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BASIC STUDIES OF ATOMIC DYNAMICS

Progress Report
for Period July 1, 1982 to August 31, 1983

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Technical Progress Report

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(14 months owing to changed date of submission)

ABSTRACT

The observed but puzzling stability of resonant statesastride potential ridges is shown to reflect a general self-focussing property of convergent waves. An approach to the solution of nonseparable wave equations is introduced which utilizes their separability in asymptotic limits. Progress is outlined in describing the properties of N-electron atoms in highly condensed states.

1. Scope of the Report. This report covers scientific activities extending over the nominal 14 months period from July 1, 1982 to August 31, 1983. The following personnel contributed to these activities.

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

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

Jiang Tan (3 months)
Michael Cavagnero (14 months)
Patrick O'Mahony (14 months)
Zhaowei Lai (2 months)
Apurba Kar (2 months)

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

The following paragraphs report summaries of progress achieved in each of the areas outlined in the Proposal for 1983, with the same numerical headings. Special weight is attached to Sec. 2 which outlines for the first time the basis and goals of a major advance dating from May 1983.

2. Particle Wave Functions on Potential Ridges. Fano's main effort has been directed towards constructing 2-dimensional WKB wave functions astride a ridge, as anticipated on page 3 of the Proposal for 1983. This effort is now following a new path which utilizes a multidimensional extension of WKB procedures drawn from an old and obscure paper by Fröman.[1]

Fröman derives his semiclassical solution of a wave equation from a variational principle, but his basic equation is in fact equivalent to the mechanical equation

$$- \vec{\nabla} V = d\vec{p}/dt \qquad (1)$$

This equation may of course be integrated by a quadrature for a given V, to obtain a trajectory with given initial conditions. The WKB approximation requires the momentum $\vec{p}$ to vary but little, in magnitude and direction[1], over a wavelength $\hbar/p$.

A novel aspect of the present application consists of studying a specific set of trajectories selected by the symmetry conditions that prevail at asymptotically large distances from the center of mass of the system. This approach contrasts with that of our previous work[2] which centered on integrating the Schrödinger equation outward toward large radial distances starting from r=0. The approach to be followed here derives instead from Harmin's solution of the Stark problem,[3] which first integrates the separate equation for the "up-field" coordinate ξ whose potential rises steadily with ξ. Harmin then studied separately the motion along the independent coordinate η, whose potential falls with increasing η. It finally combines products of these separate solutions in ξ and η to match the wavefunction emerging at short ranges from an atomic core.

We restrict this section to the prototype problem of an electron in a Coulomb+diamagnetic potential

$$V = -\frac{e^2}{(\rho^2+z^2)^{\frac{1}{2}}} + \alpha^2\rho^2 \tag{2}$$

whose broad relevance has been discussed before.[2] This potential is not separable, in contrast to Harmin's. However it separates in cylindrical coordinates in the two asymptotic regions $z \ll \rho$ and $\rho \ll z$. [The contrasting symmetries of potentials in different regions of space have been stressed by Rau.[4]] We shall find that separable solutions adapted to the limiting cases (actually we'll treat here $z \ll \rho$ only) can be continued by WKB toward smaller values of ρ (or z) preserving a local approximate separability. This essential aspect, overlooked in our earlier work, yields directly the long sought stability of resonant states astride a ridge.

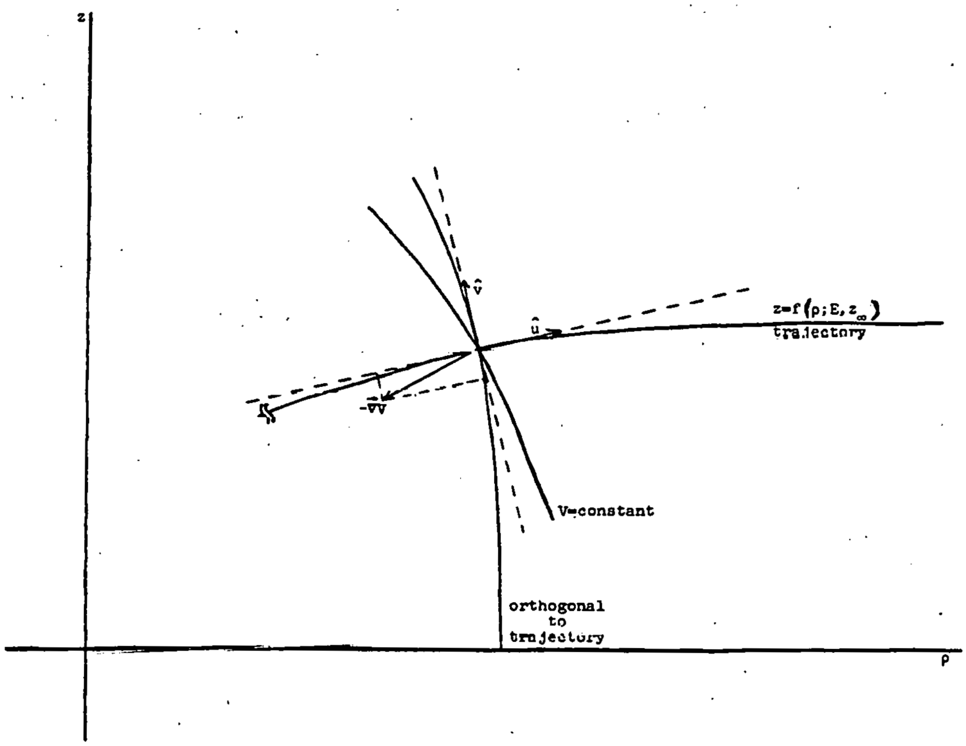
a) Boundary conditions at $\rho\to\infty$. (The converging mode.) We consider here a strip of the (ρ,z) plane with $|z| \leq \zeta \sim 100$ a.u., and the portion of this strip with $|z| \ll \rho$. The potential (2) is independent of z in the limit $\rho\to\infty$, i.e., $|z|/\rho \to 0$. Accordingly a basic set of trajectories

$$z = f(\rho;E,z_\infty) \tag{3}$$

will be considered, each starting with energy E from $(\rho\to\infty, |z_\infty| < \zeta)$ in a direction parallel to the ridge line z=0. Wave propagation along this trajectory is understood to tunnel under a potential barrier throughout the range of large ρ where $V(\rho,z) > E$.

The function (3) can be calculated, for given values of E and of z_∞, by solving Eq. (1) with the time t replaced by a distance $\vec{v}\cdot\hat{p}t$. The entire solution (3) of interest can in fact be obtained semi-analytically by expansion in powers of z/ρ in our range of interest. This problem appears essentially trivial but a fully satisfactory solution remains to be developed.

As ρ decreases, the Coulomb term in the potential (2) depends on z appreciably and the lines of force of $-\vec{\nabla}V$ no longer parallel the ρ axis but converge toward the nucleus at (ρ=0, z=0) as shown in the figure. The figure also shows that each trajectory no longer remains parallel to $\vec{\nabla}V$ when the dependence of V on z becomes appreciable. Indeed Eq. (1) shows $\vec{p}$ to change direction only in the presence of a component of $\vec{\nabla}V$ transverse to $\vec{p}$. We'll return to this essential point below.



Here we note that both the lines of force of $\vec{\nabla}V$ and the trajectories start at $\rho\to\infty$ parallel to the ridge line, z=0, and then converge to the nucleus. Proceeding in reverse both sets of lines diverge from the nucleus and then turn parallel to the ridge line. The trajectories are thus concave toward the ridge line which constitutes a symmetry element of the set of trajectories and may thus be interpreted as belonging to a convergent mode in the sense of Wannier.

b) A Theorem of Wave Optics. The present type of WKB treatment concerns solutions in which most of the kinetic energy pertains to motion along the trajectories discussed above. The wave function along each trajectory can be represented[5] by an Airy function Ai(-X), whose phase function X is given by

$$X(\rho,z) = \left(\frac{2m}{\hbar^2}\right)^{\frac{1}{3}} [V(\rho,z)-E][\hat{u}\cdot\vec{\nabla}V]^{-2/3}_{V=E} \quad . \tag{4}$$

The last factor of (4) is evaluated at the classical turning point of the trajectory, where $V(\rho,z)=E$; the unit vector $\hat{u}\equiv(u_\rho,u_z)$ points along the trajectory, i.e., $u_z/u_\rho=dz/d\rho=df/d\rho$. The function Ai(-X) is damped exponentially at $X>0$, i.e., under the potential barrier at large ρ, and oscillates as an ordinary WKB solution of $X<<-1$.

The WKB wave function also propagates in directions orthogonal to the semiclassical trajectory. This propagation has been represented in Ref.2 by an amplitude factor A(T) which multiplies the main solution Ai(-X) and which obeys a separate wave equation. (The parameter T of Ref.2 is equivalent to z_∞ of the present treatment.) It was conjectured in the 1983 proposal and in Ref.6 that oscillations of A(T) astride the ridge would have a long wavelength, being eventually confined by a potential that restricts them to a limited range of T. However the nature of this potential was not identified.

It is now apparent from a) above, that the confining force is the very same transverse component of $-\vec{\nabla}V$ that causes the trajectories to be concave toward the ridge (see the figure). It follows that the spectrum of energy levels of A(T) is necessarily discrete (at least in its lower levels) in accordance with the results shown in Fig. 8 of Ref.6. This <u>self-confinement</u> of propagation orthogonal to a set of converging trajectories thus emerges as a <u>general phenomenon</u> of wave optics.

This phenomenon in fact underlies the self-focussing of laser beams, where the transverse component $-\vec{\nabla}V$ results from nonlinearity of the optical medium rather than from its inhomogeneity. Analogous phenomena seem instead to have been overlooked in ordinary electron and light optics where the relevant beam widths are usually limited by diaphragms rather than by self-confinement.

The wave equation for the factor $A(T)$ of the complete WKB solution should itself be represented adequately by an WKB approximation because the transverse component of the field $-\vec{\nabla}V$ varies slowly as a function of z as long as $z \ll \rho$. That is, one can represent $A(T)$ itself by an Airy function $Ai(-Y)$, where Y is a function of T, i.e., of z_∞, analogous to (4). Specifically Y vanishes at the classical turning point of the transverse motion and diverges at $|z_\infty| \to \infty$, whereby $Ai(-Y)$ decays exponentially as the factor $Ai(-X)$ does at $\rho \to \infty$. Because the potential $V(\rho,z)$ is symmetric about the ridge line $z=0$, eigenfunctions $A(T)$ must be even or odd under reflection through the ridge; this condition is met by requiring $Ai(-Y)$ to have an antinode or a node at the value of Y corresponding to $z_\infty=0$, thereby determining the discrete spectrum of the transverse motion.

The approximations involved in the separation of the wave function factors $Ai(X)$ and $A(T) \equiv Ai(-Y)$ have been outlined on page 3 of the Proposal for 1983, but this aspect of the problem is only now becoming ripe for realistic investigation.

<u>c) Preliminary conclusions.</u> Two new elements have been introduced in this section, namely, the separability of coordinates at $\rho \to \infty$ (i.e., at the top of the ridge) and the spontaneous self-focussing of two-dimensional converging WKB solutions as ρ decreases from ∞ to a range where z/ρ is no longer negligible. Details of the calculation remain to be refined. Beyond details it remains to be explored how and where the WKB approximation breaks down with increasing number of nodes of the transverse oscillation $A(T)$. Some inadequate guidance is available to this end from diverse sources.[7]

An analogous study needs to be developed for WKB solutions starting from $z \to \infty$, $\rho << z$. Further steps are outlined in the Proposal for 1984.

3. Correlations in Open Valence Shells. This new project, outlined in the 1983 Proposal, has occupied the full activity of P. O'Mahony and has now taken a definite physiognomy and goal. One will study the motion of 2-5 electrons interacting among themselves and with the pseudopotential of a closed inner shell core. The study will extend to a radius r_0($\gtrsim$ 10 a.u.) such that a single electron can escape beyond it at the energies of interest. Its further escape can then be treated in terms of quantum defects μ_α evaluated at r_0, which amount to the eigenvalues of an R matrix for the range $r<r_0$. The objective is to lay down a variational base set such that the R matrix eigenfunctions will represent the electron correlation clearly.

Since Lin's recent introduction of hyperspherical bases akin to Slater orbitals,[8] and since his success in demonstrating the approximate equivalence of MCI and hyperspherical bases,[9] it was hoped that usual MCI bases would prove adequate for our purpose. O'Mahony started accordingly to reproduce Greene's hyperspherical results in Be[10] by an MCI base. The result was totally negative in that no appreciable mixture of 2snp and 2pns emerged.

The next goal is now to find a simple and appropriate base set that will reproduce Greene's results. Will the explicit admixture of a hyperspherical representation be required? Why, why not and under what conditions? A detailed understanding of correlation effects in the spectra of Groups II-VI hinges on these questions. So does the problem of excitation and ionization of atoms with open shells by collision of slow electrons. Attempts are starting in July 1983 to interpret the extensive data on this subject, accumulated particularly by A. Gallagher's group.

4. Channel Crossing in the Electron Condensation Range. This task, outlined in Sec. 4 of the proposal for 1983, has occupied the entire activity of M. Cavagnero and has made considerable progress in a novel application of group theoretical methods. The ultimate aim of the investigation is to interpret a class of correlation effects that constitute a substantial departure from the independent electron model of shell filling. To this end it was necessary to view the shell filling process in the electron configuration space using the description provided by hyperspherical coordinates. The analytical basis for this purpose was provided in calculations of nuclear binding energies but its application to atomic systems was not completely developed. To describe what has been accomplished it seems appropriate here to review the essence of the hyperspherical description in greater detail.

The gross feature of an N-electron atom are here viewed in terms of the reduced radial equation in hyperspherical coordinates

$$\left[\frac{\partial^2}{\partial R^2} - \frac{4\vec{\Lambda}^2+(3N-3)(3N-1)}{4R^2} + \frac{C(\omega)}{R} + 2E\right]F(R,\omega) = 0. \qquad (5)$$

This equation closely resembles that of the hydrogen atom and makes transparent the competition between Coulomb forces and the kinetic energy of electronic motion in determining the system's density. Here, $\vec{\Lambda}/R^2$ (where $\vec{\Lambda}^2$ is the squared grand angular momentum) represents the generalized centrifugal effect of relative electronic motion (both radial and angular). $\vec{\Lambda}^2$ must be conserved in the absence of interactions, that is, in the $R\to 0$ limit. The net effect of this term in (5) is to cause the electrons to be repelled from $R=0$. This "dispersive" tendency increases explicitly with N^2. $C(\omega)$, where ω is the set of relative position coordinates of the electrons, represents the effective charge distribution of the system in its configuration space and obviously does not commute with $\vec{\Lambda}^2$. In the fragmentation region ($R\to\infty$) the kinetic energy's dominant contribution is due to the relative motion of the fragments, the $\vec{\Lambda}^2/R^2$ term is small, and hence the symmetry properties of $C(\omega)$ play an important role. Of course the wave function concentrates at intermediate values of R in bound systems, but nevertheless depends significantly upon the boundary conditions imposed by the two limits discussed above.

No mention has yet been made of the effects of the exclusion principle in this picture. One rather obvious effect will be a greatly increased dependence on N of the $1/R^2$ term in Eq. (5). This N dependence hinges mainly upon the fact that in the condensed atom limit ($R \rightarrow 0$) only those eigenstates of $\vec{\Lambda}^2$ which are totally antisymmetric with respect to electron interchange are allowed. The antisymmetry constraint enhances the dispersive tendency of the system by raising the lowest allowed eigenvalues of $\vec{\Lambda}^2$ with increasing N, thus forcing the electrons into the larger R region corresponding to the familiar valence shells of the independent electron model.

While the dispersive nature of the Pauli principle is familiar in ordinary terms, its effects on the transition from the condensed atom limit to the region of intermediate R in the hyperspherical description are subtle. These effects were first noticed by Lin[11] for N=2. They stem from the fact that, in the presence of Coulomb interactions, the rate of expansion of the system in R (or the slope of the adiabatic energy curves) depends critically on those partitions of $\vec{\Lambda}^2/R^2$ into its radial and angular components which are allowed by antisymmetry. The varying slopes of the adiabatic curves lead to the quasi degeneracies noted by Lin. The emphasis of the present investigation, therefore, has been to trace the relative contributions of radial and angular kinetic energies in the antisymmetric eigenstates of $\vec{\Lambda}^2$ in order to extend Lin's result to an indefinitely large number of electrons. This has required a thorough investigation of the group theoretical classification of antisymmetrized 3N-dimensional hyperspherical harmonics. This preliminary step is now nearly complete.

The basis for this investigation was found in a 1977 review article concerning the nuclear shell model.[12] The scheme considered in that article classified 3N-dimensional harmonics by noting that decomposition of the 3N-dimensional space into two parts, $3N=3n_1+3n_2$, was isomorphic to vector addition in a particular group. The decomposition may be viewed as a transformation between independent particle and hyperspherical coordinate representations of the 3N-dimensional harmonic oscillator. In short, antisymmetrized states are obtained by coupling Slater determinants of 3-dimensional harmonic oscillator states according to an appropriate scheme.

To apply this principle a recursive procedure has been established. This procedure constitutes a novel extension of the standard Racah-Judd approach to antisymmetrization in the filling of each subshell. In our case, antisymmetrization of angular coordinates and spins has to be complemented by antisymmetrization in the radial coordinates. The procedure is more complicated, but the basic principles of the Racah-Judd approach have been found to apply. The recursion will serve to determine the generalized coefficients of fractional percentage. Of particular importance is the determination of the number of solutions of the recursion relations for each N and for each eigenvalue of $\vec{\Lambda}^2$. In particular, the lowest value of $\vec{\Lambda}^2$ that provides a solution has been found to increase rapidly with N. Numerical results have been obtained for N equal to 3 and 4. Initial publications should be prepared in the next several months.

5. Approach to Fragmentation. The general problem outlined in the first paragraph on page 7 of the 1983 Proposal has not been pressed forward this year. It will now have to be reformulated in accordance with the developments in Sec. 2 of the present report, particularly following their extension from propagation astride potential ridges to propagation astride potential valleys.

The study of spin-correlation in the prototype process $h\nu + K^-(4s^2) \rightarrow K(4p) + e$ (paragraph 2 on page 7 of 1983 Proposal) has been brought to completion and submitted to the Phys. Rev. A. This paper demonstrates, as expected, that the correlation between the spins of the ejected electron and of the K(4p) residue depends on the speed of electron escape, specifically on its ratio to the split of the K(4p) doublet. A novel point is then made, namely, that the spin and spin-orbit correlations exhibit quantum beats as functions of the distance of detection of the ejected electron (unless the doublet split is resolved energetically). This effect might well be observed in the next several years.

The effort to clarify details of the fragmentation, not dealt explicitly in an earlier paper (paragraph 3 on page 7 of 1983 Proposal) led Fano to prepare and submit a partial extension of that paper. Unsatisfactory aspects of such a partial contribution, noted by a referee, have caused this paper to be withdrawn.

6. Comprehensive Publications. Fano's review on "Correlation of two excited electrons," the first comprehensive article on the subject, has appeared in February 1983. A Review of Modern Physics article on "Two-Spin Systems" by Fano is to appear in October 1983 and has been discussed in a Spin-Orientation conference together with the paper on $h\nu + K^-$. The preparation of the Fano-Rau book on "Atomic Collisions and Spectra" has progressed considerably. An article by Fano in the Comments on Atomic and Molecular Physics, currently in press, reviews the newer developments on Quantum Defect Methods that were outlined on pages 8-10 of the Report for 1982. The article stresses the persisting branching out of these methods in new directions. (The same theme has been developed by Fano in an invited talk at the DEAP Meeting in May 1983.) New aspects developed in collaboration with A. Giusti-Suzor, also mentioned in 1982, are still being re-worked for final publications.

As discussed during Fano's visit at DOE in February 1983 he is drawing emphasis on viewing molecular collisions in terms of the transient complex. To this end he has organized a Symposium at the 13th ICPEAC in July 1983 and prepared for it a paper "Introductory Remarks."

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