BASIC STUDIES OF ATOMIC DYNAMICS

MASTER

Progress Report
for Period October 1, 1979 - September 30, 1980

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September 15, 1980

Prepared for
U.S. Department of Energy, Division of Basic Energy Sciences
under Contract DE-AS02-76ER01674

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Technical Progress Report

on Contract DE-AS02-76ER01674

For the Period October 1, 1979 to September 30, 1980

ABSTRACT

Potential ridges, now identified as the locus of breakdown of approximate separability of coordinates, require a special physico-mathematical treatment whose initial phase has now been completed. The role of a potential ridge in separating the pair of exit channels of lower energy two-electron excitations is circumscribed and hence accessible to numerical calculations; it has thus been studied in some detail for earth-alkaline-like configurations and for He^- . Quantum defect theory approaches have been extended to molecular predissociation and to the study of Stark effect wavefunctions; these extensions have now proved so far from the origins of the approach that a new name and description are called for.

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) Gary L. Webster, Research Associate, 9 months of full time activity supported by this project.
- c) Renato Colle, Research Associate, 9 months of full time activity supported by Italian Fellowship with additional housing support by this project.
- d) Research Assistants (Graduate Students) supported by this project as follows:

Shinichi Watanable, 12 months.
David Harmin, 12 months.

- e) Research Assistant (Graduate Student)

Chris H. Greene supported for 9 months by IBM Fellowship. In addition it reflects continuing part-time collaboration with former members of the project and with personnel of other laboratories.

2. Diffraction by a Potential Ridge.

a) A new perspective. Any atom or molecule that possesses sufficient energy to break up, or even only to become highly excited, can generally do so through alternative channels. Thus one electron can break away or another one; in a molecule, dissociation is an alternative to ionization; in a H atom placed in a magnetic field, the single electron can spiral away up-field or down-field. Break-up of the system into such alternative channels generally implies a different allotment of the available energy among the fragments. Advanced control of atomic and chemical energetics will thus require a thorough understanding of the mechanisms affecting a system's evolution into one or another channel.

Chemical reactions are usually resolved into two stages, an initial one where reactants combine into a "complex" followed by break-up of the complex into another channel. The complex must be formed with sufficient activation energy to step over the potential barrier that separates the entrance and exit channels. Our point is that the activated complex often passes through a compact state where

the kinetic energy of its particles is high, the potential deeply negative as opposite charges are closely packed, and the channels have merged. We also note that formation and break-up of the complex are reciprocal processes whose mathematical representations can be transformed into one another. What needs careful study is the evolution from the compact to fragmented stage of the complex, when particles move away from one another and potential barriers reemerge as controlling factors. The wave function that represents the joint motion of the particles must break here into separate streams within the exit channels. This wave diffraction process is thus viewed as the critical stage of reactions. Solving the relevant wave equation has been Fano's goal for a few years.

b) Progress in 1980. The problem abstracted from this analysis is to solve the Schroedinger equation in two dimensions with a potential $V(x,y) = v(x) - \beta^2(x)y^2$, where $v(x)$ rises slowly with increasing x . The line $y=0$ constitutes a "ridge" of this potential, which separates two "valleys". A particle travelling in the x direction is pulled into one valley, unless it follows the ridge exactly, while its momentum resists the deflection. Wannier had shown in a particular case the existence of two special bundles of trajectories that maintain a steady course by diverging from the ridge or converging toward it at proper rates. Fano has now shown that:

- 1) Two special modes of wave propagation exist which correspond to Wannier's eigenbundles of trajectories, and which propagate along the ridge under WKB conditions but without special requirements on the analytic form of $v(x)$ and $\beta(x)$.
- 2) Each of these modes has two eigenstates of even or odd symmetry under reflection on the ridge, $y \rightarrow -y$; their superposition can represent propagation from one valley to the other. Additional modes of propagation can of course be represented by appropriate superpositions of the base pair.
- 3) The independent WKB propagation of the two modes breaks down near a turning point where $v(x)$ has risen to equal the total energy and further propagation along the ridge is classically forbidden. Part of the diverging mode appears to be diffracted here sharply away from the ridge, but whatever part of its amplitude is transferred to the converging mode is simply reflected.

The results 1) and 2) have been presented as a general treatment in a paper (#168) accepted by the Physical Review A. Item 3) has been outlined in a Journal of Physics B letter (#169) currently in press. The further step required to exploit this progress is described in the Proposal for 1981.

3. Two-Electron Excitations. The Critical Stage. The two-electron excitations have been of central interest to this project since its origin, initially for He and H^- . A first extension of our approach to the alkaline-earth (or equivalent) atoms, which have also an ns^2 ground state configuration but an ion core instead of a bare nucleus, has been completed this year by Chris Greene. Three effects occur in this group of atoms beyond those encountered in He and H^- : a) The ionic field is non-Coulomb within the core, which has caused thus far only a minor complication. b) Two-electron excitations occur already within the valence shell and are accordingly more significant. c) Fragmentation of the atom (or ion) that leave the residue in different orbital states of the valence shell are energetically inequivalent, thus removing the symmetry of He and H^- . This last aspect leads to a new phenomenon.

The earlier studies of He and H^- , using the average radial coordinate $R = (r_1^2 + r_2^2)^{1/2}$ of a doubly excited state, had obtained the eigenvalues of the Hamiltonian with 1P symmetry at fixed R , $U_\mu(R)$, which then served as potentials to calculate a radial wave function $F_\mu(R)$ for the μ -th state. (These studies ignored the coupling between excitations to different shells which is instead the subject of Sec.2.) Greene's main calculation dealt with doubly excited states of Be with exit channels $2s\epsilon$ and $2p\epsilon$, where one electron remains attached in $2s$ or $2p$ and the other escapes with kinetic energy ϵ . In He or H^- these two channels are energetically degenerate and the states are nearly symmetric or antisymmetric (+ or - label) with respect to reflection through the potential ridge that separates their valley (see Sec.2a). Each radial wave function $F_\pm(R)$ propagates then adiabatically throughout the range $0 \leq R \leq \infty$. In the alkaline earths instead these exit channels are nondegenerate; the symmetry under their interchange obtains then only while the electron pair remains compact, i.e., at

low R , but breaks down in the transition range where the potential barrier becomes important as noted in Sec. 2a. The channel potential with lower energy, labelled $U_{2+}(R)$ at small R , takes the character $U_{2s}(R)$ at large R , while $U_{2-}(R)$ turns into $U_{2p}(R)$. Chris Greene has studied this evolution in some detail for various atoms and ions.

He then proceeded to integrate the radial wave functions $F_{\mu}(R)$ for this pair of states fully expecting a nonadiabatic behavior that would couple the two channels strongly in the transition range, distributing the wavefunction amplitudes between the two channels. Starting the integration from $R=0$ in the $2+$ channel he obtained a wavefunction $F_{2+}(R)$ which continues adiabatically until the critical range where the coupling splits it into two components $F_{2s}(R)$ and $F_{2p}(R)$. The striking result is that superposition of these two channel components at large R approximately restores the + symmetry that prevails at small R . The evolution of the state through the critical range thus proceeds nearly adiabatically much as it does in He or H^{-} , even though the state consists of two components with different energy allotment between the electrons. This result accounts for the earlier experimental observation by an IBM group that the spectra of all the alkaline earths reflect an almost even superposition of two different channels of excitation. This quasi-adiabatic behavior of the evolution from the compact to the fragmented state of the doubly excited atom seems to imply a sharp localization of the transition at a critical radius R_c , but the details of this process remain unclear. Greene's thesis paper (#170), which contains many additional details, has been accepted by the Physical Review A.

Most of the doubly excited atoms and ions have an open shell core in contrast to those studied by Greene, whereby the excited electrons can exchange spin and/or orbital angular momentum with the core. Watanabe has undertaken the extension to open shell cores as a thesis topic. His first example is He^{-} whose $n=2$ shell has several coupled channels of equal angular momentum and whose experimental study is currently pressed by R.N. Compton at ORNL and S.F. Wong at Yale. He has succeeded rapidly in adapting the programming to the open core He^{+} , to calculate several channel potentials $U_{\mu}(R)$ and to begin the assessment of nonadiabatic behavior, presenting some results at the 7th ICAP (paper #174).

4. Two-Electron Excitations. Fragmentation Properties. The calculations on He and H^- extend to large values of the radius R where one electron is ionized or even only loosely attached in a bound state well outside the rest of the system. Greene's work on the autodetaching energy levels of H^- (paper #163) has been reported in 1979. Subsequently he discovered an unexpectedly unfavored angular distribution phenomenon in the autodetachment of an electron from H^- . This striking phenomenon has been reported in a Physical Review Letter (paper #166) and further discussed in a Comment by Fano and Greene (paper #167).

In doubly excited systems with a multi-electron core, such as K^{--} , the approach to fragmentation proceeds through a second critical stage, namely, the evolution from LS- to jj-coupling. When one of the electrons is ejected with sufficient speed this evolution is clearly diabatic. That is, the final state may be still characterized as LS-coupled even though represented by a superposition of jj-coupled components whose energy is distributed somewhat differently between the escaping particle and the residue and whose amplitudes are governed by angular momentum algebra. At lower energies, on the other hand, electron escape may be energetically possible only if the residue is left in its j-state of lowest energy. The transition from one to the other of these behaviors has not been studied in sufficient detail. Falk and Geballe have measured the intensity ratio of the fluorescent emissions from the doublet levels of $K(4p_{3/2,1/2})$ residues of photo-detachment of K^- with energy 20-50 meV above threshold. They found this ratio to oscillate as a function of energy. Watanabe has not yet succeeded to reproduce this phenomenon theoretically.

5. Reformulation of Predissociation Theory by MQDT. Dr. Colle, a quantum chemist who joined our group in January, (Item 3a of 1980 Proposal), was interested in Quantum Defect Theory applications. This afforded the opportunity of extending that theory to vibrational phenomena, as Fano had suggested in 1977. Colle undertook the specific task of translating the treatment of predissociation into QDT formalism, extending the new treatment as would seem opportune. He was quickly

successful in this endeavor, presenting his approach as an invited paper at the Columbus Molecular Spectroscopy Conference in June and submitting a substantial paper (#171) to the Journal of Chemical Physics. This paper has been accepted subject to rectification of details.

Through this extension, and others in recent years, the original concept of Quantum Defect Theory has been broadened beyond recognition. It may now be described as a treatment of single- or multi-channel processes, involving bound- or scattering states and:

a) an appropriate parametrization of separate solutions of the wave equation in different regions of space and with different quantum numbers, and

b) an analytic representation of cross-sections, transition amplitudes, spectral levels, etc., in terms of the several parameters.

6. Stark Effect of Rydberg Levels. (This problem and the following one have been introduced in the 1979 Report.) David Harmin's effort to parametrize the Stark effect of hydrogen for future treatment of its transition from a perturbative to dominant influence, in accordance with item 5a above, has been progressing in a manner more rewarding than anticipated but very slowly. Preparation of a paper for the Physical Review on this parametrization is in progress. The task described in item 5b requires us, however, to treat the Stark effect of atoms other than H by combining parameters defined in different coordinate systems (polar and parabolic). Preliminary approaches to this task have been made without achieving any solution yet.

7. Zeeman Effect of Rydberg Levels. The Proposal for 1980 anticipated that Fano's progress on the diffraction by a potential ridge might provide this year the key to a basic account of the observed phenomena, but the progress reported in Sec. 2b falls short of the need. Gary Webster had formulated the wave equation for this Zeeman problem at Nebraska in a base of adiabatic channels including the nonadiabatic effects through the appropriate coupling terms. The task of solving these coupling equations over a realistic range appears

prohibitive. Inspection of his treatment showed the coupling terms to remain significant over an excessive range of the radial variable, an effect that should be corrected by bending the polar coordinates suitably to approach the cylindrical grid appropriate to dominance of the magnetic field. Such a warping of coordinates to fit different standard patterns in different regions of space appears relevant to most problems of our project. Accordingly Webster has been developing the modified coordinates and their application to construct a new base of adiabatic states.

8. Other Activities. The informal workshop planned for last January (Item 3b of 1980 Proposal), was scaled down to two outside participants (Macek and Lin) and one week's time. The week was occupied mainly in intensive discussions on $H^+ + H$ high velocity collisions. The discussions confirmed my impression that this process should be represented usefully as a superposition of H_2^+ stationary rotational states of both parities in the very high vibrational continuum.

The long standing plans of resuming work on R-matrix calculations, combining them with the hyperspherical approach, took a new turn in February when Greene felt it necessary to use both of these methods in subsidiary tests for his work reported in Sec. 3. He succeeded very rapidly in obtaining crude but significant results for He. These results were presented in an informal memo which has been circulated only to some colleagues in other laboratories.

This quick success of Greene served to dispel — also in my own mind — the belief that any new venture by R-matrix methods would require a major effort. It encouraged me in June to formulate the H_2^+ problem itself in hyperspherical coordinates, a preliminary step that has also been described in an informal memo. As a next move Greene has already performed some calculations of H_2^+ potential curves $U_\mu(R)$ at his new location at Stanford.

These new budding activities are intertwined with our expanding relationship with research groups in the Paris area (Orsay and Meudon) which I visited twice in the last year.

Actual Publications since October 1, 1979.

- COO-1674-145 Electron Scattering from Diatomic Polar Molecules. II.
146 Treatment by Frame Transformations, (Thesis) Charles W. Clark, Phys. Rev. A 20, 1875 (1979).
- COO-1674-147 Identification of States Excited by Collision: Current State of Theory, U. Fano, Coherence and Correlation in Atomic Collisions, ed. H. Kleinpoppen and J.F. Williams (Plenum Press, New York, 1979), p. 223.
- COO-1674-160 Hyperspherical Analysis of Three-Electron Dynamics, C.W. Clark and C.H. Greene, Phys. Rev. A 21, 1786 (1980).
- COO-1674-161 Atomic Polarizability in Negative Ion Photodetachment, S. Watanabe and C.H. Greene, Phys. Rev. A 22, 158 (1980).
- COO-1674-162 Dependence of Photoabsorption Spectra on Long Range Fields, Chris H. Greene, Phys. Rev. A 22, 149 (1980).
- COO-1674-163 Interpretation of Feshbach Resonances in H Photodetachment, Chris H. Greene, J. Phys. B 13, L39-44 (1980).
- COO-1674-166 Manifestation of Dynamically Unfavored Transitions in the Angular Distribution of Photofragments, Chris H. Greene, Phys. Rev. Lett. 44, 869 (1980).

Accepted for Publication.

- COO-1674-167 Unfavored Angular Distributions, U. Fano and Chris H. Greene, Phys. Rev. A.
- COO-1674-168 Wave Propagation and Diffraction on a Potential Ridge, U. Fano, Phys. Rev. A.
- COO-1674-169 Formation of Landau Standing Waves in Rydberg Spectra, U. Fano, J. Phys. B.
- COO-1674-170 Doubly-Excited States of Many-Electron Atoms I: The Alkaline Earth Atoms, (Thesis) Chris H. Greene, Phys. Rev. A.
- COO-1674-171 MQDT Analysis of Predissociation I: A Two Channel Problem with Semiclassical Scattering Parameters, Renato Colle, J. Chem. Phys.

Abstracts of Papers Presented at Various Meetings.

- COO-1674-172 Influence of the Atomic Polarizability on Negative Ion Photodetachment, presented at DEAP Annual Meeting, Rice University, Houston, December 10-12, 1979. S. Watanabe and Chris H. Greene, Bull. Am. Phys. Soc. 24, 1174-75 (1979).
- COO-1674-173 MQDT Analysis of Predissociation, presented at 35th Symposium on Molecular Spectroscopy, Ohio State University, Columbus, Ohio, June 16-20, 1980, Renato Colle.
- COO-1674-174 Hyperspherical Analysis of Doubly-Excited Atoms with an Open Shell Core, presented at 7th Int. Conf. on Atomic Physics, MIT, August 4-8, 1980, S. Watanabe
- COO-1674-175 The Role of VUV Studies of Atoms, Molecules and Condensed Matter for DEAP Annual Meeting, Los Angeles, December 1-3, 1980, U. Fano.
- COO-1674-176 Technical Progress Report 10/1/79 - 9/30/80.

Financial Statement of Estimated Costs

Special Research Support Agreement

University of Chicago

Contract DE-AS02-76ER01674

For the Period January 1, 1980 through December 31, 1980

1. Estimated Total Project Costs for the Current Period	\$95,000.00	
2. Total Amount Chargeable to DOE		\$ 95,000.00
3. Cumulative Support Costs		<u>762,379.00</u>
4. Estimated Total Cumulative Support Costs		\$857,379.00
5. Cumulative Support Ceiling		<u>857,379.00</u>
6. Anticipated difference between Estimate Total Cumulative Support Costs and the Cumulative Support Ceiling		<u><u>-0-</u></u>

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NOTICE OF RESEARCH PROJECT
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SIE NO.

AEC CONTRACT NO.

SUPPORTING DIV. OR OFFICE: BASIC ENERGY SCIENCES

NAME & ADDRESS OF CONTRACTOR OR INSTITUTION: (State the division, department, or professional school, medical, graduate or other, with which this project should be identified.)

The University of Chicago
Department of Physics
1100 East 58th Street
Chicago, Illinois 60637

TITLE OF PROJECT:

BASIC STUDIES OF ATOMIC DYNAMICS

NAMES, DEPARTMENT, AND OFFICIAL TITLES OF PRINCIPAL INVESTIGATORS AND OTHER PROFESSIONAL SCIENTIFIC PERSONNEL. (not including graduate students) engaged on the project, and fraction of man-year devoted to the project by each person.

U. Fano, Principal Investigator - 100%
Professor of Physics
Department of Physics

NO. OF GRADUATE STUDENTS ON PROJECT: 3 NO. OF GRADUATE STUDENT MAN-YEARS: 3

SUMMARY OF PROPOSED WORK: (200-300 words, omit Confidential Data). Summaries are exchanged with government and private agencies supporting research, are supplied to investigators upon request, and may be published in AEC documents. Make summaries substantive, giving initially and for each annual revision the following: OBJECTIVE; SCIENTIFIC BACKGROUND FOR STUDY; PROPOSED PROCEDURE; TEST OBJECTS AND AGENTS.

This continuing project aims at unraveling the correlations and the energy transfers between the motions of different particles in electron collisions and photoabsorption processes, to which we are now adding molecular vibrations and the related atomic and molecular collisions. All these processes are encompassed in a single framework introduced in this Proposal. The major thrusts will be directed this year at completing the mathematical description of the critical effects of potential ridges, especially on the motion of a pair of excited electrons and at treating the drastic alterations of Rydberg levels by external fields.

RESULTS TO DATE:

Since October 1, 1979 seven papers have been published and are identified as COO-1674-145-146, 147, 160, 161, 162, 163, and 166. Numbers 167, 168, 169, 170, and 171 are papers that have been accepted for publication (in press). Number 172 is abstract of paper presented at DEAP Annual Meeting, Houston; No. 173 is abstract of paper presented at 35th Symp. on Molecular Spectroscopy, Columbus, Ohio; No. 174 is abstract of paper presented at 7th Int. Conf. on Atomic Physics, MIT, and No. 175 is abstract for invited talk at the DEAP Annual Meeting, Los Angeles.

BUDGET	PROGRAM CATEGORY NO.
PRIMARY	
SECONDARY	

Signature of Principal Investigator

DATE: September 15, 1980

INVESTIGATOR DO NOT USE THIS SPACE

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