Figure 1 depicts the torsional energies as a function of dihedral angle for both our GKS and PZ LDF calculations, and compares these results with ab initio HF results of Karpfen and Beyer.17 The HF calculations used a STO-3G basis set and allowed optimization of the carbon backbone bond angle. All three sets of results agree with each other qualitatively. The rotational barriers around the eclipsed position (dihedral angle of 120°) of the carbon-carbon backbone bonds at 3.6–3.7 kcal/mol agree with the value of 4.0 kcal/mol from HF results and are consistent with typical rotational barriers for alkane systems. All three curves have a second local minimum about the all-gauche conformation of the carbon backbone, at roughly 55–60°. For our LDF results these minima lie 0.4 and 0.1 kcal/mol above the all-gauche conformation, somewhat lower than that calculated by the HF approach. All three curves exhibit a nonquadratic curvature in this gauche minimum that leads to a broadening of the well through dihedral angles of 70–80°. For the GKS calculations, we even find a third local minimum in the torsional potential curve. This undulating behavior in the

![FIG. 1. Torsional potential per CH$_2$ unit cell (kcal/mol) for a single polyethylene helical chain as a function of carbon backbone dihedral angle. Open circles and closed squares denote current GKS and PZ results, respectively. The dotted line with closed triangles denotes ab initio HF results by Karpfen and Beyer (Ref. 17).](image-url)
The gauche minimum is similar both to the ab initio HF results reported by Karpfen and Beyer,\textsuperscript{17} as well as the semiempirical complete neglect of differential overlap/2 (CNDO/2) results reported by Morokuma\textsuperscript{14,15} and Fujita and Imamura.\textsuperscript{12,13} Morokuma\textsuperscript{15} ascribes the complex behavior of this gauche minimum to competing effects between the various next-nearest-neighbor, second-nearest-neighbor, etc., interactions of the CH\textsubscript{2} units when the total energy is divided into intrasegment and intersegment contributions within the CNDO/2 approximation. Within his analysis, the nearest-neighbor (0–1) interaction is the dominant cause of the local maximum around the 120° eclipsed conformation, and has a local minimum near the 60° gauche conformation that it contributes to the total energy. Around the gauche minimum, the other contributions vary dramatically. The second-nearest-neighbor (0–2) interaction decreases monotonically as the dihedral angle is decreased, while the on-site (0–0) contributions and third-nearest-neighbor (0–3) interactions are repulsive and partially compensate the 0–2 interaction. According to Morokuma’s analysis, therefore, the gauche minimum is the result of a delicate balance between intersegment interaction, and small changes in the approach used can modify the detailed shape dramatically. We thus do not believe that this complex structure is explicitly an artefact of the choice of algorithm or exchange-correlation functional, except indirectly as any such choice will change the balance between energy contributions.

Springborg and Lev\textsuperscript{23} also reported a torsional potential using LDF methods based on LMTO basis sets in a limited range of dihedral angles from 150 to 180°. Their reported values of the torsional potential are more than an order of magnitude larger than the results reported herein or earlier HF and semiempirical results. At the 150° dihedral angle, Springborg and Lev calculate a torsional potential of 47 kcal/mol, compared to our LDF calculated values of 1.5 kcal/mol. Despite the assertion of Springborg and Lev that earlier methods might significantly underestimate the torsional potential of carbon backbone polymers, such large values are inconsistent both with our current LDF results and the general trend of alkanes to have rotational barriers less than 10 kcal/mol.

Let us now examine the one-electron band structure within our approach. Figure 3 depicts our calculated valence bands and low-lying conduction bands for the all-trans conformation using both the GKS and PZ LDF approximations. The all-trans conformation possesses a reflection plane containing the helical axis, and this reflection plane symmetry operation commutes with the helical operator. The solid lines and dashed lines for the bands in Fig. 3, therefore, denote electron states that are symmetric (\(\sigma\)-like) and antisymmetric (\(\pi\)-like) under the reflection operator. The lowest-lying valence band is seen to belong to the symmetric representation, and is typically associated with carbon 2s\(\sigma\) bonding between backbone carbons. The next two valence bands cross and belong to opposite symmetries; these bands are typically associated with the carbon-hydrogen \(\sigma\) bonds. We note that the reflection symmetry will be broken when the dihedral angle is rotated away from the all-trans conformation, and then the one-electron bands will not cross, but be expected to have avoided crossings near the all-trans conformation crossing points.

In general, we find that the GKS and PZ band structures are similar with little qualitative difference, with the predominant effect of the treatment of correlation being a shift of the PZ bands to 0.5–1.0 eV lower energy than the GKS bands. The calculated band gaps are 7.7 (GKS) and 8.0 eV (PZ), which are both in rather good agreement with the ex-
experimental result of 8.8 eV, and compare to a HF value of 13.4 eV. This agreement is unexpected insofar as LDF methods typically underestimate band gaps substantially in semiconductors by 20–50%. In general, however, our results for band gaps agree with typical expectations for LDF results that their agreement with experiment is somewhat better for certain quantities like the band gap than HF results, while qualitatively similar to results expected for a good semiempirical approach. Our one-electron eigenvalues appear to lie about 3–5 eV higher than experimental values. For example, we calculate the maximum of the valence band to be ~5.4 eV (GKS) and ~6.4 eV (PZ), compared to experimentally suggested values of the ionization potential of 9.6–9.8 eV. We see good agreement between theory and experiment in the valence bandwidths and general location of the bands in the Brillouin zone, after adjusting for a rigid shift in energy. Seki et al. report an experimental value for the low-lying carbon backbone σ-bonding bandwidth of 7.2 eV, compared to our calculated bandwidth of 6.0 eV (GKS) and 6.1 eV (PZ). For the all-trans polyethylene conformation, the next two valence bands belong to different irreducible representations of the reflection group and cross, requiring us to consider the total bandwidth of the two bands. We calculate this combined bandwidth to be 5.4 eV (GKS) and 5.3 eV (PZ), compared with an experimentally suggested value of 6.7 eV. The calculated gap between the lowest valence band and the minimum of the higher valence bands is 2.1 eV (GKS) and 2.2 eV (PZ), compared with an experimental value of 2.0 eV. Finally, our calculated total valence bandwidths are 13.3 (GKS) and 14.0 eV (PZ), compared to an experimental value of 16.2 eV. These results can be compared to a HF calculated bandwidth of 19.3 eV (Ref. 16) and a LDA calculated bandwidth using LMTO basis functions of 17.4 eV.

In Fig. 4, we compare the PZ band structure for all-trans polyethylene with the PZ band structures at two other choices of dihedral angle corresponding to the eclipsed conformation (120°) at roughly the maximum of the torsional potential, and the all-gauche conformation in the secondary minimum. We note the avoided crossing in the valence bands for dihedral angles other than 180°. We find the same general trends in the change in band energies with change in dihedral angles as earlier reported by Springborg and Ley using LMTO basis functions on the restricted range of dihedral angles.

FIG. 3. Valence- and conduction-band structure of all-trans polyethylene for (a) GKS and (b) PZ LDF results. Vertical strips denote half the helical Brillouin zone, going from zone center (κ=0) at the left-hand side to the zone edge (κ=π) at the right-hand side of each strip. Solid lines denote electron states symmetric under reflection operation; dashed lines denote electron states antisymmetric under reflection operation.

FIG. 4. Calculated valence-band structure of all-trans polyethylene for a C2H4 unit cell using PZ LDA compared with angle-resolved photoemission data of Fujimoto et al. (Ref. 8). Experimental data has been shifted up in energy 4.5 eV. Solid lines denote electron states that are symmetric under a reflection operation; dashed lines denote electron states that are antisymmetric under a reflection operation.

FIG. 5. Comparison of calculated valence-band structures of helical polyethylene using PZ LDA at dihedral angles of (a) 180°, (b) 120°, and (c) 60°.
conformational angles from 155° to 180°. In both our calculated results using GKS and PZ, the lowest valence band varies only slightly with the change of dihedral angle, with the dominant effect a raising of the band at the Brillouin-zone edge with decreasing dihedral angle. The upper two valence bands have more pronounced changes with variations in dihedral angle. As the dihedral angle is lowered from 180° the two bands increase their separation at the zone center, while decreasing their relative separation at the zone edge. In both cases their average energy rises as the dihedral angle is lowered from the all-trans planar conformation.

SUMMARY

We have carried out the first LDF total-energy calculation of the torsional potential and electronic properties of polyethylene through a range of dihedral angles encompassing both the all-trans and all-gauche local minima. Both the Gáspár-Kohn-Sham and the Perdew-Zunger local-density approximations have been used to calculate the structural and electronic properties of a single polyethylene chain with helical symmetry over a range of carbon backbone dihedral angles. The all-trans planar carbon backbone conformation was found to be the equilibrium geometry in agreement with experimental measurements and other theoretical results. In agreement with previous ab initio and semiempirical results, we find a complex structure in the all-gauche local minimum which is ascribed to long-range interactions in the helical chain. We find good agreement of the one-electron band structure with current angular resolved photoemission experiments and other theoretical work. For polyethylene, we find this LDF approach capable of both determining structural and electronic properties in agreement with experiment, and plan to extend our efforts to more complex organic and biologically-oriented polymeric systems.

ACKNOWLEDGMENTS

This work is supported partly under Grant No. 9.0053.93, and partly by the “Program for Scientific Missions” of the Belgian National Science Foundation (NFWO). It is also supported by the “Program for the Stimulation of Participation in Research Programs of the European Union” of the University of Antwerpen, and by the Concerted Action “Long Term Performance and Stability of Materials for Biomedical Applications” No. BE7317, coordinated by C.N.R.S.M., Brindisi (Italy). J.W.M. acknowledges support by the Office of Naval Research (ONR) though the Naval Research Laboratory and directly though the ONR Chemistry-Physics and Materials Divisions. V.V.D. acknowledges support from the Theoretical Division of the Los Alamos National Laboratory.