TECHNIQUE DEVELOPMENT FOR COMPLETE
ELECTRONIC-STRUCTURE CALCULATIONS IN
CRYSTALLINE SOLIDS

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Technique Development for Complete

Electronic-Structure Calculations in

Crystalline Solids

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Final report of five-year comprehensive effort in development of techniques for calculations of electronic structures of solids. Reports method based on Fourier representation theory for exact Hartree-Fock calculation; gives results for atomic and molecular hydrogen crystals and lithium crystal; preliminary studies of correlation energy; extension to surfaces or thin films and to polymers.

I. Introduction

The main goal of the research effort supported by this Grant was the systematic development of well-defined, unambiguous and practical methods for making truly ab-initio calculations of the electronic properties of crystalline solids. Prior to the grant period, nearly all calculations of solid state electronic structure had been an independent-electron approximation, and most of these studies were also characterized by approximations such as the use of empirically defined pseudopotentials, the use of a localized effective exchange potential, or the assumption of small spatial inhomogeneity in electron density. In fact, no calculations had been reported which would enable an assessment of the effects of these empirical approximations upon calculated electronic structures. Moreover, no rigorous calculation seeking to determine the energetically optimum independent-electron description of a crystalline solid had yet been carried out. This optimum description, corresponding to the solution to the Hartree-Fock problem, was expected to have significant deficiencies when directly used to estimate one-electron crystalline properties such as conductivity and spectra, but would nevertheless serve as a precise starting point not only for the discussion of electron interaction effects but also for characterizing various approximations at the independent-electron level.

In the light of the foregoing situation, the first immediate objective of this research effort was the development of computationally viable methods for approaching the Hartree-Fock description of simple crystalline solids. We introduced a Fourier representation technique, which expressed a total electronic energy of a solid in terms of a zero-order description consisting

of a lattice of point nuclei in a uniform electron distribution. This method
naturally leads to an expansion whose higher terms describe the effects of
the inhomogeneity of the actual electron distribution. The method may
readily be implemented for crystal basis functions built from Slater-type
atomic orbitals, either in lattice sums of the tight-binding variety or in
plane waves modulated by lattice inhomogeneities. Effort was directed both
to the refinement of the techniques for these calculations and to the
detailed study of the results obtained from solutions of the Hartree-Fock
problem. During the Grant period, we succeeded in developing a set of
computational methods permitting Hartree-Fock calculations to be carried
out with great efficiency, and we obtained results on atomic hydrogen,
molecular hydrogen, and lithium crystals. These results enable us to dis-
tinguish the deficiencies inherent in the Hartree-Fock method from those
introduced from approximations thereto. The Slater effective exchange
potential is found to be rather satisfactory in shape as a function of posi-
tion in the crystal, but its location on an energy scale does not vary
correctly with position in the energy band. It is also verified that cal-
culated band widths are far too wide in Hartree-Fock calculations, with
most of the error in the location of the top of the band.

In the course of developing our Fourier representation techniques, we
pointed out several features which cause the methods to have more favorable
convergence properties than was generally expected. First, the method
concentrates into its leading terms the effects due to the long-range
nature of the Coulomb force, removing many of the difficulties associated
with the fact that in ordinary space many of the lattice sums involved are
conditionally convergent. Because electron-nuclear attraction and electron-
electron repulsion are treated parallelly they cancel to a considerable

extent at an early stage in the calculations. And because the formulas for the Coulomb and exchange portions of the electron-electron interaction are relatively similar, unusual difficulties are not encountered in an exact evaluation of the exchange contribution to the electronic energy. And finally, we found that a careful symmetry grouping of terms in the lattice sums leads to a more rapid convergence in these sums than might be anticipated from the sizes of individual terms.

As has long been expected, Hartree-Fock calculations are not adequate for the description of many properties of crystalline solids, and consequently, the second immediate objective of this effort was to identify and start to implement methods for including electron correlation effects. Our initial efforts in this area consisted of critical appraisals of various procedures which had been suggested. These appraisals led us to a demonstration that for most metallic solids the introduction of an equivalent localized orbital basis would be inappropriate, with the result that we could not expect to use pair correlation methods of the types which have been successful for small atoms and molecules. An examination of various effective pair equations based on perturbation theory caused us to conclude that no justifiable formulation of this type had yet been suggested. Preliminary calculations were carried out in a random phase approximation perturbation-theoretic for the correlation energy in atomic hydrogen crystals. We found that the results depend strongly on the zero-order states employed, and that the use of Hartree-Fock zero-order states yielded much improved convergence relative to plane-wave states. This observation corroborates for moderate density solids the situation noted for atoms and molecules by comparing the work of Brueckner and Ma (based on plane waves) with that of H. P. Kelly, Das, and others (based on Hartree-Fock states). However, our preliminary

results indicated the necessity for proceeding significantly beyond the terms we found it convenient to keep in the diagrammatic perturbation theory.

Toward the end of the Grant effort we finally identified a group of methods which we believe will be ideal for the rigorous inclusion of electron correlation effects, namely the linked-cluster formalism used in nuclear physics by Kümmel and for some atomic and molecular problems by Cizek and Paldus. We examined the use of this type of formulation in solid state problems, and in preliminary work have shown that the formulation will be practical and can be carried through to a point which we expect will give the bulk of the electron correlation effects for typical systems. At the end of the Grant period, work was underway to apply this formalism to illustrative problems.

A third immediate objective was the extension of our methods to one and two-dimensional problems of practical importance: surfaces or thin films and polymers. We showed how the Fourier representation formalism could be applied to these kinds of systems, and that the computational advantages inherent in three-dimensional calculations would also be found in one and two-dimensional systems.

The immediate objectives of our effort have now largely been reached, and as the Grant period ended we were in the process of setting up the computational machinery for larger-scale calculations, using basis sets suitable for work of high accuracy and for extension to crystals with more complicated unit cells. Our computer programs can currently handle crystal orbitals built from four atomic functions of s symmetry, six p functions, and five d functions. This basis is adequate for handling both Hartree-Fock and correlation calculations at the "double-zeta" level of approximation, and should be suitable for systems containing atoms through the first transition series.

In an overall sense, our research effort exhibits several areas of scientific significance. First, we have shown that the techniques we have been developing can lead to practical results at the Hartree-Fock level and beyond, both for three-dimensional crystals and for systems exhibiting one and two-dimensional periodicity. We have shown the advantages, both conceptually and practically, of starting from crystal orbitals built from suitable atomic functions rather than from plane waves characteristic of a uniform electron gas. That these advantages are beginning to be more widely recognized is attested by the fact that an increasing number of other workers are using our kinds of methods for solid-state electronic-structure calculations. Secondly, our work moves significantly toward enabling a good assessment to be made of the errors to be associated with various empirical approximations and with the neglect of electron correlation. And finally, we believe that our recent studies point the way toward practical methods for handling correlation effects in extensive systems.

In following sections of this report we review in more detail, first the work published with Grant sponsorship, and then the work completed or in progress and not yet published. Further sections of this report list publications, the personnel participating in the work, and the individuals and organizations with whom our research group has interacted.

II. Published Work

Our initial research effort was directed at "exact" Hartree-Fock calculations for cubic metallic hydrogen crystals (Reports 1, 2, and 9). In this work we used basis Bloch functions that can be best described as atomic-orbital-modulated plane waves. Only 1s-type exponential orbitals were used. This is appropriate for these systems, as the only occupied s-type valence band is half-filled. A partitioning of the total Hartree-Fock energy could be made into physically relevant terms. Particularly noticeable is the distinction of large homogeneity and small inhomogeneity terms, the latter being associated with the non-zero vectors in the reciprocal lattice sums. Also the first hints emerged that a correct exchange treatment strongly effects the orbital energies, but not the associated Bloch orbitals. A more detailed discussion of these and other points can be found in Reports 18 and 19.

The next system we looked at was the lithium crystal, both in the face-centered and body-centered cubic symmetries. In a series of publications (Reports 5, 11, and 12) we gradually refined our methods of computation, using a frozen core and a valence 2s-band function similar to that for hydrogen. Interesting conclusions could be drawn, both when comparing our results with experimental information and other calculations. Properties were identified for which the Hartree-Fock model gives a good description. Again in Reports 18 and 19 a review has been given of this work.

In our search for computationally efficient methods to handle summations and integrations we developed techniques also useful for the evaluation of Slater-orbital product Fourier transforms (Report 3) and, consequently, of

Slater-orbital, quantum-chemical multi-center integrals (Report 6). Although
not fully implemented yet, we have great hopes for the latter approach, as
it seems to have the potential of being significantly more efficient than
current methods. In Report 13 a valuable alternative is formulated to the
"brute force" reciprocal lattice summations in evaluating the central Fourier
transform quantities.

In Reports 4, 18, and 19 the formalism appropriate for polymers has
been presented. Again the Fourier transform method is shown to be very
advantageous in handling the Madelung-type conditional convergence problem,
and the full treatment of exchange. Applications are presently underway.

Further Hartree-Fock work for three-dimensional crystals was done on
the transition from molecular to metallic hydrogen under high pressures.
In Report 16 we have published the calculations of the transition pressure
and density. Another result that attracted considerable attention was our
finding that, at least at the Hartree-Fock level, the transition is not
sudden. Rather, we found a significant pressure range over which the change
from a pure molecular solid to a metallic solid takes place. Although the
experimental situation is in considerable doubt, it is worthwhile mentioning
that the predicted transition pressure is remarkably close to that found
by a Russian high pressure group. We refer to above reports for computational
details.

In our attempts to find the most appropriate scheme for the correlation
corrections we made two important observations. In Report 8 we proved on
largely group-theoretical grounds that except for the one-dimensional case,
it is not normally possible to transform the set of occupied Bloch orbitals
to a localized equivalent-orbital form. This unfortunately rules out the
possibility to treat correlation from a localized orbitals point of view, so

successful in molecular calculations. Furthermore, we published in Report 14 a serious shortcoming in an electron-gas correlation treatment by Singal and Das, starting from a pair-correlation formulation. Although the approach seemed very attractive at face value, the treatment of certain singularities was found to be very unsatisfactory. It is remarkable, though, and possibly revealing, that the correlation energy at different electron densities is close to that obtained with quite different methods.

The most satisfactory correlation energy treatment in metallic hydrogen to date, in our opinion, was published in Report 10. Here we computed the random-phase approximated correlation energy for simple-cubic metallic hydrogen, but using the Hartree-Fock band functions and energies. The effects of using these more realistic states are quite profound. The correlation energy at the Hartree-Fock equilibrium density is cut by about one-half, bringing it in line with typical correlation energies per electron pair found in molecules. Also the density dependence of the correlation energy is much weaker compared to that of the electron gas, again in accordance with typical findings from atoms and molecules. Finally, the relative magnitude of contributions from Coulomb and exchange diagrams is drastically changed: the second order exchange now makes up only a few per cent of the total correlation energy, compared to about 40 per cent in the electron gas model.

We also investigated the applicability of plane-wave expansions for the Bloch functions in a Hartree-Fock calculation (Reports 15 and 17). We looked into this since we hoped to obtain a maximally flexible angular description of the Bloch functions for excited bands relevant in correlation studies. Although this proved to be true, the overall computational effort and the inherent poorer quality of the wave function near the nuclei does, in our

opinion, not warrant this approach for high quality work.

In Report 7 we published a note on the high-speed and high-accuracy evaluation of exponential integrals of complex arguments. This is useful in molecular calculations using mixed Gaussian-Slater orbital basis sets.

As indicated above, Report 19 contains a comprehensive review of essentially all the work done under this Grant. In addition, material related to the conditional convergence of lattice sums and two-dimensional crystals (e.g. thin films) has been included.

III. Work Unpublished at Grant Termination

When the Grant expired, several research activities were underway in a "holding pattern". One of the projects, about to give many significant results, is the development of comprehensive computer program to perform Hartree and Hartree-Fock calculations on all cubic, symmorphic structures for first and second row elements, hexagonal close packed structure (for beryllium and helium) and diamond. The wave functions will be at the double-zeta Slater orbital level (two 1s, two 2s, two 2px, two 2py, two 2pz and five 3d orbitals). The conventional "tight-binding" form of the Bloch orbitals will be used. In the course of its development, largely by graduate student J. D. Pack, several important innovations were made, particularly in the handling of reciprocal lattice summations, discovery of efficient asymptotic formulas and Brillouin Zone integrations. On this last problem we are publishing (Report 20) a paper, that already attracts attention before actual publication: workers in the solid state theory group of Dr. Freeman (at Northwestern University) are implementing the method in crystals with non-cubic symmetries. In essence we have found a better theoretical foundation and generalization of the popular Gilat-Raubenheimer methods. The significance of the method ties in the facts that it applies to all symmetries and dimensionalities, gives k-space interpolation to all orders and its convergence properties are well understood. It has greatly facilitated the integration over nearly spherical regions of the Brillouin Zone.

The second project nearing completion is the implementation of a cluster expansion method for correlation effects in the electron gas. This type of expansion was first proposed in nuclear structure calculations by Kümmel and

applied by Cizek and Paldus to a few atoms and a molecule. As explained in earlier Interim Reports the method is very well-defined, generalizable, appropriate for large systems and physically attractive. Dr. Freeman is mainly in charge of this project, and has reached the point of actually including "ladder diagrams" to all orders in the random-phase approximation. These terms are widely considered to be the "missing link" needed fo. a realistic treatment of electron gas correlation at intermediate densities. Many attempts have been made to include these terms, but essentially all approaches resort to uncontrollable approximations. If Dr. Freeman succeeds (and all indications are he will) a highly significant result for modern solid state theory will be obtained.

During the past half year we also have been spending considerable time on a study of the formal structure of the cluster expansion method. We found ways to derive the basic equations without invoking any diagrammatic methods, Wick's theorem or the occurrence of so-called "unlinked" terms. We are still finding simplifying aspects to the theory, which is neither variational nor perturbational in an order-by-order sense. The non-linearity and inhomogeneity of the equations poses special mathematical problems, such as the existence of multiple solutions and an uncertainty about the nature of these solutions. These questions are presently being investigated.

IV. Publications

1. "'Exact' Hartree-Fock Calculations for Atomic-Hydrogen Crystals," by Frank E. Harris and Hendrik J. Monkhorst, Solid State Comm. 9, 1449 (1971).

2. "'Exact' Hartree-Fock Results for Atomic Hydrogen Crystlas," by Frank E. Harris, Lalit Kumar and Hendrik J. Monkhorst, Int. J. Quantum Chem. 5, 601 (1972).

3. "Accurate Calculation of Fourier Transform of Two-Center Slater Orbital Products," by Hendrik J. Monkhcrst and Frank E. Harris, Int. J. Quantum Chem. 6 601 (1972).

4. "Fourier Representation Methods for Electronic Structures of Linear Polymers," by Frank E. Harris, J. Chem. Phys. 56, 4422 (1972).

5. "The Exact Hartree-Fock Problem for Lithium Crystals: A Preliminary Report," by Frank E. Harris, Lalit Kumar and Hendrik J. Monkhorst, in Proceedings of Colloquium on Electronic Structure in Ordered and Disordered Solids (Menton, France, September 20-24, 1971): J. Physique 33, (C3), 99 (1972).

6. "Slater Orbital Molecular Integrals with Numerical Fourier-Transform Methods. I. (Coplanar) Multi-Center Exchange Integrals Over 1s Orbitals," Ante Graovac, Hendrik J. Monkhorst and Tomislav Zivkovic, Int. J. Quantum Chem. 7, 233 (1973).

7. "Numerical Evaluation of Exponential Integrals of Complex Arguments," by Frank E. Harris.

8. "On Localized Orbitals in Infinite, Periodic Systems," by Hendrik J. Monkhorst, Chem. Phys. Letters 17, 461 (1972).

9. "Electronic Structure Studies of Solids. II. 'Exact' Hartree-Fock Calculations for Cubic Atomic Hydrogen Crystals," by Frank E. Harris, Lalit Kumar and Hendrik J. Monkhorst, Phys. REv. B7, 2850 (1973).

10. "Random-Phase Approximation Correlation Energy in Metallic Hydrogen Using Hartree-Fock Band Functions," by Hendrik J. Monkhorst and Jens Oddershede, Phys. Rev. Letters 30, 797 (1973).

11. "Electronic Structure Studies of Solids. III. Hartree-Fock Band Functions and Energies for Cubic Lithium Crystals," by Lalit Kumar, Hendrik J. Monkhorst and Frank E. Harris, Phys. Rev. B9, 4084 (1974).

12. "Electronic Structure Studies of Solids. IV. Physical Quantities for Cubic Lithium Crystals from Hartree-Fock Results," by Lalit Kumar and Hendrik J. Monkhorst, J. Phys. F4, 1135 (1974).

13. "Computation of Fourier Transform Quantities in Hartree-Fock Calculations for Simple Crystals," by Ante Graovac, Hendrik J. Monkhorst and M. L. Glasser, Int. J. Quantum Chem. 9, 243 (1975).

14. "Comments on 'Self-Consistent Pair-Correlation Approach to Many-Body Effects in Metals', by Hendrik J. Monkhorst, Phys. Rev. B12, 792 (1975).

15. "On the Hartree-Fock Limit for Metallic Hydrogen with Plane Wave Basis," by Jens Oddershede, Lalit Kumar and Hendrik J. Monkhorst, Int. J. Quantum Chem. S8, 447 (1974).

16. "Exact-Exchange Crystal Hartree-Fock Calculations of Molecular and Metallic Hydrogen and their Transitions," by David E. Ramaker, Lalit Kumar and Frank E. Harris, Phys. Rev. Letters 34, 812 (1975).

17. "Electronic-Structure Studies of Solids. V. Rigorous Hartree-Fock Treatment of Metallic Hydrogen using a Plane-Wave Basis," by Lalit Kumar, Hendrik J. Monkhorst and Jens Oddershede.

18. "Electronic Structure Calculations on Crystals and Polymers," by Frank E. Harris, in "Electronic Structure of Polymers and Molecular Crystals," Plenum Pub. Co., 1975, pp. 453-477.

19. "Hartree-Fock Studies of Electronic Structures of Crystalline Solids," by Frank E. Harris, "Theoretical Chemistry," Vol. 1, 1975, pp. 147-218.

20 "Special Points for Brillouin-Zone Integrations," by Hendrik J. Monkhorst and James D. Pack, Phys. Rev. B (to be published).

V. Personnel

The following professional personnel from the University of Utah have been active in work under the Grant:

Frank E. Harris, principal investigator (11/70-10/75).

Hendrik J. Monkhorst, principal investigator (11/70-10-75).

Lalit Kumar, postdoctoral research associate (11/70-8/73; 8/75-10/75).

Jens Oddershede, postdoctoral research associate (9/71-8/73).

David E. Ramaker, postdoctoral research associate (9/72-8/74).

Pollyanna Pixton, student programmer (6/72-6/73); research assistant (9/74-10/75).

Ante Graovac, research assistant (7/73-12/73).

James D. Pack, research assistant (1/74-10/75).

VI. Dissertations

None

VII. Patentable Inventions

None

VIII.   Individuals and Organizations Interacted With

Professional contacts have been made with a large number of individuals from various institutions. The following list represents only individuals with whom significant communication took place.

Organization	Individuals
Quantum Theory Project University of Florida	Prof. P-O. Lowdin Prof. Y. Ohrn Prof. J. W. D. Connolly Prof. D. A. Micha
Quantum Theory Group Uppsala University (Sweden)	Prof. P-O. Lowdin Dr. J-L. Calais Dr. O. Goscinski
Lawrence Livermore Laboratory	Dr. M. Ross Dr. C. Bender Dr. B. J. Alder
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