**FINAL SCIENTIFIC/TECHNICAL REPORT**

1. DE-FG02-05ER46201; Roberto Car; Strongly correlated electrons: Ground states, excited states, and transport; PI: Roberto Car

2. There were no authorized distribution limitation notices, such as patentable material or protected data

3. *Executive Summary*

The research supported by this grant focused on the quantum mechanical theory of the electrons in materials and molecules. Progress was made in dealing with electronic correlation effects in the ground state energy of molecular systems, and with topological concepts to classify the electronic state of molecules and materials, including excitation and transport properties. The physical and chemical properties of molecules and materials derive from their electronic structure, but the latter cannot be calculated exactly even with the most powerful computers because the computational cost of solving the exact equations of quantum mechanics increases exponentially with the number of electrons. The exponential cost originates from the correlations among the electrons that repel each other via Coulombic forces. In this project we have developed a new functional approximation for the ground state electronic energy that includes explicitly, and in a controllable way, the effects of the interelectronic correlations. In addition we have further developed topological concepts for classifying the electronic states of periodic ring molecules and solids. Topological concepts are very powerful because they allow us to predict subtle properties of materials and molecules using very general geometrical properties of the electron wavefunctions that do not depend on the quantitative details of the electronic interactions, which are very difficult to calculate with high accuracy.

4. The development of a new class of controlled functional approximations for the ground state energy of molecules and materials was the main goal of the project. It has been fulfilled with the formulation of the occupation-probabilities natural orbital functional theory (OP-NOFT). This approach introduces new theoretical concepts but practical application has proved to be harder than anticipated. So far it has been utilized only at its lowest level of approximation in the context of relatively small molecules (with up to 16 atoms). The study of topological properties of the electron wavefunctions in materials was not proposed in the original proposal but was prompted during the funding period by our interaction with leading experimental groups in materials chemistry and physics at Princeton University.

5. *Summary of project activities for the entire funding period*

The activities and accomplishments are summarized in the following sections, organized according to the main research themes.

*Natural Orbital Functional Theory (NOFT)*

We have developed a novel natural-orbital functional theory for the electrons, called OP-NOFT, in which the basic variables are the natural spin orbitals (NSOs), their occupation numbers, and their joint occupation probabilities (OPs). The theory and its simplest applications are presented in a paper published in the *Proceedings of the Natural Academy of Sciences*. The OP-NOFT formalism allows us to represent the two-body density matrix (2-DM) accurately, transcending the limitations of the one-body density matrix (1-DM) theories, which only require single-NSO occupation probabilities or occupation numbers. OP-NOFT's general form contains single-NSO through 4-NSO joint occupation probabilities (n-OPs) and scales as the fifth power of the basis set size. We have implemented numerically OP-NOFT-0, which is OP-NOFT in its simplest formulation, for seniority 0, i.e. when all the natural orbitals are doubly occupied. OP-NOFT-0 approximates doubly occupied configuration interaction (DOCI), a configuration interaction expansion of the many-body wavefunction in which spin up- and spin down-orbitals have the same occupation. OP-NOFT-0 contains only 1- and 2-natural-orbital (NO) OPs and retains the third-power scaling of Hartree-Fock energy functional minimization, albeit with a substantially higher prefactor. OP-NOFT-0 describes the dissociation of simple diatomic molecules and multiatom chains with accuracy that can be comparable to that of DOCI, which uses a compact basis of Slater determinants but retains combinatorial scaling. In 4-electron systems, OP-NOFT-0 yields results identical to those of DOCI. Our approach is powerful at high correlation, i.e., for static correlation at intermediate and large interatomic separations where Hartree-Fock fails due to multireference character of the ground-state wavefunction. There, the OP-NOFT-0 outperforms Hartree-Fock, density functional theory (DFT) with standard approximations, and quantum chemistry methods such as (single-reference) coupled cluster with single, double, and perturbative triple electron-hole excitations [CCSD(T)], a standard of accuracy at equilibrium separations. The introduction of higher-order OPs as variational parameters, with closure of the theory at their level, is an essential part of our work and is responsible for its favorable scaling. What distinguishes our approach from 1-DM theories is that it is based on a sequence of controlled approximations on the 2-DM. Thus it would be possible to improve its accuracy by improving on these approximations in future research.

*Topology in molecular systems and molecular-based lattices*

In a paper published in *Physical Review B* we studied ring-shaped molecules finding that hexagonal shaped molecules with nearest- and next-nearest-neighbor hopping, for a certain range of the on-site Hubbard repulsion, have a doubly degenerate ground state separated by an energy gap $\Delta$ from the excited states. Such isolated ring molecules behave like fragile Mott insulators (FMI). This state results from strong static correlation and cannot be adiabatically connected to a band insulator under the condition that time reversal and certain point group symmetries are preserved. In quantum chemistry, the distinction between a band insulator and an FMI corresponds to the difference between dynamical and static correlation. In a subsequent paper published in *Phys. Rev. Letters* we considered a

2D array of such molecules arranged to form a triangular or honeycomb lattice with intermolecular hopping small compared to $\Delta$. In this limit the doublet ground state of each molecule is described by a pseudospin 1/2 and the low energy sector of the 2D Hamiltonian is well described by the spin compass model with antiferromagnetic exchange coupling. On the triangular lattice, the compass model exhibits collinear stripe antiferromagnetism, implying *d*-density wave charge order in the original Hubbard model. On the honeycomb lattice, the compass model has a unique quantum disordered ground state that transforms nontrivially under lattice reflection. The ground state of the Hubbard model on the decorated honeycomb lattice is thus a 2D fermionic symmetry protected topological phase. This state, protected by time reversal and reflection symmetries, cannot be connected adiabatically to a free fermion phase. Our results suggest that this system could be a realization of a quantum spin liquid.

*Topological materials*

In collaboration with the groups of R. J. Cava and N. P. Ong at Princeton University we have calculated the DFT band structures of a number of three-dimensional (3D) Dirac semimetals to help establish design principles for new materials. In a paper published in *Physical Review B* three different design principles were presented (case I, II, and III), each of which yields predictions for new candidates. For case I, 3D Dirac semimetals based on charged-balanced compounds BaAgBi, SrAgBi, YbAuSb, $PtBi_2$, and $SrSn_2As_2$ are identified as candidates. For case II, 3D Dirac semimetals in analogy to graphene, $BaGa_2$ is identified as a candidate, and BaPt and $Li_2Pt$ are discussed. For case III, 3D Dirac semimetals based on glide planes and screw axes, $TlMo_3Te_3$ and $AMo_3X_3$ family, in general, (A=K, Na, In, Tl; X=Se, Te), as well as the group IVb trihalides such as $HfI_3$, are identified as candidates. Finally, conventional intermetallic compounds with Dirac cones were discussed and $Cr_2B$ was identified as a potentially interesting material. The interaction with the experimental groups of Cava and Ong attracted our attention to $WTe_2$, a material synthesized in Cava's lab, which exhibits a very large non-saturating magnetoresistance. In order to explain the unusual electronic properties of $WTe_2$ we developed a theory of topological non-symmorphic metals from band inversion. In a paper published in *Physical Review X* we expand the phase diagram of two dimensional nonsymmorphic crystals at integer fillings that do not guarantee gaplessness. In addition to the trivial gapped phase that is expected, we find that band inversion leads to a class of topological, gapless phases. These phases are exemplified by the monolayers of $MTe_2$ (M=W,Mo) if spin-orbit coupling is neglected. We characterize the Dirac band touching of these topological metals by the Wilson loop of non-Abelian Berry gauge field. Furthermore, we develop a criterion for the proximity of these topological metals to 2D and 3D $Z_2$ topological insulators when spin-orbit coupling is included: our criterion is based on nonsymmorphic symmetry eigenvalues, and may be used to identify topological materials without inversion symmetry. An additional feature of the Dirac cone in monolayer $MTe_2$ is that it tilts over in a Lifshitz transition to produce electron and hole pockets - a type-II Dirac cone. These pockets, together with the pseudospin structure of the

Dirac electrons, suggest a unified, topological explanation for the recently reported, non-saturating magnetoresistance in $WTe_2$, as well as its circular dichroism in photoemission. We complement our theoretical analysis and first-principle (DFT) band-structure calculations with a tight-binding model for the $WTe_2$ monolayer, derived from interpolating the DFT band-structure with maximally localized Wannier functions.

*Hyperuniform spin systems*
This study originated from an undergraduate senior thesis in the Princeton physics department, directed by R. Car and S. Torquato. The results of this thesis work have been published in *Physical Review B*. This project studied stealthy hyperuniform spin chains using inverse statistical mechanical techniques. Disordered many-particle systems that are stealthy and hyperuniform represent new states of matter that are unique in that they are transparent to radiation for a range of wave numbers around the origin. In this work we have considered spin chains that have this property, finding that they can be either unique or degenerate ground states of long-range spin-spin interactions. They are distinctly different from spin glasses in both their inherent structural properties and the nature of the spin-spin interactions required to stabilize them.

6. *Products developed under the award*
The following publications, in peer reviewed journals, were supported by the award.
1. Ralph Gebauer, Morrel H. Cohen, and Roberto Car: A well-scaling natural orbital theory, *PNAS* **113**, 12913 (2016)
2. L. Muechler, J. Maciejko, T. Neupert, and R. Car: Moebius molecules and fragile Mott insulators, *Phys. Rev. B* **90**, 245142 (2014) (editor suggestion)
3. C-C. Chen, L. Muechler, R. Car, T. Neupert, J. Maciejko: Fermionic Symmetry-Protected Topological Phase in a Two-Dimensional Hubbard Model, *Phys. Rev. Lett.* **117**, 096405 (2016)
4. Q.D. Gibson, L.M. Schoop, L. Muechler, L.S. Xie, M. Hirschberger, N. P. Ong, R. Car, R.J. Cava: Three-dimensional Dirac semimetals: Design principles and predictions of new materials, *Phys. Rev. B* **91**, 205128 (2015)
5. L. Muechler, A. Alexandrinata, T. Neupert, R. Car: Topological Nonsymmorphic Metals from Band Inversion, *Phys. Rev. X* **6**, 041069 (2016).
6. E. Chertkov, R. A. Distasio Jr, G. Zhang, R. Car, S. Torquato: Inverse design of disordered stealthy hyperuniform spin chains, *Phys. Rev. B* **93**, 064201 (2016) (editor suggestion)

7. *Computer modelling*
The project involved new theoretical developments, numerical calculations using the proposed theory on model systems (such as small molecules, the Hubbard model, the spin compass model etc.), as well as DFT band structure calculations for crystalline materials such as $WTe_2$ using standard and well documented electronic structure packages such as VASP and Quantum ESPRESSO. In the case of the model calculation our theory was tested against results available in the

scientific literature for the same or related models using alternative theoretical schemes. All our theoretical and numerical results have been peer reviewed.