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**NEW CONCEPTS IN ELECTRON CORRELATION WITH APPLICATION TO  
EXTENDED SYSTEMS**

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# 1. Technical Report

## Introduction

The objective of our work for ONR has been to develop and apply new, correlated electronic-structure methods for infinite-periodic systems. The methods of interest include many-body perturbation theory (MBPT) and its infinite-order coupled-cluster generalizations and complementary density-functional methods. Today we routinely do highly correlated studies of molecules (including making reliable predictions of structure, photoelectron, vibrational, and electronic spectra). The next frontier in electronic structure theory is the treatment (with the same level of confidence) of polymers, surfaces, and crystals, which are semi-conductors or insulators and are collectively termed "extended systems."

The current paradigm for molecules is SCF, MBPT(2), CCSD, CCSD(T), CCSDT, and full CI. Though convergence is not monotonic, such a sequence, augmented by experience and approximate error bars, typically offers purely *ab initio*, extrapolated solutions that are predictive. In contrast, no such paradigm exists for extended systems. Furthermore, there is no full CI so only high-level CC methods can offer reference results.

The only methods currently available for extended systems are periodic Hartree-Fock (i.e., SCF) and density functional theory (DFT), usually in the local density approximation (LDA). The former lacks the critical electron correlation effects responsible for so many of the interesting phenomena in solids, from band gaps to high  $T_c$  superconductivity, while the latter might introduce some correlation effects, but an unclear amount. In fact, the greatest weakness of DFT is that, unlike the above CC/MBPT paradigm, there is no way to systematically converge to the correct result. This causes current DFT methods to be "semi-empirical" in their application. To enable the reliable treatment of the structure, spectra, and properties of extended systems, we have embarked upon a two-pronged attack. One, we are formulating and applying CC/MBPT methods to extended systems, asking critical questions about the role of electron correlation on various properties; two, we are developing new DFT potentials by tying such potentials to high-level *ab initio* correlated results, primarily from coupled-cluster theory. This can be done in a couple of ways—by inverting the problem to extract  $V_{xc}$ 's from highly accurate coupled-cluster densities or by using CC methods to correct Kohn-Sham results as the unperturbed problem, as a function of various parameters in  $V_{xc}$ .

The following summarizes some of the principal results of our ONR grant. The reference numbers refer to our list of publications supported by ONR (Publications Section).

## Results

**A.** Choosing polyacetylene as a prototypical semi-conducting polymer, we investigated the role of electron correlation at the simplest MBPT(2) level, on its band structure [7]. Furthermore, we carefully investigated the convergence of periodic Hartree-Fock and MBPT(2) with the number of unit cells, demonstrating that prior work was inadequately converged. We also assessed the role of polarization functions in the basis set on the band structure, as prior work was limited to minimum basis sets, and, not surprisingly, found that the polarization functions were as important as they would be for molecules.

**B.** Using the methods we introduced for correlated band gaps, which requires computing the ionization potential and electron affinity for the infinite periodic system, we studied the photoelectron spectra of polyethylene [6], probably the best characterized polymer. Three experimental studies had been made, but they differed in several critical elements. Our work demonstrates that only with at least second-order correlation can the spectra be accurately assigned, and, at that level, we were also able to resolve the discrepancies among the experiments. Furthermore, we showed that neither SCF nor DFT (the latter with or without gradient corrections) could adequately explain the spectra.

**C.** An important formal question that arose in our work concerned the convergence of higher-order correlation corrections for infinite systems. Analysis shows that certain many-body diagrams could diverge in third and higher orders of perturbation theory. If so, it would be impossible to develop coupled-cluster methods for electron correlation. In two papers [4, 5], we addressed this question, proving that properly handled, all terms for the correlation energy and band structure will converge. This sets the stage for higher-order treatments of electron correlation.

**D.** In another purely formal paper [3], we develop the general theory for band structure in any order of MBPT. In this approach, we present the equations for the direct evaluation of band energies in any order of MBPT. These expressions will be used in future applications.

**E.** It is well known that electron correlation is essential in providing predictive results for the vibrational spectra of molecules, but no such study had ever been made for a polymer. Hence, we presented MBPT(2) results for the vibrational spectra of all trans polymethineimine [2], as this had been studied experimentally. Our agreement with the experiment was similar to that obtained for molecules of <5%.

**F.** Returning to our theme of convergence behavior with lattice summations, we proved formally and showed numerically that the MBPT(2) correlation correction for the total energy converges with lattice sums as  $1/N^3$ , where  $N$  is the number of cells, while for band structure, the convergence is a

much slower  $1/N^2$  [1]. This is the first proof that to obtain reliable, correlated band gaps, great attention must be paid to the lattice sums.

**G.** Polysulphur-nitride  $(SN)_x$  is a fascinating system. Under certain conditions, it is an insulator, a semi-conductor, has metallic properties, and is a superconductor below 0.26K. To investigate these aspects, we performed Hartree-Fock, DFT LDA, and Hartree calculations [8]. We find that the detailed crystal geometry can profoundly influence the electronic properties of the material. For example, for very slight differences in bond lengths, solid-state poly- $(S_4N_4)_x$  was shown to exhibit a crossing of bands accounting for its metallic, rather than semi-conducting behavior. This suggests that it should be possible to synthesize conducting polymers out of molecular crystals by polymerizing them in the solid phase.

**H.** In our DFT efforts, we have explored the relative merits of what we call HF-DFT, meaning take a Hartree-Fock density and drop it into a functional designed explicitly to account for the remaining correlation correction, and self-consistent Kohn-Sham (KS) type theory. The former was used in an extensive study of many properties and molecules to establish comparisons with CCSD(T) [12]. Such a functional based upon the Becke exchange and the Lee-Yang-Parr correlation form was found to be competitive with CCSD(T) for structures, moments, and vibrational frequencies, and superior for heats of atomization. The latter occurs due to DFT being less sensitive to basis set, as it is a one-particle theory.

**I.** Unlike Kohn-Sham DFT, HF-DFT does not satisfy a form of the Hellman-Feynman theorem, which would make it comparatively easy to evaluate analytical gradients and Hessians, readily providing the structure and vibrational frequencies. Consequently, that has not yet been done for HF-DFT. We presented the basic theory and made some applications to electric properties in [11].

**J.** In work not yet published, we have investigated the determination of molecular hyperpolarizabilities with DFT methods. It has been stated that such properties are poorly described, but we find that, unlike KS DFT, HF-DFT provides competitive results. We are currently doing such DFT studies for frequency-dependent hyperpolarizabilities using a DFT response theory that also allows the treatment of electronic excited states.

**K.** The central role of Hartree calculations instead of Hartree-Fock in making the connection between DFT and *ab initio* correlated methods is well known. Less well known is that orthogonalized Hartree orbitals offer a "localized" set of orbitals that emulate the bonds chemists tend to visualize. In other words, since Hartree orbitals involve no exchange, they are "more localized" in the sense of Edmiston and Ruedenberg's criteria of minimum exchange being used to localize orbitals. We explored this property [10] in a study of the Hartree method for molecules, demonstrating the orbital localization, which could be

used to assist a localized treatment of electron correlation with potential application to extended systems.

**L.** Related to the above, we have also considered Hartree orbitals for infinite periodic systems. Unlike the situation for molecules, Hartree orbitals for infinite systems are naturally orthogonal, since the self-energy terms vary as  $1/N$  with the number of unit cells, and vanish in the limit. We used these in the polysulphur-nitride paper [8] and in unpublished work on correlated band gaps from DFT and Hartree references. In the latter paper, we use various KS-DFT models to define a mean field, from which the proper second-order corrections are introduced with MBPT(2). Applications have been made to polyacetylene, demonstrating that the KS-DFT references, and the Hartree reference, so far, appear to offer no better unperturbed problem for band structure than HF. As we develop new  $V_{xc}$ , however, we hope to improve upon this situation.

**M.** We have also used KS-DFT reference functions for molecules, where unlike our applications to polymers, we can apply second-, third-, and fourth-order correlation corrections, and coupled-cluster theory, too. At the last level, the reference function is largely irrelevant, as CC theory is essentially invariant to orbital choice. However, there may be some hope that new  $V_{xc}$ 's can be defined that could minimize the CC corrections to the unperturbed problem for a variety of properties, like total energy, ionization potentials, electron affinities, excited states, densities, etc., all of which are available to us by virtue of our existing coupled-cluster methodology. In this way, we anticipate that we will be able to invent new exchange-correlation potentials that will have the advantage of being calibrated for properties. Those CC-generated  $V_{xc}$ 's will then be used in solid state applications as well as for molecules.

## Conclusions

The future of this work is unlimited. Obviously, we want to treat correlation at the coupled-cluster level and we are writing such programs currently. Though MBPT(2) shows prospects for a good treatment of correlation for many properties, analogous to its role for molecules, it will always be subject to the criticism of whether it is converged. CC theory alleviates this problem, offering the best possible, necessarily size-extensive approach, for extended systems.

Another alternative approach is offered by the so-called GW approximation. The idea here is that electrons interact through a screened potential, determined by a dielectric function. The dielectric function is computed at some level, typically Hartree-Fock, and then a second-order perturbation correction is made based upon the dielectric screened potential. This correction is usually done using DFT but seldomly self-consistently. Such an approximation offers an alternative way of summing higher-order diagrams to CC theory, and can be done *ab initio*. We are also planning to do this.

Another very important advance for extended systems is offered by developing analytical gradient methods, even for DFT and HF approximations. Unlike molecules, where such gradients are absolutely essential for polyatomic systems, this has never been done for infinite, periodic systems. We have recently formulated the theory for gradients and Hessians and now plan to implement it. With such a tool, the theoretical design of materials becomes more approachable.

We are also developing new  $V_{xc}$ 's by exploiting CC results for a variety of quantities, the density, ionization potential, electron affinity, excited states, and others, to attempt to "project" CC methods onto a DFT computational structure. This provides a partial answer for the failure of DFT to offer a way to systematically converge to the right answer. Such new  $V_{xc}$ 's should also play a role in establishing reliable, but practical treatments of electron correlation for extended systems.

## 2. Publications Supported by ONR N00014-92-J-1100

1. J.Q. Sun and R. J. Bartlett, "Convergence behavior of many-body perturbation theory with lattice summations in polymers," *Physical Review Letters* **80**, 349-352 (1998).
2. J.-Q. Sun and R. J. Bartlett, "Correlated vibrational frequencies of polymers. MBPT(2) for all-trans polymethinimine," *J. Chem. Phys.* **108**, 301-307 (1998).
3. J. Q. Sun and R. J. Bartlett, "Many-body perturbation theory for quasiparticle energies," *J. Chem. Phys.* **107**, 5058-5071 (1997).
4. J.Q. Sun and R.J. Bartlett, "Convergence of many-body perturbation methods with lattice summations in extended systems," *J. Chem. Phys.* **106**, 13, 5554 (1997).
5. M. Nooijen and R.J. Bartlett, "Analysis of long-range effects in many-body correlation approaches for one-dimensional periodic systems," *Int. J. Quantum Chem.* **63**, 601-614 (1997).
6. J. Q. Sun and R. J. Bartlett, "Correlated prediction of the photoelectron spectrum of polyethylene: explanation of XPS and UPS measurements," *Phys. Rev. Lett.* **77**, 3669-3672 (1996).
7. J-Q. Sun and R.J. Bartlett, "Second-order many-body perturbation-theory calculations in extended systems," *J. Chem. Phys.* **104**, 8553-8565 (1996).
8. C. J. Mei, H. J. Monkhorst, and R. J. Bartlett, "On the intrinsic conductivity of polysulphur-nitride," *Zeitschrift für. Physik.* **101**, 73 (1996).
9. R. J. Bartlett, "Coupled Cluster Theory: An Overview of Recent Developments," in *Modern Electronic Structure Theory*. (D. R. Yarkony, editor). World Scientific Publishing Co., Ltd., Singapore (1995).
10. S. A. Perera, D. E. Bernholdt, and R. J. Bartlett, "Localized Hartree product orbitals in correlated studies of molecules," *Int. J. Quantum Chem.* **49**, 559 (1994).
11. H. Sekino, N. Oliphant and R. J. Bartlett, "Property evaluation using the Hartree-Fock-density-functional-theory method: An efficient formalism for first- and second-order properties," *J. Chem. Phys.* **101**, 7788-7794 (1994).
12. N. Oliphant and R. J. Bartlett, "A systematic comparison of Hartree-Fock, a hybrid Hartree-Fock density-functional-theory, and coupled-cluster methods," *J. Chem. Phys.* **100**, 6550 (1994).

13. R. J. Bartlett and J. F. Stanton, "Applications of Post-Hartree-Fock Methods: A Tutorial," in *Reviews in Computational Chemistry*, Vol. 5, Chapter 2, p. 65-169, Eds. D. Boyd and K. Lipkowitz, VCH Publishers, New York NY (1994).

### **3. Invited Lectures at Professional Conferences, Universities and Laboratories Assisted by ONR**

- September 1997—"The Equation-of-Motion Coupled-Cluster Method and Its Similarity-Transformed (STEOM) Variant, as a Unified Treatment of Excited, Ionized, Electron-Attached States and Properties," International Conference on "Electron Correlation: From Atoms to Biomolecules" in Glumslöv, Sweden.
- June 1997—"The Interface Between DFT and *ab initio* Correlated Methods," Symposium on Density Functional Theory and Applications. Duke University, Durham, North Carolina.
- February 1997—"Electron Correlation in Extended Systems: The Next Frontier?" Ohio Supercomputer Center, Columbus, OH.
- December 1996—"Energetic Materials Workshop," Office of Naval Research, Washington, DC.
- October 1996—"Electron Correlation in Polymers," Swedish-American Symposium on the Foundations of Quantum Theory in Chemistry, Molecular Physics and Biology: A Symposium in Honor of Per-Olov Löwdin," Sanibel, FL.
- August 1996—Battelle Northwest Laboratories, EMSL Theory, Modeling and Simulation Workshop, "Recent Developments in Coupled-Cluster Theory Implemented into the ACES II Program System," Richland, Washington.
- April 1996—University of North Texas, Denton, Texas.
- April 1996—Southern Methodist University, Dallas, Texas.
- April 1996—University of Texas at Arlington, Arlington, Texas.
- April 1996—2<sup>nd</sup> International Congress on Theoretical Chemical Physics, New Orleans, LA.
- March 1996—Research Symposium on Multiconfigurational Perturbation Theory: Methods and Applications, Gandia, Spain.
- December 1995—Computational Chemistry Focus Group, Maui, Hawaii.
- October 1995—Lehigh University, Bethlehem, Pennsylvania.
- October 1995—Postec University, Pohang, Korea.
- October 1995—Korean Chemical Society, Pusan, Korea.
- October 1995—Korean Advanced Institute of Science and Technology, Taejeon, Korea.
- September 1995—Molecular Quantum Mechanics: Methods and Applications, Symposium in honor of S. F. Boys and I. Shavitt, Cambridge University, Cambridge, England.

- August 1995—12<sup>th</sup> Canadian Symposium on Theoretical Chemistry, University of New Brunswick, Fredericton, Canada.
- October 1994—"Coupled-Cluster Theory as a Unified Approach to Molecular Spectra," Workshop on Non-Perturbative Many-Body Methods (from Quantum Field Theory to Chemistry)," Bad Honnef, Germany.
- June 1994—"Coupled-Cluster Theory as a Unified Approach to Molecular Spectra," 8<sup>th</sup> International congress of Quantum Chemistry, Prague, Czech Republic.
- June 1994—"Properties in Coupled Cluster Theory," 8<sup>th</sup> International Congress of Quantum Chemistry Satellite Meeting, Bratislava, Slovakia.
- June 1994—Eötvös Loránd University, Budapest, Hungary.
- May 1994—"Excited States in Coupled-Cluster Theory: Valence, Rydberg and Core Excitations," 2<sup>nd</sup> Canadian Computational Chemistry Conference, Kingston, Ontario, Canada.
- April 1994—Florida State University, Tallahassee, FL.

#### **4. Graduate Students Supported**

Dr. Jun-Qiang Sun  
PhD Spring 1997

Mr. Kenneth Wilson

# REPORT OF INVENTIONS AND SUBCONTRACTS

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1a. NAME OF CONTRACTOR/SUBCONTRACTOR Rodney J. Bartlett		2a. NAME OF GOVERNMENT PRIME CONTRACT N00014-92-J-1100		3. TYPE OF REPORT (X one) a. INTERIM <input type="checkbox"/> b. FINAL <input checked="" type="checkbox"/>	
b. ADDRESS (include ZIP Code) Quantum Theory Project University of Florida Gainesville FL 32611-8435		d. AWARD DATE (YYMMDD) 931201		4. REPORTING PERIOD (YYMMDD) a. FROM 931201 b. TO 961130	
c. CONTRACT NUMBER		c. CONTRACT NUMBER			

## SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)

a. NAME(S) OF INVENTOR(S) (Last, First, MI)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SER. NO. OR PRIORITY NO.	d. ELECTION TO FILE PATENT APPLICATIONS				e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER
			(1) United States	(2) Foreign	(a) Yes	(b) No	
None							

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR		g. ELECTED FOREIGN COUNTRY IN WHICH A PATENT APPLICATION WILL BE FILED	
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## SECTION III - CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR		8. SIGNATURE	
a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, MI) Bartlett, Rodney J.		d. SIGNATURE <i>Rodney J. Bartlett</i>	
b. TITLE Graduate Research Professor		e. DATE SIGNED 4/24/98	
c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.		Non-Profit organization? <input type="checkbox"/> (X appropriate box)	