COO-1674-138

BASIC STUDIES OF ATOMIC DYNAMICS

Progress Report
for Period October 1, 1976 - September 30, 1977

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Technical Progress Report

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ABSTRACT

The most remarkable progress achieved this year was in the area of applications of an atomic approach to solid state problems, not only to impurity states, as planned, but unexpectedly to general band theory. The development of a post-adiabatic procedure, introduced last year, has been successful in initial tests. Studies of the interaction of electrons with polar molecules and especially of the orientation of atoms by collision are opening new and promising vistas. General comments are included on the encouraging but delayed impact of our past work.

1. Scope of the Report. This report covers the scientific activity of the following personnel:

a) U. Fano, Principal Investigator, 100% of research activity.

b) H. Klar, Research Associate, supported for 2 months by the Deutsche Forschungs Gemeinschaft, with a small supplement by this project.

c) Research Assistants (Graduate Students) supported by this project as follows:

G. Strinati, 12 months.
C. Clark, 12 months.
M. Kohmoto, 12 months.
C. Greene, 9 months.
C. E. Theodosiou, $3\frac{1}{2}$ months.

In addition it reflects continuing part-time collaboration with former members of the project and with personnel of other laboratories.

2. General Remarks. This year, in particular, evidence has accumulated of the long term successful impact of earlier work by this project, dating from about 1970, upon general progress in atomic and molecular physics. The following examples are noted:

a) Semi-empirical applications of Multichannel Quantum Defect Theory are now widespread, as reflected in extensive work of J. Armstrong et al. at IBM, C. Brown et al. at NRL and Maryland, K.T.Lu and others on actinide spectra at ANL and Livermore, Connerade et al. at Imperial College.

b) The combination of Phase-Amplitude Methods of integration of coupled radial equations with Frame Transformation procedures, which had been developed analytically by Chang and Fano in a molecular context, has now been utilized in a computational routine by Vo Ky Lan and LeDourneuf at Meudon. This routine has been tested successfully and promises to replace other methods of integration of coupled equations at large radial distances, for atoms as well as for molecules, which had caused increasing difficulties for a long time because they were proving very costly in realistic applications.

c) The atomic nature of conspicuous resonance excitations in lanthanides and transition metals as well as in molecules, was stressed here in 1971. It is now influencing much work as documented by its prominence in the recent VUV Conference. (See Travel Report by J.L. Dehmer of ANL-RER, September, 1977.)

d) The combination of Quantum Defect and Frame Transformation introduced by Fano for the analysis of rotational effects in H_2 photoabsorption is now being extended by C. Jungen et al. very successfully to the analysis of electron-vibration coupling. This work is producing a far more detailed insight into the effects of this coupling, drawing evidence from fine details of absorption, ionization and dissociation spectra.

Note that the coupling of electronic and nuclear motions in a molecular complex provides the main mechanism of chemical rearrangements. This mechanism has been studied hardly at all thus far in the energy range where it is most relevant, but the time seems to be ripe now for a serious analysis of this problem along the approach of Jungen. This point of view, and the more immediate opportunity of treating predissociation vibrational spectra from the point of view of multichannel quantum defect theory, has been raised by Fano in discussions at a conference in Aussois, France, this last June. Fano's extemporaneous remarks have now been prepared for publication in the conference volume (COO-1674-135).*

A contrasting item is also noted. The approach to R-matrix theory and calculations developed by Fano and by C.M. Lee in his 1974 thesis, has not yet attained a wide impact. Discussions have been in progress with P.G. Burke of Belfast and his collaborators — notably I. Shimamura — on the comparative significance of our approach and of the classical approach utilized in their extensive calculations. These discussions have led Fano to devote considerable effort this year to identifying more sharply the conceptual differences of the two approaches. Conclusions have been formulated in his invited report to the R-Matrix Symposium at the X ICPEAC in Paris last July (COO-1674-134).

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*Entries of the form (COO-1674-xxx) in this Report refer to items of the "List of Reports."

Another story, reported as Item 4 below, may also warrant a general remark. Fano had outlined in 1973 an approach to the treatment of impurity states in crystals through the construction of electronic states with central symmetries in the crystal that surrounds an impurity; these states are viewed as analogs of the spherical waves in the free space surrounding a single atom or molecule. Strinati has endeavored to develop this program since 1974. In the Summer of 1976 he remarked that the construction of central symmetry states in crystals opens a new path that would allow him to approach and solve long-standing problems of crystal band theory. The results obtained thus far form a very substantial Ph.D. thesis which is now ready for final examination and publication. Here again one can just discern very broad potential implications of this progress but it will probably take years before they can be fully assessed or exploited.

3. Two-Electron Excitations. This problem remains central to our program, but progress on it remains slow, partly because other tasks with smaller objective difficulties receive higher priority. Work on the new post-adiabatic approximation, developed in 1976, has led to a second more detailed paper by Klar published early in 1977 (COO-1674-124). A program of numerical applications was initiated by Klar after his return to Freiburg. As a first test he repeated C.D. Lin's calculation of e-H scattering introducing in it the post-adiabatic corrections; the results removed altogether the increasing discrepancies with experiment and with more elaborate calculations that had been obtained by Lin. It now appears likely that the post-adiabatic approximation will prove a very valuable adjunct to the Macek-Lin adiabatic approach to two-electron and other processes.

The preliminary studies by Fano on other aspects of the two-electron problem, indicated in Item 3 of the 1976 Report, have scarcely advanced this year. Greene has done some exploratory calculation and Fano has reformulated and discussed the newer approaches in his invited talk at the X ICPEAC, which is now in press (COO-1674-134).

4. Solid State Theory from an Atomic Approach. This work has made very gratifying and promising progress, as indicated above. The principal points developed by Strinati are summarized here:

a) When a wave with central symmetry (of the crystal's point group) is constructed as a superposition of Bloch waves with equal energy but with different wave vectors $\vec{k}$, all but very limited ranges of integration over $\vec{k}$ give contributions that depend on $\vec{k}$ smoothly. As the integration amounts to the inversion of a Fourier transform, these contributions reflect only the effect of short range interactions. On the other hand, the integrand varies rapidly in the neighborhood of singularities of its dependence on $\vec{k}$, mainly branch points, which are points of degeneracy of the band structure in directions with a nontrivial "small group", i.e., lying on planes of symmetry or on the outer surface of the Brillouin zone. Theorems of Fourier analysis show that the characteristics of each singularity are reflected in the behavior of long tails of the Wannier functions and hence reflect the influence of the long range interactions which distinguish crystalline from amorphous structures. This distinction between regions of a Brillouin zone that do or do not reflect the characteristic features of a crystal lattice is believed to be both new and fundamental. However, its physical interpretation remains to be developed.

b) The regions of singularity in $\vec{k}$ space separate portions of this space that are equivalent geometrically, but may be forced by the analytic structure of the integrand to yield contributions of opposite sign. The problem of identifying the relative phase normalization of Bloch waves with different $\vec{k}$ had been raised — but not solved — by Kohn and others. It appears now that its solution required an approach that considers an integration over $\vec{k}$ and the analytic properties of the integrand in critical ranges.

c) Singularities on the outer surface of the Brillouin zone have a special effect. Depending on their symmetry, they may cause the Wannier functions, resulting from further integration over a band's energy, to shift their center from the center of an atom to an interstitial position. This phenomenon was noticed by Kohn long ago in a one-dimensional model but was not investigated further; it may imply a special role of particular bands for the formation of bonds but its interpretation remains to be developed.

These developments have been utilized thus far for the construction of electron wave functions with central symmetry for the s-d bands of Cu. The calculation started from previously known APW Bloch function, fitted them to an analytic approximation by the Slater-Koster method and then proceeded to numerical integration over the $\vec{k}$ space. The results have been described in a separate paper (COO-1674-131) which is now ready for submission. The general theoretical development has been described in a larger paper (COO-1674-136) which is now also ready for submission.

5. Interaction of Electrons with Polar Molecules. This project was introduced in the Report for 1976, with reference to its MHD relevance. Early in this reporting period, Clark found that the influence of the electron-dipole interaction is not generally confined within the range of moderate distances accessible to a body-frame treatment. At larger distances, where a laboratory frame treatment is appropriate, the electron-dipole interaction can be readily treated in Born approximation but Clark observed that this approximation does not hold for all combinations of dipole strength, radial distances and energies which may be relevant.

To circumscribe the range of parameters where greater difficulties would be encountered, Clark undertook then the task of identifying the combined range of energies, dipole strengths and orbital momenta (equivalent to radial distances) within which the Born approximation can be applied to any prescribed accuracy. Scaling procedures, inherent in this approximation, permitted the answer to this problem to be formulated in terms of universal

three-dimensional graphs. These graphs were constructed and presented in a paper for the October Physical Review A (COO-1674-132) as well as in reports at the X ICPEAC in Paris (COO-128- and 129). Clark is now studying further the critical joint between the range of moderate radial distances where a body-frame treatment is applicable and the larger distances where a lab-frame may be combined with Born approximation.

The general understanding of the electron-polar molecule system obtained by Clark was utilized by him in a critical study of a preprint by Dubé and Herzenberg of Yale University. He pointed out the limited significance of this work, contributing remarks that were incorporated and acknowledged in the final version of the paper which appeared in the Physical Review Letters of 11 April 1977.

6. Angular Distribution of Collision Products. Theodosiou's study of the distribution of secondary electrons from autoionizing states, described in the 1976 Report, was concluded as planned about January 1, 1977. A new development occurred in the terminal months, through comparison of the calculated distribution for Na with newer measurements by K. Ross et al. at 10° intervals. The agreement was quite good except in some narrow ranges of direction where the experiment is believed erroneous. A "letter" version of Theodosiou's thesis has been published (COO-1674-125), while the major paper has undergone extensive editorial revisions after submission and is now accepted by the Physical Review.

7. Orientation of Atoms by Collision. This work has been activated early this year, but Fano's interest in it dates from the first observations in 1973-4 by Kleinpoppen et al. of electrons inelastically scattered by He in coincidence with photons emitted by the excited atoms. The experiments indicated clearly that these atoms had received in the collision a net angular momentum perpendicular to the scattering plane. Calculations in the Distorted Wave Born Approximation by Madison and Shelton reproduced the experimental result with surprising accuracy, but it remained totally unclear which mechanism determines even only the sign of the angular momentum transfer.

After unsuccessful efforts to elicit from the authors of the calculation an interpretation of their results, a new student, M. Kohmoto, was directed to this task. The initial approach was to reformulate the calculation in some more transparent way, by means of Racah algebra. A new formulation was thus obtained which relates the induced orientation of the atoms more directly to the deflection experienced by the scattered electron. In particular, this formulation establishes a preliminary result anticipated by a classical argument, namely, that the sign of the orientation would be reversed by a reversal of the sign of all the electron-atom interactions. However, the final result is still expressed as the sum of a large number of terms whose combined contribution cannot yet be surmised on qualitative grounds. Efforts are continuing to obtain a still better formulation.

These efforts have been stimulated further by the realization that a known identity, which has a central role in the present formulation, may have unsuspected mechanical significane. The results obtained last Spring have been reported at the X ICPEAC (COO-1674-127), in a Satellite Conference and in a Lyon seminar by Fano.

8. Further Developments of Quantum Defect Theory (QDT). During the last year,work of other groups applying and extending our earlier semi-empirical development of the QDT, as indicted in Item 2, brought out unclear or incomplete aspects of that theory. In two occasions we were led to undertake further development.

a) Jungen's work on the photoabsorption spectrum of H_2, now published in the Journal of Chemical Physics of June 15, attempted to derive the QDT's formulation from a standard Born-Oppenheimer approach followed by configuration mixing due to the interactions disregarded in this approach. Editorial review of the paper pointed out that the derivation was not substantiated in any detail. Discussions among Jungen, Dill and Fano suggested that the bridging between the two formulations should involve considerations of Green's function properties. Fano followed up this suggestion by

showing that the QDT and configuration mixing formulations correspond to two well-known alternative representations of the Green's function for the motion of an electron in the outer field of an atomic or molecular residue. This point of view also led to an extension of the equation for the reaction matrix of an electron-ion collision to the energy range where the electron may remain bound in some or all the channels. Thereby one extends the range of Seaton's original formulation of the QDT. This material has been submitted for publication in the Physical Review A (COO-1674-130).

b) John Armstrong's work on the absorption spectra on alkaline earths led him to stress the following point. While the multichannel QDT had proved very helpful to him in classifying long series of Rydberg levels, it failed to indicate the lower energy level at which each series would terminate. Fano's reaction was that QDT assumes a slow and smooth variation — if any — of quantum defects and of other parameters, an assumption that clearly breaks down at some point, about 3-5 eV below the ionization threshold. This breakdown, however, had only been indicated in Seaton's work but had never been documented. Documentation could be provided by an array of calculations by the Phase Amplitude or other methods, but this work would require dealing with instabilities of quantum defects as functions of energy.

These considerations led us to undertake an extended series of exploratory calculations and of related analytical studies, carried out mainly by C. Greene with contributions by Fano and Kohmoto and with much guidance by J.L. Dehmer of ANL. An extended report is planned but the work is far from complete.

9) The Manifold Aspects of Rydberg States. Fano has been invited to particpate in a Colloque on highly excited states of atoms and molecules organized by the French National Research Council. In fact he had been asked to comment on the subject and program of this Conference early in its preparation. He took this occasion to prepare an essay aimed at a synthesis of extensive

work developed with quite different intents and with diverse experimental or theoretical approaches. This essay (COO-1674-133) also afforded an opportunity to outline:

a) prospective developments in the theory of the motion of an electron subjected to the Coulomb field of an ion and, simultaneously, to an external electric or magnetic field, and

b) the view, held by him and Inokuti, that the study of the perturbation of Rydberg leves by foreign atoms or molecules should provide evidence on the early stages of formation of molecular complexes by excited species, and possibly also by unexcited species with a single loosely bound valence electron.

The conference itself, which proved unusually lively and successful, also stimulated another small contribution by Fano, noted in Item 2 of this Report.

10. Other Activities. The extensive calculations on the properties of highly stripped ions, undertaken earlier in co-operation with ANL-RER and other groups and partially described in Item 5 of the 1976 Report have not been pressed actively, nor have the available results been prepared for publication, owing to reduced priority and to lack of suitable manpower, at Chicago or at ANL. Nevertheless we have not abandoned this task.

The work on line profiles and threshold intensities, outlined in Item 9 of the 1976 Report, was accepted for publication subject to minor adjustments. However, upon further examination, Fano found the paper unsatisfactory and withheld its publication pending clarification of related matters, some of which form the subject of Item 8 of the present Report. This work has accordingly been shelved for the present.

List of Reports

COO-1674-123 Electron Distributions from Resonant and Nonresonant Fast Particle Collisions (Thesis), C.E. Theodosiou, Phys. Rev. A.

COO-1674-124 Post-Adiabatic Analysis of Atomic Collisions. II. Properties of Velocity-Coupled Channels, H. Klar, Phys.Rev. A 15, 1452 (1977).

COO-1674-125 Electron Distributions from Fast e^-+Na Collisions, C.E. Theodosiou, J. Phys. B 10, L253 (1977).

COO-1674-126 Multipole Wave Functions for Photoelectrons in Crystals, G. Strinati and U. Fano, Abstract for the 5th Int'l Conf. on Vacuum Ultraviolet Radiation Physics, Montpellier, France, Sept. 5-9, 1977.

COO-1674-127 Polarization of Atoms by Collision, M.Kohmoto and U.Fano, Abstract for the X ICPEAC, Paris,France, July 21-27,1977.

COO-1674-128 Rotational Excitation of Polar Molecules: Delimiting the Range of Born Approximation, Charles W.Clark and U.Fano, Abstract of talk for the X ICPEAC, Paris, France, July 21-27, 1977.

COO-1674-129 Characteristics of Continuum and Bound States of the Electron-Dipole System, Charles W. Clark, Abstract of talk for the X ICPEAC, Paris, France, July 21-27,1977.

COO-1674-130 Connection between Configuration Mixing and Quantum Defect Treatments, U. Fano, Phys. Rev. A

COO-1674-131 Multipole Wavefunctions for Photoelectrons in Crystals. II. Examples of Constant Energy Surface Harmonics. Application to s-d Band of Cu, (Part I of Thesis) G. Strinati, to be submitted to Phys. Rev.

COO-1674-132 Electron Scattering from Diatomic Molecules I. The Limitations of the Born Approximation, Charles W.Clark, Phys. Rev. A (in press).

COO-1674-133 The Manifold Aspects of Rydberg States, U. Fano, Invited talk at the Colloque Int'l no 273,"Atomic and Molecular States Coupled to a Continuum. Highly Excited Atoms and Molecules, June 13-17,1977, Aussois, France and published by C.N.R.S.

COO-1674-134 Perspective and Prospectives, U. Fano, Invited paper for the R-Matrix Symposium, X ICPEAC, ed. by G. Watel, (North Holland Publ. Co., Amsterdam, 1977).

COO-1674-135 Remarks on Predissociation and Autoionization, U. Fano, Colloque Int'l no.273, Aussois, France and published by C.N.R.S.

COO-1674-136 Multipole Wavefunctions for Photoelectrons in Crystals. III. The Role of Singular Points in the Band Structure and the Tail of the Wannier Functions, (Part II of Thesis), G. Strinati, to be submitted to Phys. Rev. A.

COO-1674-137 Foreign Travel Report.

COO-1674-138 Technical Progress Report 1977.