0 0 0 0 4 3 0 0 2 5 9

Submitted to Chemical Physics Letters

LBL-3971
Preprint c.1

CALCULATION OF AUTOIONIZATION STATES OF He AND H^-

Albert P. Hickman, Alan D. Isaacson, and
William H. Miller

July 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-3971 c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 4 3 0 6 2 6 0

Calculation of Autoionization States of He and H^-*

Albert P. Hickman, Alan D. Isaacson, and William H. Miller†

Department of Chemistry, and Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, University of California,
Berkeley, California 94720

ABSTRACT

The positions and lifetimes of several ^1S and $^{1,3}P$ autoionizing states of He and H^- are obtained by two methods involving standard techniques of electronic structure calculation which can be extended to more complicated systems. The first method involves an approximate evaluation of Miller's "Golden Rule" formula; the second is an application of the recently developed complex coordinate method.

I. INTRODUCTION.

Recent calculations[1,2] of the autoionizing states of two-electron systems have been carried out to a very high degree of accuracy. However, these calculations utilize Hylleraas basis sets and other techniques which cannot easily be extended to more complicated systems. We have performed calculations of the positions and lifetimes of several autoionizing states of He and H^- by two methods involving standard techniques of electronic structure calculation. The first method is a direct extension of the stabilization method[3] and involves an approximate evaluation of Miller's[4] Golden Rule formula. The second method is an application of the recently-developed complex coordinate approach,[2,5] in which the coordinate operators $\vec{r}_j$ in the Hamiltonian are replaced by $e^{i\alpha}\vec{r}_j$, and matrix elements are evaluated in an appropriate basis set. The complex eigenvalues $E_r - \frac{i}{2}\Gamma$ of this matrix give directly the position and width of autoionizing states. We have obtained results accurate to about ten percent using Slater-type basis sets of modest size. Both of these methods may be extended to molecular systems, and thus may prove useful in the calculation of electron-molecule scattering resonances and widths for Penning Ionization.

II. GOLDEN RULE CALCULATIONS.

The familiar Golden Rule of Miller[4] is given by

$$\Gamma = 2\pi\rho|\langle\psi_r|H-E_r|\chi_c\rangle|^2 \tag{1}$$

ψ_r is the resonance electronic wave function corresponding (for example) to a doubly excited state of He. χ_c is then a continuum wave function of the system $He^+ + e^-$. ρ is the density of continuum states.

Our approach is to approximate χ_c by one of the non-resonance eigenfunctions of the Hamiltonian matrix constructed by the CI procedure. That is, we begin with a basis set of N orthonormal configurations $\{\Phi_i(\vec{r}_1,\vec{r}_2)\}$, and diagonalize the matrix $H_{ij} = \langle\Phi_i|H|\Phi_j\rangle$. As in the standard stabilization procedure, we identify one root as the resonance:

$$\psi_r = \sum_{i=1}^{N} a_{ri}\,\Phi_i \tag{2}$$

It has been found[3] that some of the other N-1 eigenfunctions of H_{ij} correspond to "continuum-like" solutions of H, i.e., to $He^+ + e^-$:

$$\tilde{\chi}_c = \sum_{i=1}^{N} a_{ci}\,\Phi_i \tag{3}$$

Before substituting into the Golden Rule formula, it is necessary to "project out" from ψ_r all configurations which

correspond to continuum-like solutions; otherwise the orthonormality of the eigenfunctions ψ_r and $\tilde{\chi}_c$ would yield a zero result. It is then easily shown that

$$\Gamma = 2\pi\rho\,(E_r - E_c)^2\,|\Sigma'\,a_{ri}\,a_{ci}|^2 \qquad (4)$$

where the prime on the solution emphasizes that certain configurations are not included.

Calculations were performed on the $2s2p\ ^{1,3}P$ states of He using the basis sets shown in Table I. Several diffuse basis functions have been included to represent the continuum orbital. Typically we used nine configurations: 1s2p, 2s2p, 1s2p', 1s3p, ..., 1s8p (where each STO has been orthogonalized to those preceeding it in Table I). Initially it was hoped that the roots would correspond to the resonance state closely bracketed by continuum-like solutions. The continuum roots, however, proved not to be so closely spaced. We therefore decided to adjust the Z of the 2p'-8p basis functions in order to have one continuum solution very close to the resonance solution. This was effective. As Z was varied, the energy of the continuum root closest to resonance moved continuously through an interval about E_r. Eq. 4 breaks down and gives zero if $E_c = E_r$, so we determined Γ for several values of Z which gave E_c close to E_r and interpolated. The value of E_r was relatively stable against variation in Z. As previously stated, all continuum-like configurations 1s2p', 1s3p, ...,1s8p are exluded from the sum. Γ is thus a direct measure of the amount

of the resonance 2s2p configuration in the continuum state, or, alternatively, of the amount of continuum configurations in the resonance states.

We determined the density of continuum states ρ by using a result discussed previously by Hazi and Taylor.[3] They found that the use of square integrable functions which form a flexible basis out to some large distance L, but which then decay rapidly, corresponds approximately to the boundary condition of an infinite potential barrier at L. The energies of the continuum states of $He^+ + e^-$ should then be approximately $E_n = -\frac{1}{2} Z^2 + \frac{1}{2} k_n^2$, where $-\frac{1}{2} Z^2$ is the energy of the He^+ core, and

$$k_n \approx \frac{2\pi n}{L} \tag{5}$$

If the integral of $\psi^*\psi$ is normalized to unity (as is done automatically in our CI calculations), then $\rho(E_n)$ is given by

$$\rho = \left(\frac{1}{2} k^2_{n+\frac{1}{2}} - \frac{1}{2} k^2_{n-\frac{1}{2}}\right)^{-1} \tag{6}$$

k_n was determined for each continuum eigenvalue, and found to be very nearly linear in n near the resonance. We were therefore able to determine ρ with an accuracy of 10-15%. Figure 1 shows our results for He(2s2p ^{3}P); the value obtained for Γ agrees quite well with the accurave values of Bhatia and Temkin.[1] For He(2s2p ^{1}P) the method gave Γ about a factor of two small. These results are summarized in Table II.

III. COMPLEX COORDINATE METHOD.

A more direct approach for calculating the energies of autoionizing states is the recently developed complex coordinate method.[2,5] In this approach all the radial coordinates in the Hamiltonian are considered to be complex ($\vec{r} \rightarrow e^{i\alpha}\vec{r}$), and the resulting Schrödinger's Equation is

$$[-\frac{e^{-2i\alpha}}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^{-i\alpha}}{r_1} - \frac{Ze^{-i\alpha}}{r_2} + \frac{e^{-i\alpha}}{r_{12}} - E]\psi = 0 \quad (7)$$

It has been shown[6] that the bound state eigenvalues E of this transformed equation are independent of α, and that the continuum solutions have energies along rays in the complex plane which make an angle 2α with the real axis, and which intersect the real axis at each eigenenergy of the one electron system. The location of autoionizing states (which correspond to scattering resonances or poles of the S matrix) is also independent of α; the wave functions for these states decay asymptotically for α in a certain range. Thus, after a coordinate rotation, autoionizing states and genuine bound states are both described by square integrable wave functions, and both may be calculated with the same techniques. Using modest but carefully selected basis sets of Slater orbitals, we have calculated the spectrum of eigenvalues of certain ^1S and $^{1,3}P$ states of He and H^-, and found behavior of the bound, autoionizing, and continuum states in accord with the prediction for an exact calculation. Previous complex

coordinate calculations[2,5] of two electron systems have dealt only with the ^1S state of H^-.

We typically chose basis sets of about 13 STO's, and formed linear combinations of them to construct 40 to 60 configurations which were eigenfunctions of L^2, M_L, S^2, and M_S. As in the previous section, we chose several very diffuse basis functions, to allow the wave functions to have a flexible asymptotic form. Figure 2 illustrates our results for the ^3P symmetry of H^-. States were accurately obtained belonging to two different continua, e^- + H(1s) and e^- + H(2s). States were also found which seem to belong to the e^- + H(3s) continuum, but they do not lie exactly on the ray as expected. This presumably reflects the limited nature of our basis.

Figure 3 shows the trajectory of the energy of the 2s2p ^3P autoionizing state of He. For $\alpha = 0$, this is just the energy obtained in a stabilization calculation. For $\alpha > 0$, the root should rapidly approach the exact pole location and remain there. Instead, we observe the same behavior as did Doolen _et al._[2]; the root trajectories approach the exact pole locations, hesitate, and then move rapidly away. We calculated $|dE/d\alpha|$ along the trajectory, and defined our best estimate of the pole's location as the point where this quantity was a minimum. Thus in Figure 3 the root location is plotted for equal increments $\Delta\alpha = \pi/96$; a range of α exists over which both the real and imaginary parts of the energy are nearly stationary.

An explanation for this behavior is suggested by the results of calculations we carried out using the same model potential as Bain, et al. viz., $V(r) = 7.5\ r^2 e^{-r}$ au. For several α, we calculated the complex wave functions numerically and compared them with those generated by the complex matrix diagonalization. For small α, the basis set was flexible enough to reproduce accurately the real and imaginary parts of the wave function, and the resonance eigenvalue was stationary. However, as α was increased, the exact wave function exhibited additional oscillations which the basis set could not reproduce. At this point the trajectory followed by the resonance root moved away from the exact pole, in a seemingly random direction.

It is likely that the behavior of the resonance roots for the two electron system is also related to the adequacy of the basis set at each angle α. We found the following expansion a useful guideline for choosing basis functions:

$$r^n e^{-Zre^{i\alpha}} = r^n [e^{-Z\cos\alpha\ r} - iZ \sin\alpha\ r\ e^{-Z\cos\alpha} + \ldots] \quad (8)$$

Thus if an STO of order n and charge Z is important in describing a particular state for $\alpha = 0$, one might expect higher order STO's of charge $Z \cos\alpha$ to be appropriate at the rotation angle α. We normally included only one higher order function, and used double-zeta basis sets to span a range of Z's.

Table II summarizes the results of our calculations. We feel that of the two methods we have tried, the complex coordinate method

is the more promising. This method yields lifetimes accurate to about ten percent for a variety of autoionization states, and requires very little effort beyond that for a standard, real, bound state calculation. Undoubtedly, this accuracy could be improved by the use of more elaborate basis sets. However, we are presently working to extend the method to molecular systems.

REFERENCES

* Supported in part by the U. S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.

† Camille and Henry Dreyfus Teacher-Scholar.

1. A. K. Bhatia and A. Temkin, Phys. Rev. A. 11, 2018 (1975).
2. G. D. Doolen, J. Nuttall, and R. W. Stagat, Phys. Rev. A 10, 1612 (1974).
3. Andrew U. Hazi and Howard S. Taylor, Phys. Rev. A 1, 1109 (1970).
4. W. H. Miller, Chem. Phys. Lett. 4, 627 (1970).
5. R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukumar, J. Phys. B 7, 2189 (1974).
6. B. Simon, Commun. Math. Phys. 27, 1 (1972).

TABLE I. Basis Sets for Golden Rule Calculations

	^3P	^1P
1s	Z = 2.00	Z = 2.00
2s	.74	.56
2p	.85	.99
2p', 3p-8p	1.71 - 1.81	1.71 - 1.81

TABLE II. Summary of Results

State		Golden Rule Method		Complex Coordinate Method		Accurate Values	
		E_r (au)	Γ (eV)	E_r (au)	Γ(eV)	E_r (au)	Γ (eV)
He	^1S			-.7767	.1170	-.7788	.125
	^1P	-.6577	.021	-.6618	.0412	-.6929	.0374
	^3P	-.7504	.0085	-.7552	.0079	-.7615	.0084
H^-	^1S*			-.1484	.0574	-.1488	.0476
	^3P			-.1382	.0072	-.1426	.0063

* Results for this state are also obtained in references 2 and 5.

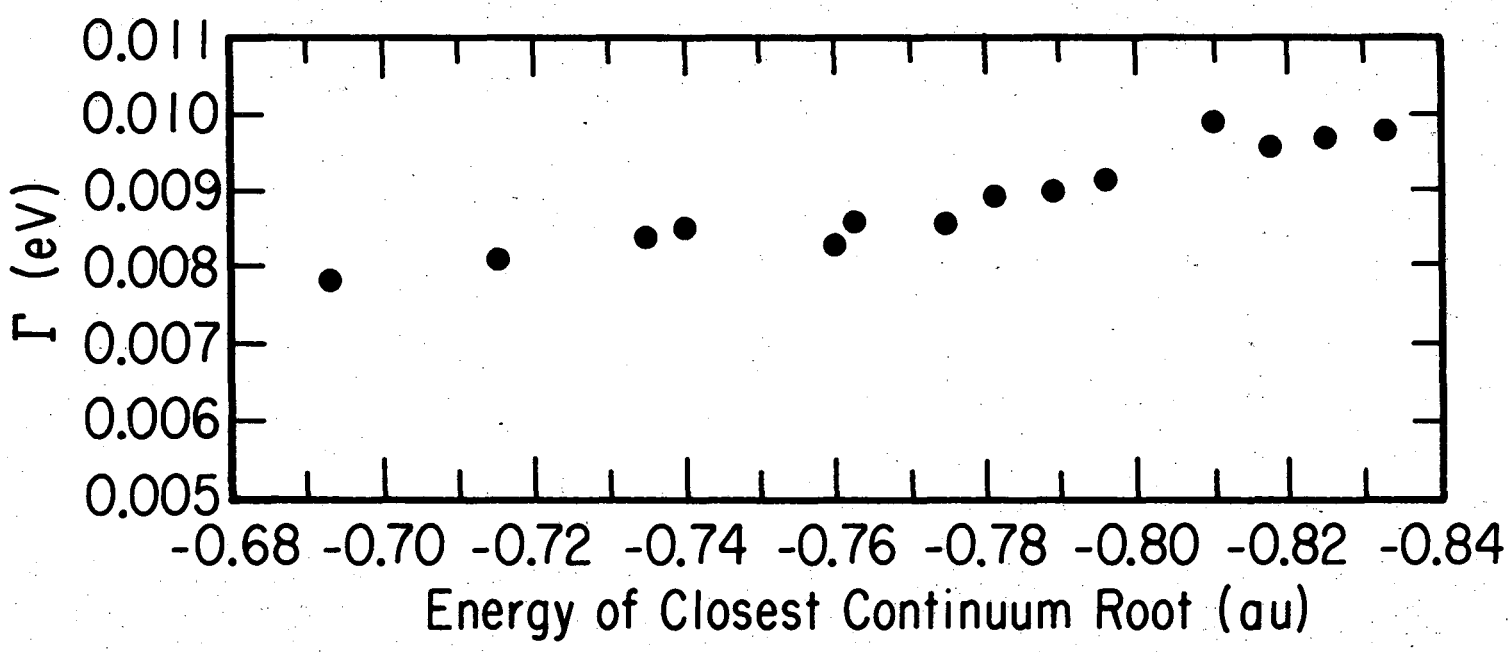
FIGURE CAPTIONS

Figure 1. Γ as determined from the Golden Rule Eq. 4 for several basis sets giving continuum roots in a range near the resonance energy $E_r = -0.7504$ a.u.

Figure 2. Several eigenvalues of the 42 configuration complex matrix diagonalization are shown. The diagonal lines make an angle 2α with the real axis and represent the various branch cuts of the exact continuum spectra, which are rotated by the complex coordinate transformation.

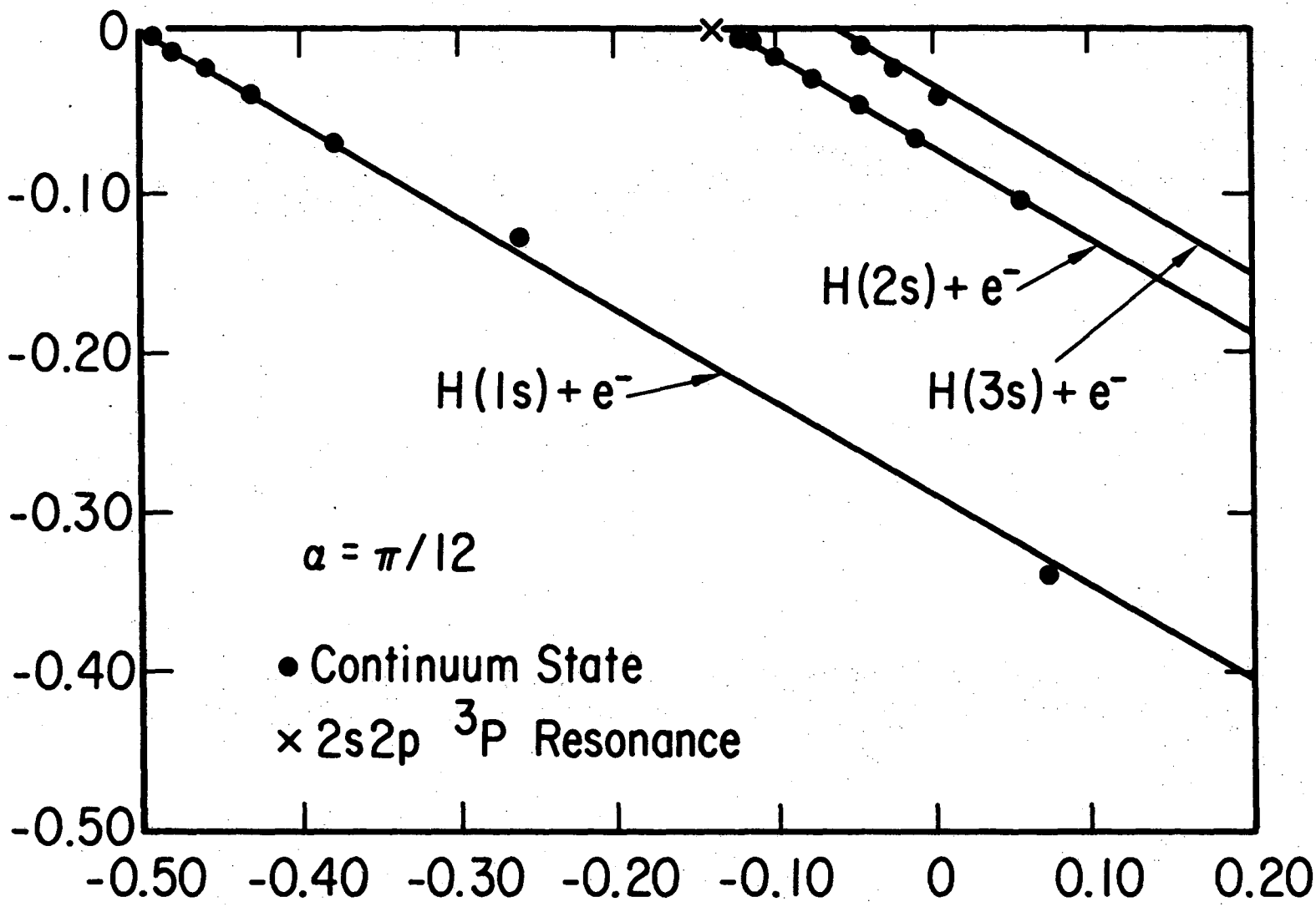
Figure 3. The trajectory of the 2s2p resonance eigenvalue of the He ^3P system. The points are shown at $\alpha = 0$ (on the real axis) and then for equal increments $\Delta\alpha = \pi/96$.

0 0 0 0 4 3 0 6 2 6 7



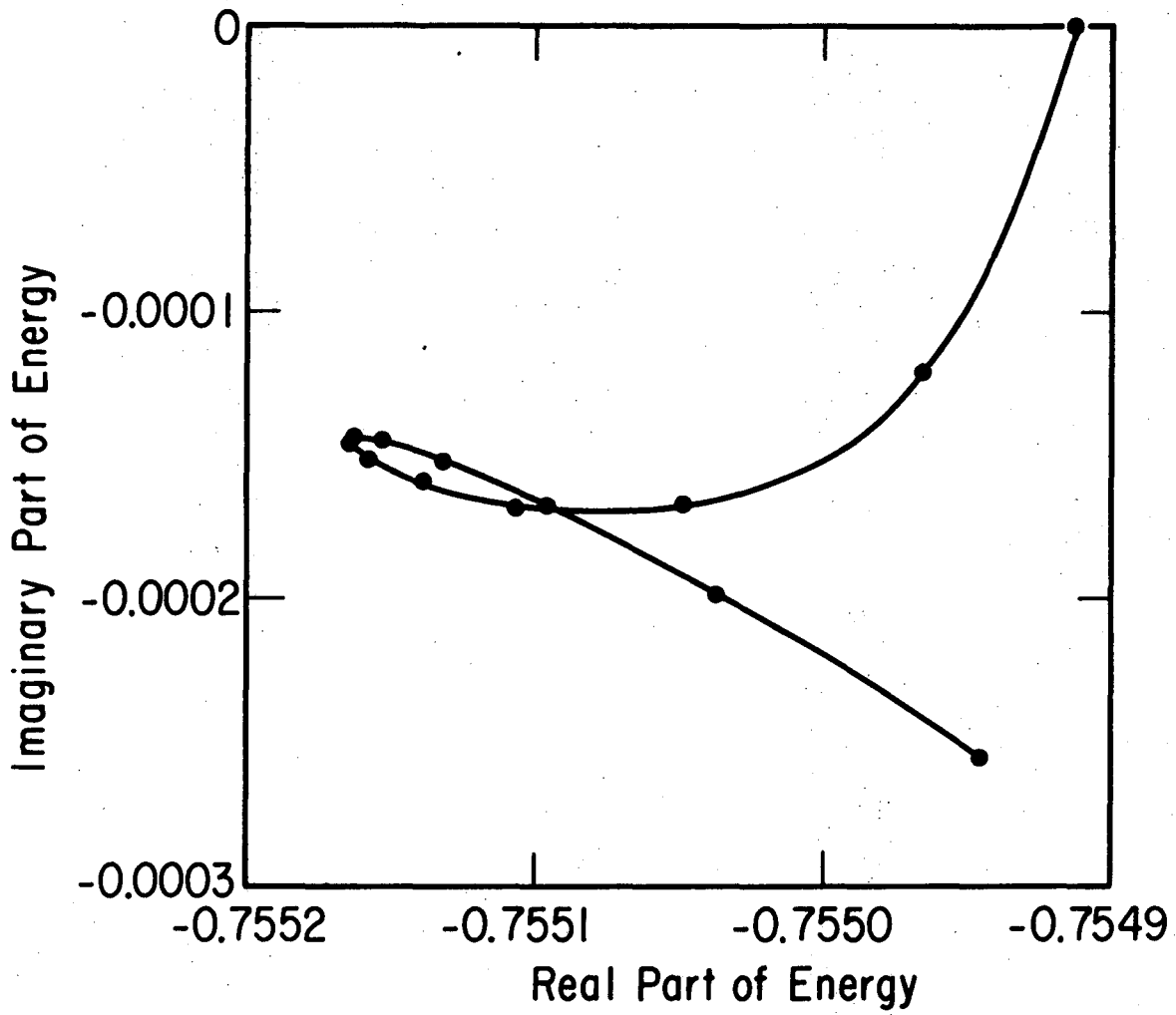
XBL 757-6625

Fig. 1.



XBL 757-6626

Fig. 2.



XBL 757-6627

Fig. 3.

0 0 0 3 4 3 0 0 2 3 9

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720