

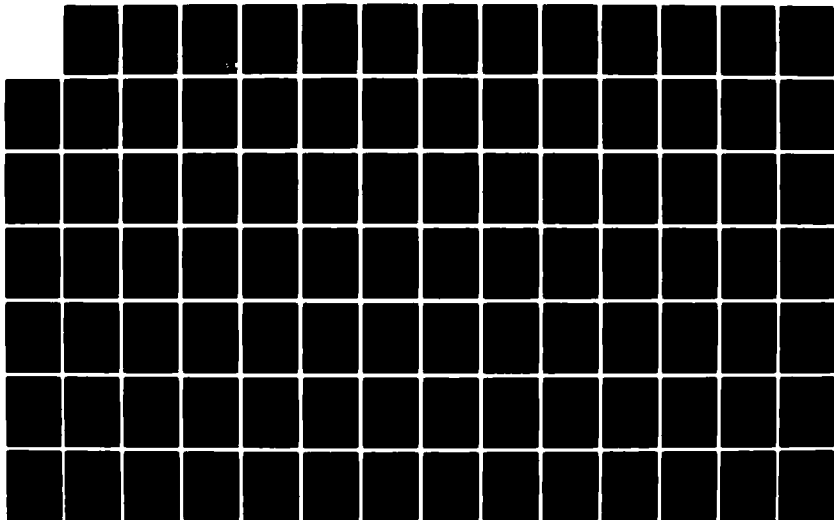
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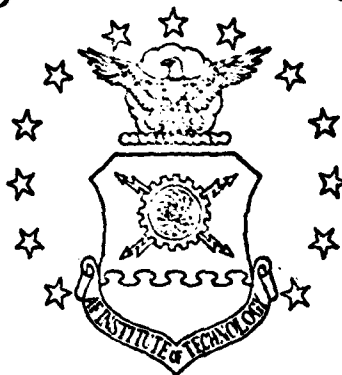
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AIR FORCE INSTITUTE OF TECHNOLOGY



AIR UNIVERSITY
UNITED STATES AIR FORCE

NUMERICAL METHODS FOR THE PREPARATION
OF POTENTIAL ENERGY CURVES OF
DIATOMIC MOLECULES

THESIS

AFIT/GNE/PH/83M-12

Lyle L. Rutger
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NUMERICAL METHODS FOR THE PREPARATION
OF POTENTIAL ENERGY CURVES OF
DIATOMIC MOLECULES
(with applications for lead-oxide)

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology

Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

by

Lyle L. Rutger, B.S.

Capt USAF

Graduate Nuclear Engineering

March 1983

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Preface

This work has been prepared to provide researchers at the Air Force Institute of Technology and the Weapons Laboratory with the computer programs necessary to analyze spectroscopic data. I am grateful for the learning opportunity provided by this thesis and hope the results are helpful to those who follow me.

I am indebted to my thesis advisor, Dr. Ernest Dorko, for his guidance and encouragement throughout the development of the project. I wish to thank C. R. Vidal for his timely response in providing his program for generating potential energy curves at the start of my research. Finally and foremost, I thank my wife Vivian and children for their support in this endeavor.

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Abstract

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This thesis presents the tools necessary to transform spectral data from diatomic molecules into potential energy curves which are most consistent with the experimental data and the quantum mechanical model (i.e., the Schroedinger wave equation (SWE)) for a diatomic molecule. The first of these tools, a computer program called DUNCON, generates spectroscopic constants by performing least-squares fits to spectroscopic data. The program performs fits to separate groups of data and then merges the results in a manner based upon the relative errors and correlations of the separate data sets. The second tool is a computer program provided by C. R. Vidal which contains two major routines. The first routine generates potential energy curves using the Rydberg-Klein-Rees (RKR) method. The second routine through an inverted perturbation analysis (IPA) adjusts the RKR curve so it is consistent with the SWE model. Finally, techniques are presented for extending potential energy curves to the dissociation energy, D_e , when the spectroscopic data alone is inadequate for the purpose.

↙
Use of the programs is demonstrated for the diatomic molecule lead-oxide. Constants are produced for the A, B, D, a, b, and X states from previously published experimental

data. A new set of assignments is made for the b state experimental data producing constants with significantly improved accuracy over those reported in literature. The b state constants are:

$$T_e = 16325.1 \pm 11.2 \text{ cm}^{-1}$$

$$W_e = 430.99 \pm 2.47 \text{ cm}^{-1}$$

$$W_e X_e = -0.757 \pm 0.441 \text{ cm}^{-1}$$

These are one standard error limits. Potential energy curves are generated for the a, A, and X states of lead-oxide. The X state potential energy curve is extended to its dissociation energy.

NUMERICAL METHODS FOR THE PREPARATION
OF POTENTIAL ENERGY CURVES OF
DIATOMIC MOLECULES

I Introduction

The construction of accurate potential energy curves is essential to the understanding of data gathered in pursuits ranging from the study of gas kinetics to the study of stellar structures. Potential energy curves are used to calculate Franck-Condon factors which can be used to predict the probabilities of an electronic transition. Discussed in this paper are Dunham coefficients with the corresponding model used to represent experimental data. A computer program called DUNCON is developed for generating a minimum-variance linear unbiased (MVLU) fit to independent sets of spectroscopic data. This program has a provision for merging these fits, as appropriate, to obtain weighted, correlated estimates of constants for data sets which exhibit different accuracies or are correlated. The Rydberg-Klein-Rees (RKR) method of generating potential energy versus internuclear separation curves is presented. A computer program which performs RKR calculations and then uses an inverted perturbation approach (IPA) (Ref 23) to improve the accuracy of the RKR curve is

discussed in detail. The RKR-IPA program was developed by C. R. Vidal and H. Scheingraber (Ref 41). Utility of the programs is demonstrated using data reported for the diatomic molecule lead oxide (PbO).

The accuracy of any potential energy curve depends upon the analytic model used to represent experimental data and the manner in which the constants in the model are generated. The Dunham model was chosen to represent the data because of the large number of terms that can be incorporated.

The RKR method is a semi-classical WKB method which has been shown to agree quite well with quantum mechanical calculations for simple molecules (Ref 34). Because of its accuracy, it has been chosen by several researchers to ascertain the accuracy of other methods such as the Morse formula for generating potential curves (Refs 47 and 32).

A recent improvement on the RKR method, though still an approximate method, is the IPA approach which starts with an RKR curve and adjusts it to obtain an approximate but more accurate solution to the Shroedinger equation.

Methods developed by Leroy, by Tellinghuisen, and by Vidal and his coworkers are discussed. These methods can be used to extend potential energy curves when the available experimental data does not cover the entire range of the potential curve.

II Literature Background and Theory

Modeling Spectroscopic Data for Diatomic Molecules

Spectroscopic data resulting from the emission of energy by a diatomic molecule during a transition from an excited electronic state to a lower state may be represented as follows:

$$\nu(\nu', J', \nu'', J'') = T'(\nu', J') - T''(\nu'', J'') \quad (1)$$

where ν is the observed line frequency in wave numbers, and the term values for the upper and lower electronic states, T' and T'' respectively, are represented by the Dunham type expression:

$$T(\nu, J) = \sum_{ij} A_{ij} (\nu + 1/2)^i J^j (J + 1)^j \quad (2)$$

(Ref 48:1866).

Although Eq (2) has the same form as that associated with the Dunham coefficients, Y_{ij} , (Ref 18), i.e.,

$$T(\nu, J) = \sum_{ij} Y_{ij} (\nu + 1/2)^i J^j (J + 1)^j \quad (3)$$

researchers M. M. Hessel and C. R. Vidal make the distinction that their A_{ij} values are not necessarily identical to Dunham's Y_{ij} 's (Ref 22:4443).

Dunham arrived at the expression in Eq (2) by using the Wentzel-Brillouin-Kramer method (WKB) (Refs 51; 9 and 29) to solve the Schroedinger equation for the rotating diatomic vibrator for the energy levels within one electronic state:

$$\frac{d^2\psi}{d\xi^2} + \frac{8\pi^2\mu r_e^2}{h^2} \left[E - V(\xi) - \frac{h^2 J(J+1)}{8\pi^2 r_{e\mu}^2 (1+\xi)^2} \right] \psi = 0 \quad (4)$$

where:

$$\xi = (r - r_e)/r_e$$

r_e = the equilibrium nuclear separation

μ = the reduced mass

V = potential of the function, with a minimum at r_e

V_r = the last term which is due to the centrifugal force of rotation.

He expressed the potential energy by expanding V about $\xi = 0$.

$$V = hca_0\xi^2(1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots) \quad (5)$$

where $a_0 = w_e^2/4B_e$; w_e is the classical frequency of small oscillations expressed in cm^{-1} and $B_e = h/(8\pi^2\mu r_e^2 c)$ (Ref 18:732). Finally, he obtained expressions for the Y_{ij} 's in terms of the a_k 's in Eq (5).

Hessel and Vidal distinguish their constants, A_{ij} , from the Dunham constants, Y_{ij} , by pointing out that the latter are theoretically derived, while the A_{ij} 's are the results of a least-squares fit. Inherent in the least-squares

fitting procedure is the fact that the A_{ij} coefficients absorb the effects of inaccuracies in the data, and are somewhat dependent upon the values of their neighboring constants and upon any missing constants (Ref 22:4447). For these reasons, the A_{ij} 's are only estimates of the theoretical Y_{ij} derived by Dunham.

Some further discussion of the A_{ij} and Y_{ij} constants is appropriate. First, a listing of the correspondence of Dunham's constants and the classical spectroscopic constants is desirable. They are given in Table I-1.

TABLE I-1
Correspondence Between Dunham Coefficients and
Classical Spectroscopic Constants

Y_{00}^*	$Y_{01} \sim B_e$	$Y_{02} \sim D_e$	$Y_{03} \sim F$	$Y_{04} \sim H$
$Y_{10} \sim w_e$	$Y_{11} \sim -\alpha_e$	$Y_{12} \sim \beta_e$		
$Y_{20} \sim -w_e x_e$	$Y_{21} \sim \gamma_e$			
$Y_{30} \sim w_e y_e$				
$Y_{40} \sim w_e z_e$				

* Y_{00} is defined as:

$$Y_{00} = 1/4 Y_{20} + 1/4 Y_{01} ((Y_{11}Y_{10}/(6 Y_{01}^2)) - 1)^2 \quad (6)$$

This is the expression normally reported in the literature based upon the work of Dunham (Ref 18), although the expression for Y_{00} is not explicitly stated in Dunham's work. Sandeman

(Ref 40) and Jarmain (Ref 25) expand on Dunham's work. Using this material, the expression given in Eq (6) can be verified. In addition to this derivation, the expression for Y_{00} was found in the following works: (Refs 49; 28:325; 35:117; and 41:4450). The expression for Y_{00} was found to be in error in two publications. First, Herzberg's Y_{00} is larger than that in Eq (6) by $+3/4 Y_{20}$ (Ref 21:109). Second, in McKeever's work, due to a typographical error, $+1/4 Y_{20}$ was omitted (Ref 3:47). The works of Sandeman and Jarmain compliment Dunham's work, making easier the understanding of Dunham's work.

Returning to Eq (1), it should be noted that when a least-squares fit is performed using Eq (2), the bottom of the potential energy curve of the lower state is typically assigned a value of "0." This is done by omitting the A''_0 term from the fit. When A'_0 is found from the least-squares fit, it is not equivalent to Dunham's Y'_0 for the upper state. For this reason, Vidal assigns an asterisk to A'_0 and calls it A_{00}^* . This term is made up of three components as shown (Ref 44):

$$A_{00}^* = A'_0 + Te - A''_0 \quad (7)$$

A'_0 and A''_0 are estimated from Eq (6). These A'_0 and A''_0 are then the best estimates of Dunham's Y'_0 and Y''_0 . Eq (7) can be solved for Te , the electronic term energy of the upper state:

$$T_e = A_{00}^* - A_{00}' + A_{00}'' \quad (8)$$

In applying Dunham's expression, one should be aware of its inadequacies. Expressions such as the Morse potential (Ref 21:57):

$$U(r-r_e) = D_e (1 - \exp(-B(r-r_e)))^2 \quad (9)$$

are constructed to guarantee that as $r \rightarrow r_e$, $U \rightarrow 0$ and as $r \rightarrow \infty$, U approaches the dissociation energy, D_e . Eq (5) on the other hand does not necessarily satisfy these two criteria. Sandeman showed that if Morse's equation is expanded about $(r-r_e) = 0$, it takes on a form similar to Dunham's Eq (5), but is expressed in terms of two constants and additional numerical coefficients as follows:

$$U = a_0(1 - a + 0.583a^2\xi - 0.250a^3\xi + 0.086a^4\xi - \dots) \quad (10)$$

A comparison of Eqs (5) and (10) shows that Dunham's expression is a more general form of Morse's equation. Sandeman also applies a similar expansion to an equation for potential energy developed by Kratzner (Ref 30) and obtained a similar correspondence with Dunham's expression. Because of the increased number of variables and, in turn, the increased flexibility, Dunham's expression has the potential for being more accurate. But, because of this freedom, obtaining constants which satisfy the convergence criterion is more difficult and is not guaranteed for large values of r or v .

Jarman made a term-by-term comparison of similar expressions developed from Dunham's work and by the RKR method and showed that, upon neglecting Dunham's small corrections, the potentials produced by the two are mathematically identical (Ref 25:217). Based upon this, the use of Dunham's expression (Eq (3)) to represent spectroscopic data for input to an RKR program for generating potential curves is justified and appropriate.

In applying Dunham's expression, one should remember that his equations are developed for small oscillations about r_e . At energy levels approaching the dissociation limit, Eq (2) may no longer be appropriate. Eqs (1) and (2) are for simple cases. In cases where Λ -type doubling occurs, or where isotopic effects are being considered, more complex models must be substituted for Eqs (1) and (2). Works cited in the bibliography by Vidal and his coworkers present variations of Eq (2).

Spectroscopic Constants by Merging Least-Squares Fit Data

The large quantities of data obtained in a spectroscopic analysis requires that the data be reduced to a more manageable form. For example, Eqs (1) and (2) in the previous section are used to calculate reportable constants. To make these models usable, the A_{ij} coefficients must be determined. The most widely used method of generating these coefficients

is to perform a linear least-squares fit to the experimental data. For spectroscopic data, a model is created, typically involving a power series expansion based upon the rotational and vibrational quantum numbers as expressed in Eqs (1) and (2). If only band head data is being analyzed, the model takes the following form:

$$v = \sum_{i=0} A'_{i0} (v' + 1/2) - \sum_{i=0} A''_{i0} (v'' + 1/2)^i \quad (11)$$

If several different transitions are involved, different values of the A''_i ground state constants may be obtained. In addition, the accuracy of the A''_i 's may be different. It is desirable to merge these constants and obtain a best estimate of the ground state constants. This can be done by accomplishing a weighted least-squares fit of the data. Such a merging can produce more accurate estimates of the constants and reduce the error limits associated with them. The merged fit may also improve the upper state constants.

Merging may also be desirable for the case when two groups of data are available with significantly different standard errors. For example, if infrared data for vibration-rotation band transitions and microwave data for transitions between adjacent rotational levels are available, the greater accuracy of the microwave data can improve the accuracy of the other constants if a weighted merged fit is performed.

There are other methods of data fitting available. These methods include least absolute deviation, least-squares

deviation, maximum likelihood, and minimum chi-squared. All have different fit criteria (Ref 2:3). Also, nonlinear least-squares fits are possible (Refs 4 and 15). The present report deals only with the least-squares fit techniques.

The least-squares method or "regression" method minimizes the sum of the squared deviations between observed values and values calculated using the constants obtained from the fit. The least-squares method provides the minimum-variance linear unbiased (MVLU) estimates of the constants; that is, the least-squares method introduces no bias. The fits produced are linear functions of the data. When the fit is used to reproduce data, the generated data exhibits the smallest possible variance from the original data that can be achieved with the model and data used (Ref 2).

In performing a least-squares fit, the following assumptions are made:

1. The model (equation) chosen to represent the data is a perfect description of the physical event.
2. The model is linear in the constants to be estimated.
3. The mean error of the experimental data is zero. Any systematic error present must be small compared to the variances and random errors of the data.
4. The variance-covariance elements must be finite and their relative values known if different groups of data are to be merged (Ref 2:7).

In reducing spectroscopic data, three methods are available:

1. The reduction of each band, i.e., each a group of transitions from one electronic state to another, separately.
2. The reduction of a number of bands simultaneously.
3. The reduction of the bands separately and then merging the resulting data.

The first and third techniques are developed in this paper. The method of approach is now described. Least-squares fitting techniques are based upon the following matrix equation:

$$v = X\beta + \epsilon \quad (12)$$

where v is a column matrix containing the experimentally observed line frequencies expressed in wavenumbers, X is a matrix made up of the $(v + 1/2)$ and the $J(J + 1)$ terms as dictated by the model in Eqs (1), (2), or (11) as chosen. β is a column matrix made up of the A_{ij} constants which are to be calculated. The ϵ column matrix contains the unknown errors associated with each observed experimental data point. These matrices are written out explicitly in Appendix A to aid the user in understanding the program DUNCON.

Eq (12) is then solved for β as:

$$\beta = (X^T X)^{-1} X^T v \quad (13)$$

The estimated variance of the fit is expressed as follows:

$$\sigma^2 = (v - X\beta)^T (v - X\beta) / f_m \quad (14)$$

where f_m is the degree of freedom of the calculation. The degrees of freedom, f_m , is equal to the number of experimental values v used in the fit minus the number of constants to be obtained in the β matrix. The variance-covariance matrix for the constants obtained in Eq (13) is calculated by the following relation:

$$\theta = \sigma^2 (X^T X)^{-1} \quad (15)$$

The diagonal elements of the θ matrix are the variances of the constants and the off diagonal elements are their covariances. The correlation between the calculated constants is expressed by the correlation coefficients which are obtained using the variances and covariances in the following manner:

$$C_{ij} = \theta_{ij} / (\theta_{ii} \theta_{jj})^{1/2} \quad (16)$$

The subscripts refer to the two constants for which the coefficient expresses the correlation.

As mentioned earlier, the performance of separate fits to each band will yield several values for the constants associated with the lower electronic state. The variances for different bands may also differ significantly. If the variances of the bands are the same, the data can be combined

in one large data group and reduced simultaneously. If estimates of the errors are available, a weighted fit based upon the error may and should be performed.

Albritton describes an approach, the correlated least-squares fit, which is more general than the weighted least-square fit (Refs 2 and 3). Albritton showed that one need not use all raw data at one time to obtain a merged fit. He showed that a weighted simultaneous multiband fit and a merged band-by-band fit are equivalent. The merged fit is presented in this paper.

The bands or other groups of data are first reduced in a least-squares manner as previously discussed.

Then the data obtained in the initial least-squares fit may be expressed in the following manner:

$$y = X\beta^M + S \quad (17)$$

where y is a column matrix made up of the constants obtained from the separate least-squares fits and β^M is a column matrix which will hold the desired merged constants. The y matrix will often contain several values for the same constant. Each constant will be represented only one time in the β^M matrix. The X matrix relates the redundant values in the y matrix to the corresponding constants in the β^M matrix. Explicit examples of these matrices are given in Appendix A.

To perform a weighted, correlated least-squares fit, a matrix composed of the variance-covariance matrices from a separate least-squares fit is required. This matrix is given the symbol " θI ." It is structured as follows:

$$\theta I = \begin{bmatrix} \theta_1 & 0 & 0 \\ 0 & \theta_2 & 0 \\ 0 & 0 & \theta_3 \end{bmatrix} \quad (18)$$

where θ_1 , θ_2 and θ_3 are the variance-covariance matrices of Eq (15). The formula required to obtain the merged constants is as follows:

$$\beta^M = (X^T \theta I^{-1} X)^{-1} X^T \theta I^{-1} y \quad (19)$$

The estimated variance of the new merged fit is given by:

$$\sigma^2 = (y - X\beta^M)^T \theta I^{-1} (y - X\beta^M) / f_m \quad (20)$$

where f_m is the degree of freedom. The variance-covariance matrix of the merged constants is obtained by the following calculation:

$$\theta^M = \sigma^2 (X^T \theta I^{-1} X)^{-1} \quad (21)$$

The formulas are discussed in future detail in the appendices.

As in all analysis, the data should be checked to insure that the errors predicted by the least-squares fit follow a normal distribution pattern. Albritton provides a

fairly complete discussion of the checks commonly used
(Ref 2:14-31).

Having established that the errors of the data are normally distributed, one should then construct confidence limits for the constants based upon the degrees of freedom and the confidence one wishes to have that the true value is within the assigned limits. The placing of too much reliance upon error limits specified by one standard deviation, $1 \times \theta_{ii}^{1/2}$, should be avoided. Even if a large sample of data is taken, one can only be about 68% certain that the "true value" lies within a range of $\pm 1 \times \theta_{ii}^{1/2}$. If a 95% confidence level is desired and the degrees of freedom, f_m , is greater than 30, one must assign limits of $\pm 2 \times \theta_{ii}^{1/2}$. The multiplier of $\theta_{ii}^{1/2}$ is student's t-factor. It is named after its originator, W. S. Gosset (1876-1937). It is a function of the degrees of freedom of the calculation and the desired confidence level, "1- α ." Dixon and Massey (Ref 17) give a tabulation of student's t-factor as a function of the degrees of freedom and the degree of confidence. The confidence limits for the constant are then expressed as follows:

$$\beta_i + t(f_m, 1-\alpha) \theta_{ii}^{1/2} \quad (22)$$

Having established the limits, one can assume that the probability of the true value of falling within the limit $\pm t \theta_{ii}^{1/2}$ is "1- α " where α may vary between 0 and 1.

With the confidence limits for the estimated constants properly established, one can then determine if the constants are significant (Ref 27). For example, if a constant has a value of 3 and an assigned error limit of ± 5 , the range in which the true value of the constant might be found is -2 to +8. This range includes 0; hence, the constant is not significant. If the assigned confidence limits, $\beta_i \pm t \theta_{\alpha}^{1/2}$ includes zero, then the constant is insignificant and may normally be discarded. Two exceptions to this rule may be encountered.

The first exception concerns the case where a non-zero correlation between two molecular constants exists. If non-zero correlation coefficients are involved, standard errors must be calculated using the most general formulation involving both variances and covariances. If large correlations exist, the rounding of a constant to the number of significant digits dictated by the standard error of the constant, may result in loss of information, i.e., rounding may introduce unnecessary inaccuracies into the calculated data (Ref 2:2).

Albritton suggests that one digit beyond the "one standard error digit" should suffice for most fits. A simple check is to use the rounded constants and see that they reproduce to some desired accuracy the values calculated using the unrounded constants obtained from the fit.

The second exception occurs, where it may prove necessary to retain a constant when not justified by the standard

error, in the extension of the potential curve to its dissociation limits (Ref 10:83).

Before merging data from separate least-squares fits, a check should be made for systematic errors. A simple check is to verify that for a given set of confidence limits, say 95%, the error limits for the common constants obtained in two independent fits overlap each other. If they do not, then it is probable that one set contains a systematic error. A second more sophisticated test involves the computation of the confidence limits for the differences for pairs of corresponding constants checking to see if they include zero (Ref 2:45). Calculation of the confidence limits of differences involves student's t-factor and methods are given by Bennet and Franklin (Ref 5); and Dixon and Massey (Ref 17). A more extensive discussion of the covariance-variance data and how it may be used is presented by Albritton (Refs 2 and 3).

Finally, Albritton provides a recommendation as to what data should be provided in a report on the results of a spectroscopic study. He lists the following as essential data:

1. The observed line numbers (with assignments).
2. If room permits, the variance-covariance matrix used to merge the data.
3. The model used to represent the experimental data.

4. The estimated molecular constants.

5. The standard error of the constants and the degrees of freedom involved in the calculations. This data will enable the reader to establish his own confidence limits.

6. The estimated variance of the variance, σ_{σ} , may be helpful. An estimate of this value for large samples of normally distributed data may be obtained by the formula (Ref 16):

$$\sigma_{\sigma} = \sigma / [2f_m]^{1/2} \quad (23)$$

Other data which may be appropriate include the variance-covariance matrix of the final merged constants and the results of the testing to determine the normality of the data sample.

Rydberg-Klein-Rees Potential Energy Curves

Potential energy curves for diatomic molecules are plots of potential energy versus the internuclear distance between atoms. Figure II-1 shows a typical curve. From this plot of energy versus internuclear distance, it can be seen that as the nuclei approach each other the potential becomes infinite; and as their separation increases, the curve asymptotically approaches the dissociation energy, D_e . The equilibrium internuclear distance, r_e , is the distance at which the potential energy of the molecule is at a minimum.

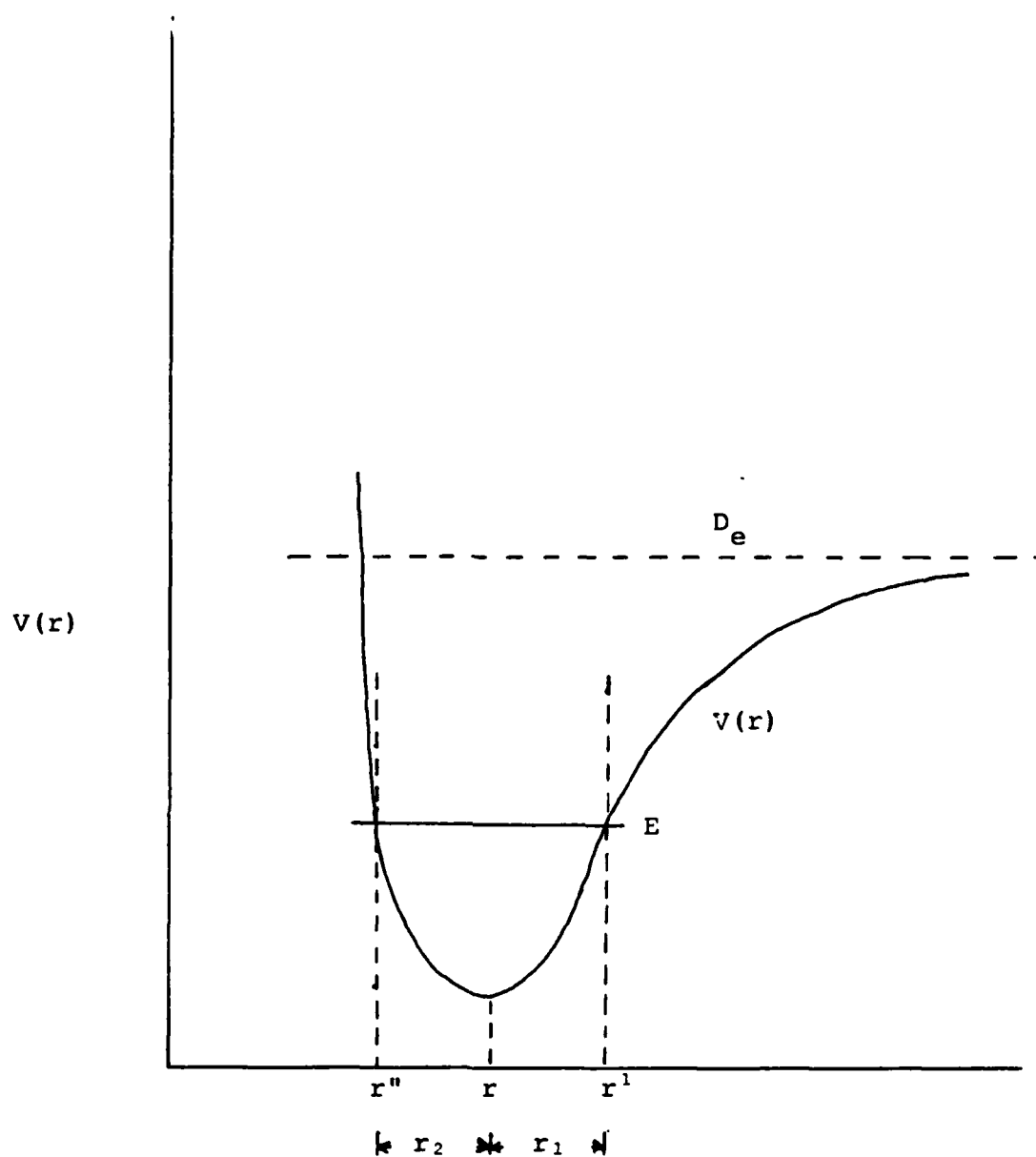


Fig II-1. Potential Energy Versus Internuclear Distance for a Diatomic Molecule

The Rydberg-Klein-Rees (RKR) model for the potential energy curve is developed in this section. Rydberg started with the expression for the total energy, E , for a rotating-vibrating diatomic molecule:

$$E = p^2/2\mu + V(r) \quad (24)$$

The $p^2/2\mu$ term in Eq (24) is the kinetic energy of the system, p in turn, is the linear momentum. The second term, $V(r)$ is defined as follows:

$$V(r) = U(r) + \kappa/r^2 = U(r) + P^2/2\mu r^2 \quad (25)$$

where $U(r)$ is the potential energy of the system, P is the angular momentum of the system, and μ is the reduced mass.

Based on this energy expression, Rydberg developed a procedure for graphically determining the classical turning points for a diatomic molecule (Ref 39). Klein modified Rydberg's derivation so that the turning point could be calculated numerically (Ref 52). Reese obtained quadratic and cubic analytic solutions approximating Klein's formulas (Ref 38).

Klein's mathematical development is given here. Terms used in the development are shown in Fig II-1 as an aid in following the presentation. The classical turning points are denoted r' and r'' . Klein defined the turning points in terms of the quantities r_1 and r_2 . For his analysis,

r_1 and r_2 are measured from r_e , r_1 being positive and r_2 negative. Then r' and r'' are defined as follows:

$$r' = r_1 + r_e \quad (26)$$

$$r'' = r_e + r_2 \quad (27)$$

Then

$$dr' = dr_1 \quad (28)$$

$$dr'' = dr_2 \quad (29)$$

$$dr = dr_1 \text{ or } dr_2 \quad (30)$$

Klein designated the width of the potential curve as $2f$ and from Eqs (26) and (27), it follows that:

$$2f = (r_1 + r_e) - (r_2 + r_e) = r_1 - r_2 \quad (31)$$

The energy in Eq (24) may be expressed as a function of "I," the action integral for a rotating vibrator and " κ ." These terms are defined as follows:

$$I = \oint P dr \quad (32)$$

$$\kappa = P^2 / (2\mu) \quad (33)$$

The following relationships which involve the period, τ , and the average position of a harmonic oscillator, $\overline{1/r}$, are known:

$$1/\tau = \partial E / \partial I \quad (34)$$

$$\overline{1/r^2} = (\partial E / \partial \kappa) \quad (35)$$

$$\rho = \tau (\partial E / \partial \kappa) \quad (35')$$

Using Eqs (32) and (34) and solving for the differential of E and adding the results, the following is obtained:

$$\delta E = (1/\tau) \delta I + (\rho/\tau) \delta \kappa \quad (36)$$

Inverting Eq (32), the following is obtained:

$$\tau = \partial E / \partial I \quad (37)$$

Setting Eq (36) equal to zero and solving for ρ , the following is obtained:

$$\rho = -\partial I / \partial \kappa \quad (38)$$

From the equation for the momentum, $p = \mu v = \mu (dr/dt)$, one can, by integrating over one cycle, obtain an expression for the period of vibration for a harmonic oscillator:

$$\tau = \oint \mu (dr/p) \quad (39)$$

Solving Eq (24) for p and substituting into Eq (39), the period of oscillation may be expressed as:

$$\tau = (\mu/2) \oint (E - V(r))^{-1/2} dr \quad (40)$$

The integral in Eq (40) can be broken into two parts, one to be integrated from r_e to r_1 , and the other from r_2 to r_e (as depicted in Fig II-1). This operation yields:

$$\tau = 2(\mu)^{\frac{1}{2}} \left[\int_{r_e}^{r_1} dr / (E - V(r))^{\frac{1}{2}} - \int_{r_2}^{r_e} dr / (E - V(r))^{\frac{1}{2}} \right] \quad (41)$$

The factor of two is introduced to account for one vibration cycle from r_e through r_1 and r_2 and back to r_e again. Rearranging Eq (41) and recombining the integrals, one obtains:

$$\tau = (2\mu)^{\frac{1}{2}} \int_{r_2}^{r_1} (dr_1 - dr_2) / (E - V(r))^{\frac{1}{2}} \quad (42)$$

Now to change the variables of integration, Klein defined the following terms:

$$y = V(r) - V(r_e) \quad (43)$$

and

$$x = E - V(r_e) \quad (44)$$

where x is constant for a given E . Then r may be expressed as a function of y as follows:

$$r = r_1(y), \quad r > r_e \quad (45)$$

$$r = r_2(y), \quad r < r_e \quad (46)$$

and when at r_e , $r_1(0) = r_2(0) = r_e$. Subtracting Eq (43) from Eq (44):

$$x - y = E - V(r) \quad (47)$$

and if the "f" of Eq (31) is function of y , then as defined

$$r_1(y) - r_2(y) = 2f(y) \quad (48)$$

then

$$dr_1/dy - dr_2/dy = 2df(y)dy \quad (49)$$

or

$$dr_1 - dr_2 = 2f'(y)dy \quad (50)$$

Using Eqs (45), (46), (47), and (50) to change the variable of integration and integration limits in Eq (42), Klein obtained:

$$\tau = 2 (2\mu)^{1/2} \int_{y_2}^{y_1} 2 f'(y) dy / (x-y)^{1/2} \quad (51)$$

From Eq (43) when $r = r_e$, then $V(r) = V(r_e)$ and $y = 0$.
Thus, the integral in Eq (51) may be evaluated from 0
(defined as the bottom of the potential well) to some value
 x .

$$\tau = 2 (2\mu)^{1/2} \int_0^x f'(y) dy / (x-y)^{1/2} \quad (52)$$

This is the first of two integral equations central to Klein's derivation.

Combining Eqs (28), (35), (35'), and (40) yields:

$$\rho = \tau \overline{(1/r^2)} = (\mu/2)^{1/2} \oint (1/r^2) [dr/E-V(r)]^{1/2} \quad (53)$$

By definition:

$$dr/r^2 = -(1/r) \quad (54)$$

Then Eq (53) becomes:

$$\rho = -(\mu/2)^{1/2} \oint d(1/r)/(x-y)^{1/2} \quad (55)$$

Again, the integral in Eq (55) may be broken into two parts. Then for $r > r_e$:

$$r'' = r_2 + r_e \quad (56)$$

$$1/r'' = 1/(r_2 + r_e) \quad (57)$$

and if r_e is set equal to "0" then:

$$1/r'' = 1/r_2 \quad (58)$$

Similarly for $r < 0$:

$$1/r' = 1/r_1 \quad (59)$$

Then for small oscillations about r_e , Eq (53) may be written as the difference between the integrals:

$$\rho = 2 (\mu/2)^{1/2} \left[\int_{1/r_e}^{1/r_1} -d(1/r_1)/(x-y)^{1/2} - \int_{1/r_2}^{1/r_e} -d(1/r)/(x-y)^{1/2} \right] \quad (60)$$

$$\rho = (2\mu) \int_{1/r_2}^{1/r_1} d(1/r_2 - 1/r_1)/(x-y)^{1/2} \quad (61)$$

Klein established the following definition:

$$2g(y) = 1/r_2 - 1/r_1 \quad (62)$$

Differentiating with respect to y yields:

$$2dg(y) = (d/dy) (1/r_2) - (d/dy) (1/r_1) \quad (63)$$

Changing the notation yields:

$$2g'dy = d(1/r_2) - d(1/r_1) \quad (64)$$

Substituting Eq (64) into Eq (61) yields:

$$\rho = 2 (2\mu)^{1/2} \int_0^y [g'(y) dy / (x-y)^{1/2}] \quad (65)$$

with the limits of integration assigned in the same manner as for Eq (52). This is the second integral which is central to Klein's derivation.

In the next step of his development, Klein derives expression for $r_{\max}$ and $r_{\min}$, the classical turning points for a harmonic oscillator. Klein recognized that the integrals for τ and ρ (Eqs (52) and (65)) were of the Abelian type. He multiplied both sides by $dx/(\alpha-x)^{1/2}$ and integrated both sides from $x = 0$ to $x = \alpha$, where $\alpha = E - (V(r)$ (Ref 35:25), i.e.,

$$\int_0^{\alpha} \frac{dx}{(\alpha-x)^{\frac{1}{2}}} = 2 (2\mu)^{\frac{1}{2}} \int_{y=0}^{y=\alpha} f'(y) dy \int_{x=y}^{x=\alpha} \frac{dx}{[\alpha-x](x-y)^{\frac{1}{2}}} \quad (66)$$

In Eq (66)

$$f'(y) = f(\alpha) \quad (67)$$

and

$$\int_y^{\alpha} \frac{dx}{[(\alpha-x)(x-y)]^{\frac{1}{2}}} = \frac{dx}{(-x^2+y\alpha-\alpha y)^{\frac{1}{2}}} \quad (68)$$

Eq (68) may be integrated as follows (Ref 6:300):

$$\int \frac{dx}{(uv)^{\frac{1}{2}}} = 2/(bd)^{\frac{1}{2}} \tan^{-1} [(-bd uv)^{\frac{1}{2}}/bv],$$

for $bd > 0$ (69)

where $u = a+bx$, and $v = a'+dx$ and for the present integral:

$$a = \alpha \quad a' = -y$$

$$b = -1 \quad d = 1$$

$$bd = -1$$

then the integral can be evaluated to be π . Finally, the left side of Eq (68) is evaluated as:

$$\int_0^{\alpha} \frac{dx}{(\alpha-x)^{\frac{1}{2}}} = 2 (2\mu)^{\frac{1}{2}} \frac{1}{\pi} f(\alpha) \quad (71)$$

or solving Eq (71) for $f(\alpha)$:

$$f(\alpha) = 1/(2\pi(2\mu)^{1/2}) \int_0^{\alpha} dx/(\alpha-x)^{1/2} \quad (72)$$

and for $\alpha = y$:

$$f(y) = 1/(2\pi(2\mu)^{1/2}) \int_0^y dx/(y-x)^{1/2} \quad (73)$$

Similarly, Eq (65) for "g" may be transformed into the following:

$$g(y) = \frac{1}{2\pi(2\mu)^{1/2}} \int_0^y \frac{\rho dx}{(y-x)^{1/2}} \quad (74)$$

From the definitions for x given in Eq (43):

$$dx = dE \quad (74')$$

Substituting Eq (74') into Eq (34) yields:

$$\tau dx = dI \quad (75)$$

Recalling that E is a function of I and κ , and using Eq (47), Eq (73) becomes:

$$f(V) = 1/(2\pi(2\mu)) \int_0^I dI/(V-E(I,\kappa))^{1/2} \quad (76)$$

From Eqs (34), (35'), and (74'):

$$\begin{aligned} \rho dx &= \rho dE = (\partial E/\partial \kappa) d\kappa = \tau (\partial E/\partial \kappa) (\partial I/\tau) \\ &= (\partial E/\partial \kappa) \partial I \end{aligned} \quad (77)$$

and Eq (74) becomes:

$$g(V) = 1/(2\pi(2\mu)^{1/2}) \int_0^{I'} \partial[E(I,\kappa)/\partial\kappa] dI / (V-E(I,\kappa))^{1/2} \quad (78)$$

As $E(I,\kappa)$ approaches V in Eqs (76) and (78), the integrals become infinite. To avoid these singularities, Klein instead evaluated the following expression:

$$S(V,\kappa) = 1/(\pi(2\mu)^{1/2}) \int_0^{I'} (V-E(I,\kappa))^{1/2} dI \quad (79)$$

This expression has the following relation to the f and g of Eqs (76) and (78):

$$f = \partial S / \partial V \quad g = -\partial S / \partial \kappa \quad (80)$$

As shown in Eq (2), spectroscopic energy levels can be represented as power series of $(v+1/2)$ and $J(J+1)$. It is convenient then to express the integrals for f and g in terms of the quantum numbers v and J .

The expression for the radial action variable in quantum mechanical terms is

$$I = (v+1/2)h \quad (81)$$

Then

$$d(I) = d(v+1/2)h \quad (82)$$

The quantum mechanical expression for κ is:

$$\kappa = P^2/2\mu = J(J+1) \hbar^2/2\mu \quad (83)$$

Then

$$\partial/\partial\kappa = 2\mu/\hbar^2 (\partial/\partial J(J+1)) \quad (84)$$

Finally, the expressions for f and g become:

$$f(V, J(J+1)) = \hbar/(2\mu)^{1/2} \int_0^{v'+1/2} \frac{d(v+1/2)}{[V-E(v+1/2, J(J+1))]^{1/2}} \quad (85)$$

$$g(V, J(J+1)) = (2\mu)^{1/2}/\hbar \int_0^{v'+1/2} \frac{\partial E/\partial (J(J+1))|_{v+1/2} d(v+1/2)}{[V-E(v+1/2, J(J+1))]^{1/2}} \quad (86)$$

where the upper limit of integration v' is selected such that $V = E(v'+1/2, J(J+1))$ for the fixed value of $J(J+1)$ used in the integrals (Ref 35:27,28).

If the RKR calculations are evaluated for $J=0$ then Eq (2) reduces to:

$$T = \sum_{i=1} Y_{i0} (v+1/2)^i = G(v) \quad (87)$$

more commonly referred to as G_v .

Eq (85) becomes:

$$f = \int_{v_0}^{v'} (G(v) - G(v'))^{1/2} dv' \quad (88)$$

(Ref 24:2), where Kaiser (Ref 26:1686) defined the lower limit of integration by the following:

$$G(v_0) = -Y_{00} \quad (89)$$

where Y_{00} is the Dunham constant previously defined in Eq (6). The variable v_0 in $G(v_0)$ may be expressed in terms of Dunham coefficients as:

$$v_0 = -1/2 - \Delta = -1/2 - (Y_{00}/Y_{10}) (1 + Y_{00}Y_{20}/Y_{10}^2 + \dots) \quad (90)$$

For $J = 0$

$$\partial E / \partial J(J+1) = \sum_{n=0} Y_{ni} (v+1/2)^n = B(v) \quad (91)$$

(Ref 24:2), where $B(v)$ is the spectroscopic term defined as follows:

$$B_v = B_e - \alpha(v+1/2) + \gamma(v+1/2)^2 \dots \quad (93)$$

(Ref 21:108).

Using these definitions, Eq (86) for g becomes:

$$g(v) = \int_{v_0}^v B(v') (G(v) - G(v'))^{1/2} dv' \quad (94)$$

(Ref 24:2).

From the definitions in Eqs (22) and (62) for f and g the following expressions for inner and outer turning points may be obtained:

$$r = (f^2 + f/g)^{1/2} + f \quad (95)$$

Solutions of the equations for f and g are discussed in the section on the RKR Program by C. R. Vidal.

This completes the theoretical background required for the RKR calculations. Second order semiclassical RKR formulations are not presented in this work. Several articles on the RKR method which were not referenced in this work are listed in Appendix C.

Methods for Extending RKR Curves

In many cases, because of the lack of experimental data, the constants necessary to construct an RKR curve may not be obtainable from straightforward least-square fits or their quality may be insufficient to construct accurate curves. Two techniques for improving existing constants which may, in turn, be used to produce improved RKR curves are presented here (Refs 10; 53).

As depicted in Fig II-1, the potential energy curve of a diatomic molecule should have a minimum at some intermediate distance, approach the dissociation limit for large internuclear separations and increase rapidly as the atoms approach each other. Ideally, curves generated using the RKR method should satisfy these criteria.

For many diatomic molecules, only two and, at most, three vibrational constants are available. The available rotational constants are even more limited. Attempts to generate curves based upon these constants using the RKR method can be expected to produce curves which do not meet the dissociation criteria or which do not exhibit an increasing

potential for small internuclear distances. These results occur because the experimental data upon which the constants are based may represent only a fraction of the vibrational levels which exist between the bottom of the potential well and the dissociation limit.

To develop potential energy curves which obey the known constraints, Leroy and Burns have reported on a new technique which shows promising results. While they start with constants obtained from experimentally observed transitions, they then adjust these constants slightly until the new RKR potential energy curve is most consistent with all of the known constraints.

Leroy and Burns used their knowledge of the desired shape to adjust the constants. They worked with the G_v and B_v quantities as expressed in Eqs (87) and (91). Expressed in terms of these two quantities, their criteria for adjusting the molecular constants are:

1. $V(\alpha)$ asymptotically approaches the dissociation energy (De) and the difference between energy levels, $\Delta G_{v+\frac{1}{2}}$, becomes 0 for the same value of v . $\Delta G_{v+\frac{1}{2}}$ is defined as:

$$\Delta G_{v+\frac{1}{2}} = G(v + 1) - G(v) \quad (95')$$

2. The slope of the inner portion of the RKR curve must be negative. Hence:

$$dV(r)/dr < 0 \quad (96)$$

3. The slope of the inner portion of the curve must become increasingly steeper; that is, the second derivative with respect to the internuclear separation must be positive:

$$d^2V(r)/dr^2 > 0 \quad (97)$$

A study of Eq (88) reveals that as $\Delta G_{v+1/2}$ becomes smaller, the quantity f becomes larger. In turn, Eq (94) shows that f determines the width of the RKR curve. Examination of Eq (94) further reveals that the value g determines the center of the potential curve for a given energy level. In turn, Eq (93) shows that having determined the constants necessary to generate the $G(v)$'s, the other factor affecting the value of g is $B(v)$, a quantity whose value is determined by the rotational constants, Y_{ni} . From Eqs (88), (93), and (94), it follows that the width of the curve, as determined by the RKR method, and the value at which $\Delta G_{v+1/2} = 0$ depends only upon the vibrational constants which make up G_v . On the other hand, having selected suitable constants for G_v , the behavior of g , the rate at which the outer portion of the curve approaches D_e , and the behavior of the slope of the inner portion of the curve depends solely upon the constants which constitute B_v .

Following this logic, Leroy applied the criteria in 1 above first. If the constants obtained from experimental

data do not satisfy this criteria, the value of the last experimental constant is adjusted or a value is selected for the next constant, Y_{n_0} , in the series given by expression (8). The contribution from that constant, $Y_{n_0}(v+1/2)^n$, is then subtracted from the $G(v)$ values calculated from the original experimentally based constants. A least-squares fit is then performed on the adjusted experimental data, Gv_j^* :

$$Gv_j^* = \sum_{i=1}^{n-1} Y_{i_0} (v_j + 1/2)^i - [Y_{n_0} (v_j + 1/2)^n] \quad (98)$$

For a given Y_{n_0} the experimental data fixes the values of the other constants. This new set of constants is tested to determine if Gv approaches a maximum value of D_e . Leroy and Burns say that if this value approaches D_e within $< 2 \text{ cm}^{-1}$ then the criteria in 1 is satisfied. If 1 is not satisfied, then a new trial value for Y_{n_0} is chosen and the process repeated until 1 is satisfied.

At this point, a new RKR curve is generated using the new vibrational constants, Y_{i_0} , and the experimental rotational constants, Y_{i_1} . The curve is then evaluated according to criteria (2) and (3). If the inner portion of the curve diverges, the process followed for adjusting the constants for Gv is repeated for the constants making up Bv . The value for the last experimental constant is adjusted or a value for the next rotational constant in the

Y_{i1} series is selected. Then the B_v values given by the experimental constants are adjusted as follows:

$$B_{v_j}^* = \sum_{i=0}^{n-1} Y_{i1} (v_j + 1/2)^i - [Y_{n1} (v_j + 1/2)^n] \quad (99)$$

Then a least-squares fit is performed to obtain a new set of rotational constants Y_{01} through Y_{n1} . The new constants are then used to produce a new RKR curve. If the curve does not satisfy the criteria in 2 and 3, then the Y_{n1} constant is adjusted and the process repeated until 2 and 3 are satisfied.

In this manner, Leroy and Burns obtained a set of constants consistent with the experimental data and with criteria 1-3.

Tellinghuisen and Henderson describe a technique for constructing RKR based curves when experimental data does not permit the direct calculation of the rotation constants (Ref 20). Their technique is based upon a combination of the Morse and RKR potentials; hence, Morse-RKR curves.

As explained, vibrational constants provide all the information necessary to calculate f , Eq (88) and, thus, the width of the potential curve, $2f$, as defined by Klein for a given vibrational energy level. Having established the width of a potential, the remaining piece of information required to construct a potential curve is the location of either the inner or outer branches of the potential curve, or

the center of the potential well, i.e., g as obtained from the RKR calculations.

Tellinghuisen and Henderson point out that inner turning points on a potential curve might be approximated by the Morse potential (Ref 21:101).

$$U(r) = D_e (1 - e^{-\beta(r-r_e)})^2 \quad (100)$$

where:

D_e = dissociation energy, cm^{-1}

r_e = equilibrium internuclear distance, A

$$\beta = 0.12777 w_e (\mu/D_e)^{1/2} \quad (101)$$

where

w_e = the vibration frequency, cm^{-1}

μ = reduced mass, amu

Or because of the relation

$$D = w_e^2 / 4 (w_e x_e) \quad (102)$$

β may be expressed as follows:

$$\beta = 0.243555 (\mu w_e x_e)^{1/2} \quad (103)$$

Using these relations, Tellinghuisen investigated 25 different well-known potentials and found errors at the dissociation limit for the inner portion of the curve to be typically less than $0.02 \overset{\circ}{\text{A}}$ and r_e to be in error by seldom more than 1%.

Further, Tellinghuisen states that a potential curve in error by $\Delta r_{\min}$ has identical classical and almost identical quantum eigenvalues for $J = 0$. The wavefunctions derived from a shifted curve would be skewed with respect to a proper wavefunction.

If possible, Tellinghuisen recommends the construction of curves by formulas (102) and (103) using the experimental w_e and $w_e x_e$. If only w_e and D_e are known, then a value of D_e 40% larger than the experimental D_e should be used.

Tellinghuisen also speculates that α_e might be calculated using an expression derived by Pekeris from the Morse function:

$$\alpha_e = \frac{6B_e}{w_e} \left[\left(\frac{w_e x_e}{e} \right)^{\frac{1}{2}} - 1 \right] \quad (104)$$

(Ref 21:109). Tellinghuisen found that for 23 of the 25 cases he investigated, the α_e calculated per formula (104) had an average absolute error of 13% and an average signed error of 6%.

If one is seeking the rotational constant D_e (Y_{02}), the following relation might be used:

$$D_e = \frac{4B_e^2}{w_e^2} \quad (104')$$

(Ref 21:10).

Tellinghuisen cautions against using B_v values made up of only two terms, i.e.,

$$B_v = B_e - \alpha (v+1/2) \quad (105)$$

because the Morse expression for B_v does not terminate with two terms as does G_v . Further, for high values of v , the Morse B_v will differ from the Morse-RKR B_v . The Morse-RKR B_v value must be determined by numerical methods.

Inverted Perturbation Analysis

Having constructed a semiclassical RKR curve, the next step is to determine if that curve is consistent with the Schroedinger wave equation; or, even better, to adjust the curve so it agrees with the SWE. This leads to the use of the inverted perturbation approach. The goal of the inverted perturbation approach (IPA) is to adjust the potential energy curve of rotationless molecules, $V_0(r)$, so that the quantum mechanical eigenvalues, E_{vJ} , obtained from a solution of the Schroedinger wave equation agree in a least-squares sense with the measured term values, $T(v,J)$.

The IPA technique was first demonstrated by Kosman and Hinze (Ref 23). Vidal and Scheingraber expanded the use of the IPA method. Vidal, in conjunction with several authors, has applied the IPA method to a number of molecules.

The Schroedinger wave equation (SWE) for a vibrating rotator (Eq (4)) is the basis of the IPA method. To develop

the IPA method, the SWE can be expressed as follows

(Ref 41):

$$(H_0^0 + H_{\text{rot}}) \psi_{\text{vJ}}^0(r) = E_{\text{vJ}}^0 \psi_{\text{vJ}}^0(r) \quad (106)$$

E_{vJ}^0 is the energy eigenvalue specified by the vibration and rotation quantum numbers. H_0 is the Hamiltonian of the non-rotating molecules and is made up of the terms:

$$H_0 = - \left(\frac{\hbar}{4\pi\mu c} \right) \frac{d}{dr^2} + V_0(r) \quad (107)$$

where $V_0(r)$ is the potential energy of the rotationless molecule.

This formulation has been simplified by neglecting terms describing electronic coupling contributions (Ref 46).

The rotational motion of the molecule is described by:

$$H_{\text{rot}} = \left(\frac{\hbar}{4\pi\mu c} \right) \frac{J(J+1)}{r^2} \quad (108)$$

In the inverted perturbation approach, one starts with an approximate potential $V_0(r)$, for example an RKR potential. Eq (106) is solved numerically for the zeroth order eigenvalues E_{vJ}^0 and the radial wavefunction $\psi_{\text{vJ}}^0(r)$. Then an energy correction ΔE_{vJ} is calculated according to the following formula:

$$\Delta E_{\text{vJ}} = E_{\text{vJ}} - E_{\text{vJ}}^0 \quad (109)$$

where E_{vJ} is the measured term value as calculated from the spectroscopic constants and quantum numbers v and J . If the difference between the experimentally determined term values and the eigenvalues obtained from the SWE is sufficiently small, the calculation is stopped.

If the difference exceeds a specified limit, then one proceeds. As stated, the goal is to obtain some correction to $V_0^0(r)$, i.e., $\Delta V(r)$, such that the calculated and experimental E_{vJ} 's agree. Following this reasoning, then the true potential, $V_0(r)$, being sought may be expressed as a sum of the approximate potential and some delta potential:

$$V_0(r) = V_0^0(r) + \Delta V_0(r) \quad (110)$$

In turn, it follows that the true Hamiltonian differs from the approximate zero order Hamiltonian " $H_0^0 + H_{\text{rot}}^0$ " by $\Delta V_0(r)$:

$$H_0 + H_{\text{rot}} = H_0^0 + H_{\text{rot}}^0 + \Delta V_0(r) \quad (111)$$

First order perturbation theory gives the following relationship between the perturbation to the Hamiltonian $\Delta V_0(r)$ and the energy change ΔE_{vJ} :

$$\Delta E_{vJ} = \left\langle \psi_{vJ}^0 \left| \Delta V_0(r) \right| \psi_{vJ}^0 \right\rangle \quad (112)$$

To obtain a correction to $V(r)$, a mathematical expression of the following form is assumed to represent $\Delta V_0(r)$:

$$\Delta V_0(r) = \sum_i c_i f_i(r) \quad (113)$$

The selection of the specific form of the function $f_i(r)$ is critical to the convergence and solution of the SWE. Discussion of the form of $f_i(r)$ will be postponed until the section describing Vidal's IPA program.

Using the $f_i(r)$ and the radial wavefunctions, ψ_{vJ} , obtained from the numerical solution of Eq (106), the expectation values for $f(r)$ are calculated:

$$\left\langle \psi_{vJ}^0 \left| f_i(r) \right| \psi_{vJ}^0 \right\rangle \quad \begin{matrix} v = 0, 1, 2, 3 \dots \\ J = 0, 1, 2, 3 \dots \end{matrix} \quad (114)$$

From Eqs (112) and (113), it follows that:

$$\Delta E_{vJ} = \sum_i c_i \left\langle \psi_{vJ}^0 \left| f_i(r) \right| \psi_{vJ}^0 \right\rangle \quad (115)$$

Having obtained ΔE_{vJ} from Eq (109), Eq (115) can be solved for the c_i coefficients. Using these coefficients in Eq (113), $\Delta V_0(r)$ may be calculated. From this, a new $V_0^0(r)$ is obtained.

$$V_0^0(r) \text{ (new)} = V_0^0(r) \text{ (old)} + \Delta V_0(r) \quad (116)$$

Then using the new $V_0^0(r)$, the calculation is repeated to obtain new energy eigenvalues. Again, the calculated E_{vJ}^0 are compared with the experimental term values $T(v,J)$ for agreement. If the agreement is not acceptable, the process is repeated.

Elaboration upon the specific numerical calculations to solve Eqs (106) through (116) is postponed until the discussion of Vidal's routine for performing the IPA calculations.

III Computer Programs

A computer program called DUNCON has been developed to generate spectroscopic constants. DUNCON is presented in Appendix A. The program generates the constants by separate least-squares fits and provides for the merging of the separate fits in a weighted manner as previously described. A description of the program, a listing with a sample fit and instruction on how to use it are contained in Appendix A.

A second program, provided by C. R. Vidal of the Max-Planck Institute for Exterrestriche Physik, West Germany, has provisions for the generation of potential energy curves by the Rydberg-Klein-Reese (RKR) method and adjustments of those curves by the inverted perturbation approach (IPA). The IPA routine adjusts the potential energy curve so it is consistent with the Shroendinger wave equation. A copy of the program with a sample problem, a description of the program, and instructions on using the program are included in Appendix B.

The DUNCON program and the RKR-IPA program may be used in a variety of combinations to generate constants and potential energy curves. Presented in Fig III-1 is a flow diagram describing the logic used in applying these programs in this work.

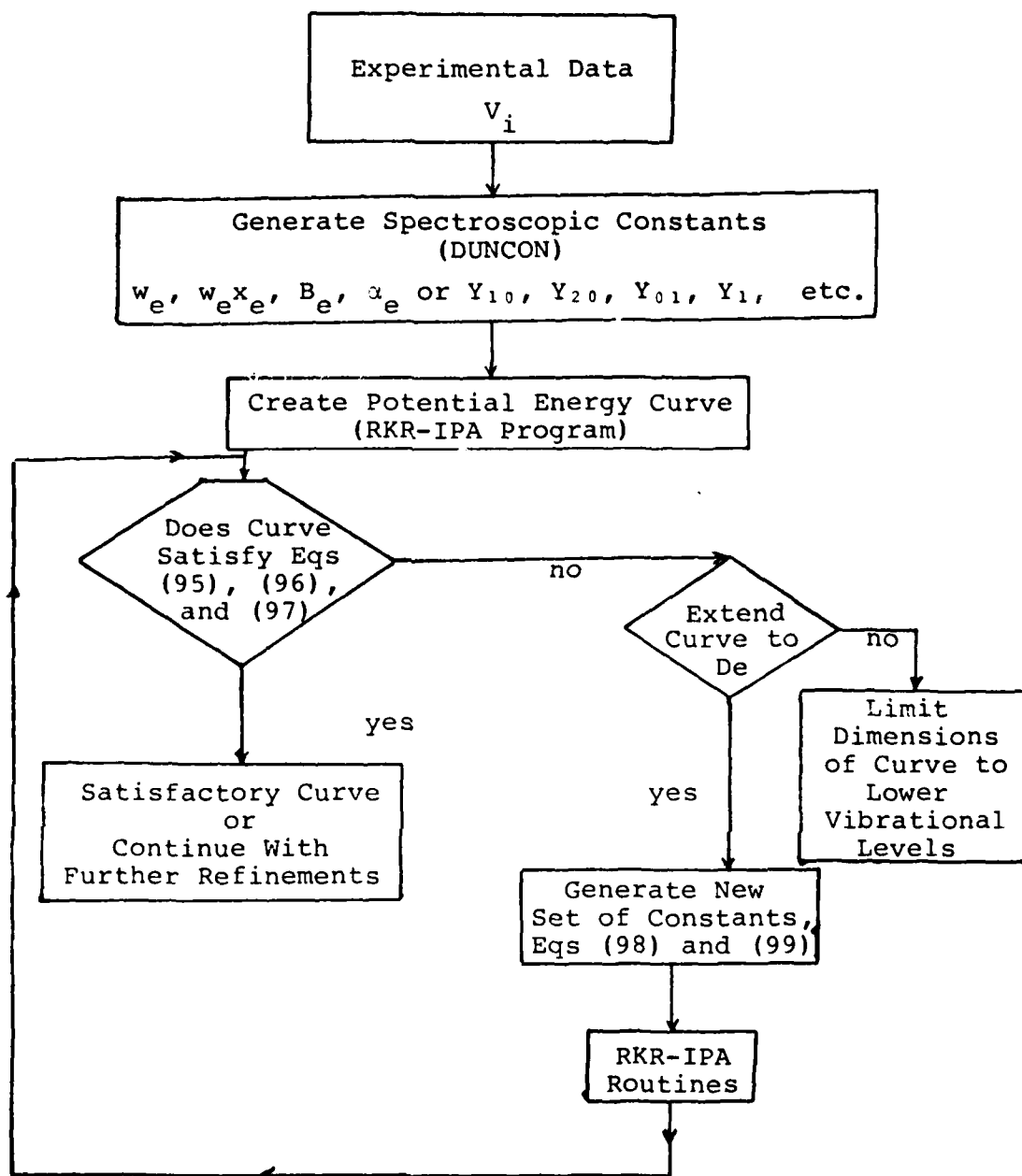


Fig III-1. Flow Diagram for Creation of Potential Energy Curves

DUNCON is used to generate spectroscopic constants by performing least-squares fits to the experimental data. These constants are then used as inputs to the RKR-IPA program. This program produces an RKR curve which is then adjusted by the IPA portion of the program.

Several options are available in the use of the RKR-IPA routines. The RKR routine can be used independently of the IPA routine. The range over which the curve is generated can be restricted to low vibrational energy levels or extended to the dissociation energy. If limited to small vibrational numbers initially, the RKR-IPA routine may be used iteratively to generate new constants and extend the curve to the dissociation limit.

In this paper, after initially generating an RKR-IPA curve, the curve is evaluated according to the criteria of Leroy and Burns, Eqs (95), (96), and (97). If a satisfactory curve is obtained, the calculation is complete. If not satisfactory, then the constants are adjusted as previously described. A modified version of the program DUNCON is used to perform the least-squares fit necessary to produce these constants. The constants are then again input into the RKR-IPA routine. The process is repeated until a satisfactory curve is obtained.

Programs demonstrating the use of DUNCON and the RKR-IPA programs are presented in Appendices A and B. Results of applying the program to the lead-oxide molecule are presented in the following chapter.

IV. Analysis of Spectroscopic Data for Lead-Oxide

This chapter contains the results of an analysis of spectroscopic data for lead-oxide (PbO). The program DUNCON was used to obtain spectroscopic constants for the X, a, b, A, B, and D electronic states of PbO . Constants from published literature were used to generate potential energy curves using the IPA-RKR routine. The potential energy curve for the ground state of lead-oxide was extended almost to the dissociation limit using the extension techniques and the RKR-IPA routine.

The experimental data of three investigations was reduced using DUNCON to yield spectroscopic constants. The data from these investigations is presented in Table IV-5. Two of the investigators, Glessner and Synder (Refs 19; 42), obtained least-squares fits, but did not have the computer routines necessary to generate error estimates and merge the data in a weighted-correlated manner. Their data is reduced, error estimates obtained, and merged using DUNCON. Lead-oxide data produced by Linton and Broida (Ref 33) is reduced using DUNCON and the A-X and a-X data is merged. Also, the results of all three investigations is merged using DUNCON. The results of reducing the data of each investigator for each transition separately is presented in Table IV-1. This

data is then merged in several combinations. The constants resulting from these mergings are presented in Table IV-2. Presented in Table IV-3 are the unmerged and merged estimates for the D-X transitions. The D-X data is merged with other data in a separate fit to prevent its large variance from degrading the constants for the other transitions. Finally, the merged results of Glessner and Snyder's data, are compared in Table IV-4 with the best previous published values available.

The constants presented in columns I and II of Table IV-1 are not identical to those reported by the original investigators. When transforming their experimental data from angstroms to wavenumbers, they did not make corrections for the index of refraction of air as previously discussed. The constants listed in column III of Table IV-1 are also different from the values reported by Linton and Broida. For the A-X transition, they listed only their new band head data. They used data of other researchers to generate their constants. Their published constants are included in Table IV-4. The constants for the a-X transition of column III, Table IV-2 are also slightly different from those reported by Linton and Broida. Presumably, the slight difference arises from the difference in weighting schemes used in this report and that used by Linton and Broida.

TABLE IV-1
 Constants from Separate Least-Squares Fits
 for Each Electronic Transition (cm^{-1})

Electronic Transition	Constant	Source of Experimental Data		
		I Glessner	II Snyder	III Linton and Broida
a-x	Te	[10.03]	[9.875]	[6.310]
	We'	16021.54(2.81)	16021.68(2.59)	16023.12(1.38)
	We'Xe	482.93(1.26)	484.51(1.09)	481.831(0.438)
	We"	2.814(0.170)	2.970(0.146)	2.4590(0.0432)
	We"Xe"	719.36(2.19)	722.785(0.961)	720.166(0.469)
b-x		3.067(0.455)	3.712(0.105)	3.4600(0.0462)
		[2.035]		
	Te	16336.43(6.08) ²		
	We"	428.98(1.46)		
	We'Xe	-0.944(0.114)		
A-X	We"	722.00(1.92)		
	WeXe	3.554(0.193)		
		[41.70]	[33.07]	[4.817]
	Te	19846.0(25.8)	19858.52(6.88)	19864.79(2.38)
	We'	453.5(18.5)	446.30(4.92)	443.31(1.12)

TABLE IV-1--Continued

Electronic Transition	Constant	Source of Experimental Data		
		I Glessner	II Snyder	III Linton and Broida
B-X	We'Xe'	2.04(2.74)	0.479(0.8632)	0.443(0.146)
	We"	715.7(11.3)	724.69(2.93)	720.933(0.374)
	We"Xe"	2.80(1.58)	4.012(0.390)	3.5334(0.0239)
		[52.02]	[64.63]	
	Te	22290.9(10.3)	22286.22(9.06)	
	We'	495.70(4.34)	483.00(8.13)	
	We'Xe'	2.22(1.39)	-1.07(1.71)	
	We"	731.52(6.99)	721.11(3.85)	
	We"Xe"	5.06(1.11)	3.532(0.477)	

¹The quantities in brackets are the variances of the least-squares fits (Eq (14)). Errors reported in parenthesis are one standard deviation. Column I contains least-squares fit to data produced by Glessner (Ref 19). Column II constants are based upon data produced by Snyder (Ref 42). Column III constants are the results of performing least-squares to data published by Linton and Broida (Ref 33).

²The constants for b-x were obtained by combining the data observed by Glessner and Snyder.

TABLE IV-2
Merged PbO Constants (cm-1)¹

Electronic State	Constant	Source of Experimental Data		
		I Merging of Glessner and Snyder Data	II Merging of Linton and Broida Data	III Merging of Glessner, Snyder, Linton, and Broida Data
a	Te	16021.51(1.69)	16024.06(1.16)	16023.16(1.80)
	We'	484.239(0.808)	481.800(0.439)	481.488(0.769)
	We'Xe'	2.949(0.109)	2.4595(0.0434)	2.4339(0.0818)
b	Te	16335.44(2.89)		16331.83(4.77)
	We'	428.43(1.21)		428.34(2.27)
	We'Xe	-0.99552(0.0983)		-1.014(0.186)
A	Te	19856.22(3.31)	19864.11(2.14)	19860.04(3.13)
	We'	447.88(3.50)	443.39(1.12)	445.32(1.83)
	We'Xe'	1.013(0.6007)	0.446(0.145)	0.655(0.249)
B	Te	22282.80(3.67)		22280.52(7.08)
	We'	489.50(2.63)		489.79(5.25)
	We'Xe'	0.149(0.363)		0.225(0.720)
X	We"	721.905(0.620)	720.736(0.244)	720.890(0.395)
	We"Xe"	3.5900(0.0683)	3.5201(0.0171)	3.5316(0.0292)

TABLE IV-2--Continued

Electronic State	Constant	Source of Experimental Data		
		I Merging of Glessner and Snyder Data	II Merging of Linton and Broida Data	III Merging of Glessner, Snyder, Linton, and Broida Data
Variance of Fit		1.0248	1.008	4.076

¹Column I is the result of merging with DUNCON the separate fits in Columns I and II of Table IV-1.

Column II is the result of merging the separate fits in Column III of Table IV-1.

Column III is the result of merging all separate fits in Table IV-1 with DUNCON.

Errors reported in parenthesis are one standard error.

TABLE IV-3
Spectroscopic Constants for D-X Transition of PbO (cm⁻¹)

Electronic State	Constant	Unmerged	Merged
D		[322.3]	[4.19]
	Te	29897.8(67.4)	30115.8(46.1)
	We'	490.0(30.8)	542.2(54.9)
	We'Xe'	-16.53(7.72)	-1.99(13.1)
X	We"	606.1(33.3)	720.989(0.401)
	We"Xe"	-8.32(3.53)	3.5312(0.0296)

Errors Reported in Parenthesis are One Standard Error

TABLE IV-4
Final Spectroscopic Constants for PbO^3

Merged Constants	State	T_e (cm^{-1})	W_e (cm^{-1})	W_{eX_e} (cm^{-1})
This Study (Glessner and Snyder, Refs (19) and (42))	D	30115.8(46.1)	542.2(54.9)	-1.99(13.1)
	B	22282.80(3.67)	489.50(2.63)	0.149(0.363)
	AO+	19856.22(3.31)	447.88(3.50)	1.013(0.6007)
	2b	16335.44(2.89)	428.43(1.21)	-0.99552(0.0983)
	a	16021.51(1.69)	484.239(0.808)	2.949(0.109)
	x		721.905(0.620)	3.5900(0.0683)
Linton and Broida, Ref (33)	AO+	19862.6(1.5)	444.3(0.8)	0.54(0.12)
	a1	16024.9(1.45)	481.5(0.7)	2.45(0.07)
	XO+		720.97(0.36)	3.536(0.025)
Bloomenthal, Ref (8)	D	30197.0	530.6	1.05
	B	22289.8	496.3	2.33
	X		722.3	3.73
Oldenborg, Dickensen and Zare, (Ref 36)	b	16379 $\pm$ 430 ¹		

¹This value is based upon estimate by Oldenborg, Dickensen and Zare that the b state is 350 $\pm$ 430 cm^{-1} above the a state.

²Based upon six data points marked with asterisk in Table IV-7.

³Errors reported in parenthesis are one standard deviation.

TABLE IV-5

Lead-Oxide Spectral Lines Assigned to the
D-X, B-X, A-X and a-X Transitions

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
Investigator: Snyder (Ref (42))				
28589.0	28607.2	-18.2	0,2	D-X
28432.8	28453.7	-20.9	1,3	D-X
27648.9	27625.7	23.2	2,5	D
27534.6	27501.3	33.3	3,6	D
27076.0	27075.5	00.5	1,5	D
26788.7	26829.9	-41.2	3,7	D
26555.3	26529.3	26.0	0,5	D
26394.0	26387.0	-3.0	1,6	D
24122.4	24120.5	1.9	4,0	B
23630.9	23632.5	-1.6	3,0	B
23146.1	23144.0	2.1	2,0	B
22640.3	22655.1	-14.8	1,0	B
22175.3	22165.8	9.5	0,0	B
21450.0	21452.0	2.0	0,1	B
20749.4	20745.2	4.2	0,2	B
20055.5	20045.5	10.0	0,3	B
19646.0	19645.5	0.5	2,5	B
19346.0	19352.9	-6.9	0,4	B
18772.8	18784.0	-11.2	3,7	B
17802.4	17806.7	-4.3	1,7	B
17631.6	17631.2	0.4	2,8	B
21054.4	21051.1	3.3	3,0	A
20166.0	20167.0	1.0	1,0	A
19811.0	19809.6	1.4	5,3	A

TABLE IV-5--Continued

Energy (cm-1)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
19719.7	19723.0	-3.3	0,0	A
19456.0	19453.2	2.8	1,1	A
18996.1	19009.1	-3.0	0,1	A
18741.8	18746.4	-4.6	1,2	A
18293.3	18302.4	-9.1	0,2	A
17593.4	17602.7	-9.3	0,3	A
17338.3	17354.1	-15.7	1,4	A
16905.6	16910.0	-4.4	0,4	A
16224.6	16224.5	0.1	0,5	A
15315.4	15318.5	-3.1	1,7	A
19127.0	19137.9	-10.9	7,0	a
18679.9	18690.4	-10.5	6,0	a
18244.2	18238.2	6.0	5,0	a
17972.0	17976.6	4.6	6,1	a
17778.6	17781.0	-2.4	4,0	a
17520.3	17524.3	4.0	5,1	a
17320.6	17319.0	0.4	3,0	a
17064.6	17067.2	-2.6	4,1	a
16855.4	16852.1	3.3	2,0	a
16601.3	16605.2	-3.9	3,1	a
16384.7	16380.4	4.3	1,0	a
16135.6	16138.3	-2.7	2,1	a
15896.7	15898.4	-1.7	3,2	a
15662.6	15666.5	-3.9	1,1	a
15657.9	11650.4	7.5	4,3	a
15431.5	15431.5	0.0	2,2	a
15187.9	15189.9	-2.0	0,1	a
14958.6	14959.8	-1.2	1,2	a

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
14732.2	14731.8	0.4	2,3	a
14481.2	14483.1	-1.9	0,2	a
14260.0	14260.1	-0.1	1,3	a
13782.7	13783.4	-0.7	0,3	a
13561.7	13567.4	-5.7	1,4	a
13353.6	13353.6	0.0	2,5	a
13083.0	13090.8	-7.8	0,4	a
12932.2	12932.5	-0.3	4,7	a
12874.0	12881.9	-7.9	1,5	a
12473.5	12470.5	3.0	3,7	a
12399.9	12405.2	-5.3	0,5	a
12266.0	12268.2	-2.2	4,8	a
12199.5	12203.3	-4.3	1,6	a
12065.8	12068.0	-2.2	5,9	a
11801.3	11806.1	-4.8	3,8	a
Investigator: Glessner (Ref (19))				
23629.2	23632.5	-3.3	3,0	B
23162.7	23144.0	18.7	2,0	B
22661.3	22655.1	6.2	1,0	B
21444.6	21452.0	-7.4	0,1	B
20745.1	20745.2	0.1	0,2	B
20042.7	20045.5	-2.8	0,2	B
19840.6	19842.2	-1.6	1,4	B
19453.7	19455.5	-1.8	3,6	B
18928.1	18924.9	3.2	6,9	B
18759.8	18761.3	-1.5	7,10	B

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
21921.0	21929.9	-8.9	5,0	A
20163.9	20167.0	-3.1	1,0	A
19004.8	19009.1	-4.3	0,1	A
18299.6	18302.4	-2.8	0,2	A
17609.8	17602.7	7.1	0,3	A
16906.1	16910.0	-3.9	0,4	A
16219.6	16244.5	-25.0	0,5	A
15980.3	15990.0	-9.7	1,6	A
15762.6	15761.2	1.4	2,7	A
19127.7	19137.9	-10.2	7,0	a
18682.3	18690.4	-8.1	6,0	a
18237.9	18238.2	-0.3	5,0	a
17783.0	17781.0	2.0	4,0	a
17513.3	17524.3	-11.0	5,1	a
17316.7	17319.0	-2.3	3,0	a
17064.3	17067.2	-2.9	4,1	a
16852.8	16852.1	0.7	2,0	a
16603.2	16605.2	-2.0	3,1	a
16382.0	16380.4	1.6	1,0	a
16135.8	16138.3	-2.5	2,1	a
15898.0	15903.7	-5.7	0,0*	a
15668.5	15666.5	2.0	1,1	a
15433.4	15431.5	1.9	2,2	a
15193.0	15189.9	3.1	0,1	a
14963.5	14959.8	3.7	1,2	a
14732.4	14731.8	0.6	2,3	a
14483.8	14483.1	0.7	0,2	a
14261.4	14260.1	1.3	1,3	a

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
13781.7	13783.4	-1.7	0,3	a
13564.1	13567.4	-3.3	1,4	a
13085.4	13090.8	-5.4	0,4	a
Investigator: Linton & Broida (Ref (33))				
22364	22367.4	-3.4	6,0	A
21930	21929.9	0.1	5,0	A
21654	21653.6	0.4	6,1	A
21494	21491.2	2.8	4,0	A
21221	21216.1	4.9	5,1	A
20949	20946.8	2.2	6,2	A
20777	20777.3	-0.3	4,1	A
20245	20247.1	-2.1	6,3	A
20069	20070.6	1.6	4,2	A
20168	20167.0	1.0	1,0	A
19366	19370.9	-4.9	4,3	A
19117	19117.0	0.0	5,4	A
18679	18678.2	0.8	4,4	A
17994	17992.7	1.3	4,5	A
17083	17081.5	1.5	5,7	A
14483	14880.9	2.1	3,9	A
14440	14439.5	0.5	2,9	A
14229	14230.7	-1.7	3,10	A
14217	14210.1	6.9	0,8	A
13998	13996.8	1.2	1,9	A
13789	13789.3	-0.3	2,10	A
13585	13587.5	-2.5	3,11	A
13390	13391.4	-1.4	4,12	A

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
13201	13201.1	-0.1	5,13	A
13347	13346.6	0.4	1,10	A
13146	13146.1	-0.1	2,11	A
12951	12951.3	-0.3	3,12	A
12761	12762.3	-1.3	4,13	A
12580	15279.1	0.9	5,14	A
12511	12509.9	1.1	2,12	A
12323	12322.3	0.7	3,13	A
12141	12140.3	0.7	4,14	A
11964	11964.2	-0.2	5,15	A
20448	20450.9	-2.9	10,0	a
20022	20018.1	3.9	9,0	a
19582	19580.4	1.6	8,0	a
19307	19304.2	2.8	9,1	a
19139	19137.9	1.1	7,0	a
18877	18866.6	10.4	8,1	a
18691	18690.4	0.6	6,0	a
18597	18597.5	0.5	9,2	a
18431	18424.0	7.0	7,1	a
18236	18238.2	-2.2	5,0	a
18160	18159.8	0.2	8,2	a
17977	17976.6	0.4	6,1	a
17782	17781.0	1.0	4,0	a
17526	17524.3	1.7	5,1	a
17317	17319.0	-2.0	3,0	a
17272	17269.8	2.2	6,2	a
17067	17067.2	-0.2	4,1	a
16854	16852.1	1.9	2,0	a

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
16819	16817.6	1.4	5,2	a
16609	16605.2	3.8	3,1	a
16386	16380.4	5.6	1,0	a
16361	16360.4	0.6	4,2	a
16140	16138.3	1.7	2,1	a
16117	16117.9	0.9	5,3	a
15902	15898.4	3.6	3,2	a
15668	15666.5	1.5	1,1	a
15662	15660.7	1.3	4,3	a
15434	15431.5	2.5	2,2	a
15423	15425.2	-2.2	5,4	a
15191	15189.9	1.1	0,1	a
14961	14959.8	1.2	1,2	a
14734	14731.8	2.2	2,3	a
14510	14506.1	3.9	3,4	a
14485	14483.1	1.9	0,2	a
14286	14282.5	3.5	4,5	a
14261	14260.1	0.9	1,3	a
14071	14061.1	9.9	5,6	a
13828	13820.5	7.5	3,5	a
13784	13783.4	0.6	0,3	a
13569	13567.4	1.6	1,4	a
13355	13353.6	1.4	2,5	a
13146	13142	5.2	3,6	a
13092	13090.9	1.1	0,4	a
12884	12881.9	2.1	1,5	a
12667	12675.1	1.9	2,6	a
12407	12405.2	1.8	0,5	a

TABLE IV-5--Continued

Energy (cm ⁻¹)			Assignments	
Observed	Calculated	Obs-Calc	v',v''	Transition
12006	12003.6	2.4	2,7	a
11807	11806.1	0.9	3,8	a
11728	11726.7	1.3	0,6	a
11534	11531.9	2.1	1,7	a
11341	11339.3	1.7	2,8	a
11149	11148.8	0.2	3,9	a
11057	11055.3	1.7	0,7	a
10869	10867.5	1.5	1,8	a
10498	10498.6	-0.6	3,10	a
10391	10390.9	0.1	0,8	a
10212	10210.2	1.8	1,9	a

*Later reassigned as the "(3,2) a-X" transition.

Examination of Table IV-1 reveals values of w_e for the X-state ranging from 715.7 to 731.5 cm^{-1} . DUNCON permits the merging of the data listed in Table IV-1 in a weighted-correlated least-squares fashion.

The results of the merging are presented in Table IV-2. Error limits for w_e of the X-state are reduced from a maximum standard error of $\pm 11.3 \text{ cm}^{-1}$ to $\pm 0.620 \text{ cm}^{-1}$ when the data in columns I and II of Table IV-1 are merged. The results are presented in column I, Table IV-2.

Column II, Table IV-2 contains the smallest error estimate for the constants of the a-, A-, and X-electronic states. The variances for the merged fits of columns I and II are similar, 1.0248 and 1.008, respectively. But when the data in columns I and II are merged to yield column III, Table IV-2, the estimated variance of the fit and, in many cases, the standard errors of the individual constants increase. Examination of (columns I and II) the a- and X-states reveals term electronic energies, T_e , with error limits of comparable magnitude which do not overlap. Because of this, when merged, the error limits reflect the equal weighting of the "almost significant" differences and, hence, the increased error limit reflects a bias in one or both of the data sets.

Column III of Table IV-2 reflects the most conservative error estimate of the three columns in Table IV-2. It is also based upon the largest quantity of data.

In reporting constants, a researcher may be tempted to manipulate the constants of the ground state and report the constants obtained from the least-squares fits for the upper state. For example, if a routine for merging fits is not available, one might average the constants for the ground state or obtain a weighted average based upon the error estimates. The temptation then is to report the averaged ground state constants and the upper state constants obtained from the original least-squares fits. Reporting constants in this fashion is undesirable for two reasons. First, the constants reported in this manner will not faithfully reproduce the experimentally observed data. Second, a better estimate of the ground state has been obtained. This new estimate of the ground state constants should, in turn, be used to ascertain how well the upper state constants are known. This can be done by removing (adding) the energy contributions of the ground state from the experimental data and performing a least-squares fit to obtain the upper state constants. These new upper state constants and the average ground state constants should provide an accurate reproduction of the experimental data and an accurate set of constants for the generation of potential energy curves. The approach just described is not necessary if a routine such as DUNCON is available for merging data. Even though it is available, the use of DUNCON to form a merged fit may not be desirable

if large quantities of data are involved and the ground state constant has already been well defined.

Often the data merged from different investigators may contain different experimental values for the same assignment (v', v''). If after using DUNCON to obtain the best estimate of the constants, one of the experimental values agrees with the fit and the other does not, then one might remove the poorer data point and perform the fit again. This approach should be used with caution.

Presented in Table IV-4 are the constants obtained by merging the experimental data of Glessner and Snyder. Presented for comparison are results published by other researchers.

The data used to produce the constants of Tables IV-1 and IV-2 is presented in Table IV-5. The calculated values of Table IV-5 were obtained using the constants of column III, Table IV-2 and Table IV-3 for the D state.

The D-state constants were obtained in a separate merged fit from that used to obtain the other constants because of their large error. The values reported by Bloomenthal (Ref 8) produced a better fit for his data; hence, his constants are the preferred constants.

The B-state constants reported by Bloomenthal provide a better fit to his data than the constants reported here fit the B data listed in Table IV-5. This statement must be modified slightly. Bloomenthal did not provide "observed-

calculated" values for all the data he listed. Hence, these values may not have been included in his estimate of the constants.

The A-state constants reported in Table IV-4 provide a reasonable agreement with those reported by Linton and Broida (Ref 33). The reported constants are based upon the merging of data reported by Glessner and Snyder.

The small a-state constants reported in Table IV-4 rival those reported by Linton and Broida in accuracy. Table IV-2 shows that the merged data of Glessner and Snyder produces constants with error limits of magnitude comparable to that reported by Linton and Broida.

The ground state (x) constants reported in Table IV-4 agree well with those reported by Linton and Broida. The merging of Glessner's and Snyder's data resulted in constants for the X-state with significantly smaller errors than those obtained in separate fits of their data.

The discussion of the b-state data was reserved until last, because they were obtained by making reassignments of many transitions that were published in previous works.

The b-state constants listed in Table IV-1, column I are based upon the six assignments marked by asterisks in Table IV-7. The assignments were made by Glessner and Snyder (Refs 19; 42) based upon the works of Kurylo, et.al. (Ref 31). The variance of the constants in Table IV-2 is remarkably

small considering that only six data points with five constants were used yielding a degree of freedom of one. A review of Kurylo's tentative assignments and tentative assignments made by Oldenberg, Dickson, and Zare (Ref 36) show a much greater difference between the observed and calculated values than would be expected from the constants of Table IV-1.

Using the b-state constants of Table IV-1, new assignments were made for the experimental data which had been marked as belonging to the b-X transition by Kurylo and Oldenberg. It was possible to make new assignments for 29 of 34 observed values which had been reported as belonging to the b-state. Twenty-six of those were used in a least-squares fit to generate new b-state constants. DUNCON was used to perform separate least-squares fits to the data of Snyder and Glessner, and to the data of Kurylo and Oldenberg. Then DUNCON was used to merge the results of these fits. A copy of the program with the results is presented in Appendix A.

The resulting b-state and X-state constants are presented in Table IV-6. The 26 assignments used to obtain the constants are listed in Table IV-7. The "observed-calculated" values are presented for comparison with those of the original investigators. For the 26 values used in the new fit, a standard error of +10.5 cm was obtained. For the 15 values which the investigators reported "observed-calculated" values, their standard error was +47.4 cm. It should be noted

TABLE IV-6

Spectroscopic Constants for b-X
Transition for Lead Oxide

State	Te	We	WeXe
b	16325.1(11.2)	430.99(2.47)	-0.757(0.165)
X		721.41(4.35)	3.700(0.441)

that this error was due to uncertainties in the assignments and not the quality of the data.

The second part of Table IV-7 contains those values which were published as b-X transitions for which no assignments had been made at the time the fit was performed. After the new constants were calculated, assignments were made for three more b-X transitions.

The new assignments presented in this paper were made without access to the raw spectral data and, hence, information concerning the relative intensities of each transition. It is also probable that some of the assignments of the transitions to the b-state are incorrect. For example, the last value of Table IV-7, an experimentally observed value of 15672 cm^{-1} was assigned as a b-X transition. This value corresponds closely with the value of 15662 cm^{-1} observed by Linton and Broida and assigned to the a-X transition series.

TABLE IV-7
Lead-Oxide Spectrum for the b-X Transition

This Work				Original Investigator	
Assignment	Observed (cm^{-1})	Calculated (cm^{-1})	Obs-Calc	Assignments	Obs-Calc
(14,1)	21643	21659.8	-16.8	(12,0) O	
	21636			(12,0) K	-24
(13,1)	21200	21207.6	- 7.7	(11,0) O	
(10,1)*	19869.8	19860.2	9.6	(10,1) G	4
(7,1)	18515	18526.3	-11.3	(5,0) K	-15
(3,0)	17488.4	17483.1	5.3	(3,0) S	- 5.5
(4,1)	17212	17206.1	5.9	(2,0) K	13
(7,3)	17108	17120.5	-12.5	(8,4) K	56
(2,0)	17033	17047.5	-14.5	(5,2) K	-75
(5,2)	16915	16938.0	-23.0	(1,0) K	-62
(3,1)	16773	16769.0	4.0	(1,0) K	16
(1,0)	16614	16613.5	- 0.5	(4,2) K	50
(4,2)	16488	16499.5	-11.5	(2,1) K	3
(7,4)	16434	16428.7	5.3	(10,5) K	67
(17,11)	16297	16292.4	4.6	(0,0) K	-18
(14,9)	16215	16214.1	0.9	(3,2) K	- 5
(3,2)*	16066.8	16062.4	4.4	(3,2) S	- 5.7

TABLE IV-7--Continued

This Work				Original Investigator	
Assignment	Observed (cm^{-1})	Calculated (cm^{-1})	Obs-Calc	Assignments	Obs-Calc
(13,9)	15773	15762.0	11.0	(2,2) K	- 5
(2,2)	15623	15627.0	- 4.0	(0,1) K	22
(3,3)	15363	15363.2	- 0.2	(1,2) K	28
(9,7) *	15281.9	15285.4	- 3.5	(9,7) S	- 6.1
(3,4)	14687.8	14671.4	15.6	(3,4) S	8.4
(8,8)	14180.1	14178.5	1.6	(8,8) S	- 2.2
(0,4)	13367.30	13369.4	- 2.1	(0,4) S	10.5
(1,5) *	13117.5	13117.4	0.1	(1,5) S	5.9
(1,6) *	12440.1	12440.4	- 0.3	(1,6) S	- 7.4
(3,8) *	11968.9	11978.2	- 9.3	(3,8) S	- 8.9
	20786			(10,0) O	
	20354			(9,0) O	
	19923			(8,0) O	
(19,5)	21169	21161.4	7.6	(11,0) K	58
	20338			(9,0) K	24
	19904			(8,0) K	37

TABLE IV-7--Continued

Assignment	This Work		Original Investigator	
	Observed (cm ⁻¹)	Calculated (cm ⁻¹)	Assignments	Obs-Calc
(18,12)	16108	16618	(6,4) ^K	-52
(17,12)	15672	15660	(5,4) ^K	-43
	or 15662		a(4,3) ^{L&B}	

*These are the six transitions used to obtain the b-state constants of Table IV-1, column I.

O - Oldenborg (Ref 36)

S - Snyder (Ref 42)

G - Glessner (Ref 19)

K - Kurylo (Ref 31)

L&B - Linton and Broida (Ref 33)

This concludes the discussion of program DUNCON and the results of its application to lead-oxide. Only a small portion of the PbO data available was used in the present analysis. Rotational data, if used, should increase the quality of the constants. A more extensive evaluation of the literature data with the selective discarding of "erroneous" data points should yield better constants.

Lead-Oxide RKR-IPA Curves

To demonstrate the use of the RKR-IPA program, the X-, a-, and A-states were selected for evaluation. Curves were drawn for the X-, a-, and A-states using the results of the RKR routine alone or using the combined RKR and IPA routine (RKR-IPA curve). The resulting potential energy curves are presented in Fig. IV-1 for the X-, A-, and the a-states. For the A-state, the curve presented in Fig. IV-1 is an RKR curve, while for the X- and a-states, they are RKR-IPA curves. The RKR and IPA results are presented for the X- and a-states in Tables IV-8 and IV-9, respectively. The RKR data for the A-state is presented in Table IV-10. The constants used to generate these curves for each state is presented in Table IV-11.

The ultimate use of a potential should be to predict what transitions should occur. A sophisticated analysis would involve the calculation of Franck-Condon factors from the wave functions resulting from the solution of the Schroedinger wave

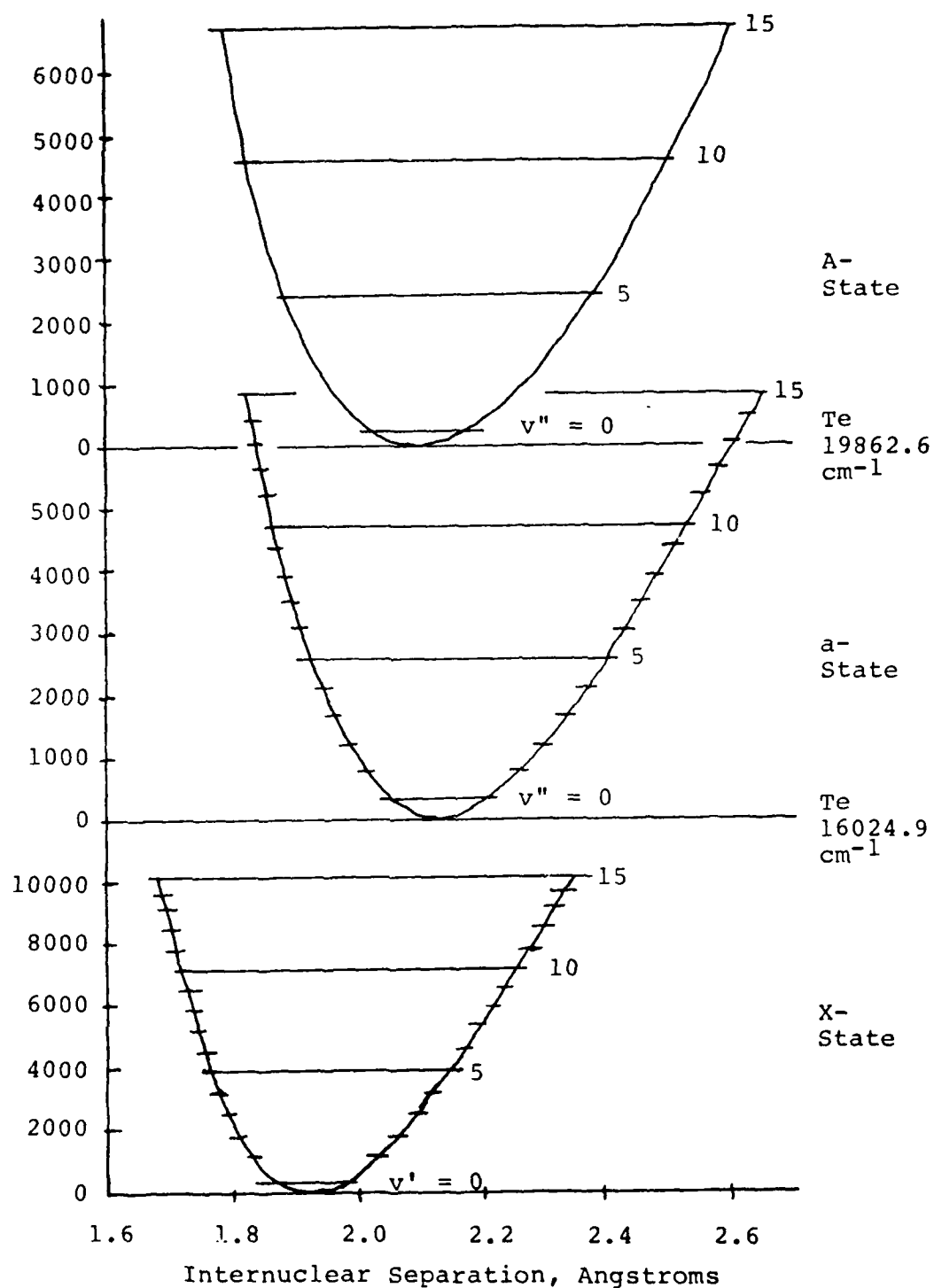


Fig IV-1. Potential Energy Curves for Lead-Oxide
X, a, and A Electronic States

TABLE IV-8
RKR and IPA Potential for Ground State of Lead-Oxide

RKR				IPA			
V	Gv (cm ⁻¹)	R- (Å)	R+ (Å)	Gv (cm ⁻¹)	R- (Å)	R+ (Å)	Bv (cm ⁻¹) X100
-½			1.921				
0	359.62	1.868	1.980	359.918	1.867	1.979	30.687
1	1073.52	1.832	2.027	1073.901	1.831	2.027	30.469
2	1780.34	1.809	2.062	1780.716	1.808	2.062	30.256
3	2480.10	1.790	2.092	2480.445	1.791	2.092	30.048
4	3172.78	1.775	2.118	3173.120	1.776	2.119	29.844
5	3858.39	1.762	2.143	3858.743	1.763	2.144	29.645
6	4536.93	1.751	2.167	4537.299	1.752	2.168	29.452
7	5208.40	1.740	2.189	5208.773	1.741	2.190	29.264
8	5872.79	1.731	2.211	5873.161	1.732	2.212	29.082
9	6530.11	1.722	2.231	6530.471	1.723	2.236	28.905
10	7180.36	1.714	2.251	7180.713	1.715	2.253	28.731
11	7823.54	1.706	2.271	7823.891	1.707	2.273	28.557
12	8259.65	1.699	2.291	8459.997	1.700	2.292	28.378
13	9088.68	1.693	2.311	9089.028	1.693	2.311	28.192
14	9710.64	1.686	2.330	9711.015	1.686	2.330	27.998
15	10325.53	1.680	2.349	10326.059	1.680	2.349	27.796

$Y_{00} = 0.0233501$

$Y_{00} = 0.37952$

TABLE IV-9

RKR and IPA Potential for the a-State of Lead-Oxide

V	RKR			IPA		
	Gv (cm ⁻¹)	R- (Å)	R+ (Å)	R- (Å)	R+ (Å)	Bv (cm ⁻¹) X100
- $\frac{1}{2}$			2.122			
0	240.13	2.075	2.172	2.054	2.192	25.163
1				2.011	2.250	24.988
2				1.982	2.293	24.822
3				1.960	2.329	24.658
4				1.942	2.363	24.495
5	2574.13	1.928	2.394	1.925	2.392	24.328
6				1.911	2.421	24.157
7				1.899	2.448	23.979
8				1.887	2.457	23.795
9				1.877	2.501	23.607
10	4785.63	1.868	2.528	1.868	2.527	23.419
11				1.859	2.552	23.236
12				1.850	2.576	23.060
13				1.842	2.600	22.893
14				1.834	2.624	22.729
15	6874.63	1.827	2.647	1.827	2.648	22.562
$Y_{00} = 1.5566 \times 10^{-5}$ $Y_{00} = 0.16759$						

TABLE IV-10

RKR Potential for the A-State of Lead-Oxide

V	$Gv(\text{cm}^{-1})$	$R-\overset{\circ}{A}$	$R+\overset{\circ}{A}$
0.0	222.30	2.025	2.168
2.5	1328.32	1.937	2.288
5.0	2427.60	1.890	2.367
7.5	3520.12	1.856	2.432
10.0	4605.90	1.829	2.491
12.5	5684.92	1.807	2.546
15.0	6757.20	1.788	2.597
$Y_{00} = 0.28500$			

TABLE IV-11
Input Constants and Data Used to Generate
Potential Energy Curves

Constants	State		
	X	a	A
Te*	0.0	16024.9(1.45)	19862.6(1.5)
Y ₁₀ *	720.97(0.36)	481.5(0.70)	443.3(0.8)
Y ₂₀ *	- 3.536(0.025)	- 2.45(0.07)	- 0.54(0.24)
Y ₀₁	0.307519**	0.252(0.10)*	0.2588**
Y ₁₁	- 1.9167X10 ^{-3**}	- 1.6761X10 ^{-3#}	1.4X10 ^{-3**}
Y ₀₂	2.2X10 ^{-7**}	2.2X10 ^{-7##}	3.3X10 ^{-7**}

Mass : Oxygen - 1.5994 amu; Lead - 207.19 amu.

*Source: Linton and Broida (Ref 33).

**Source: Suchard (Ref 45).

#Source: Calculated from Linton and Broida's Y₀₁ using Eq (104).

##Source: Used X-state value for a-state Y₀₂. The a-state Y₀₂ should be calculated according to Eq (104'). The error due to this substitution should be small.

equation. But, it is possible to arrive at certain conclusions without calculation of the Franck-Condon factors. For example, examination of the a-state and X-state curves show that no overlap exists between the " $v'=0$ " energy level for the a-state, and " $v=0$ " for the X-state. This indicates that such a transition is classically forbidden. In Table IV-5, a transition observed at 15898 cm had been assigned to the a-X (0,0) transition. Reevaluation showed that the 15898 band head should be the a-X (3,2) transition. Both assignments were acceptable within the error limits of fit. The relative positioning of the potentials indicate that only the (3,2) transition is possible. The calculated value for the a-X (3,2) transition is 15898.4 cm^{-1} .

The next step should be the generation of a new set of constants using the formulas for G_v and B_v and the newly obtained energy eigenvalues G_v and B_v values generated by the IPA routine. This technique was applied to the ground state IPA potential of Table IV-8. From this, the following constants were generated for the ground state:

$$Y_{10} = 720.991(0.058) \text{ cm}$$

$$Y_{20} = 3.5357(0.00479)$$

The calculation of new values for the rotational constants Y_{01} , Y_{11} , etc., from B_v was not performed.

The calculations using only Vidal's RKR-IPA method were halted at this point. Attempts to extend the curves to the dissociation limit "in one jump" produced a potential

which diverged as the curve approached the dissociation limit (see Fig IV-2). Not having data for vibrational levels above about $v=15$, the iterative techniques of gradually extending the curve, as discussed by Vidal and Stawalley (Ref 43), were not attempted. They used the IPA method to improve the RKR curve at lower levels, and then on successive trials, extended the curve slowly to the dissociation limit.

The reader is referred to Vidal's works listed in the Bibliography and in Appendix C for further information concerning the generation of new constants and the extension of potential curves to the dissociation limit using the IPA routine.

This completes the discussion of the use of the RKR-IPA program by itself to generate potential curves. The next section presents use of the RKR-IPA technique in conjunction with Leroy's extension techniques to produce a potential energy curve which extends to the dissociation limit.

Extension of the X-State Lead-Oxide
Potential Energy Curve to the
Dissociation Limit, D_e

The potential energy curve for the ground state of lead-oxide was selected as the likely candidate for extension to the dissociation energy, D_e . This selection was based upon the fact that the constants for the ground state have the smallest standard errors.

The vibrational constants of Linton and Broida were selected as starting values because of their small error

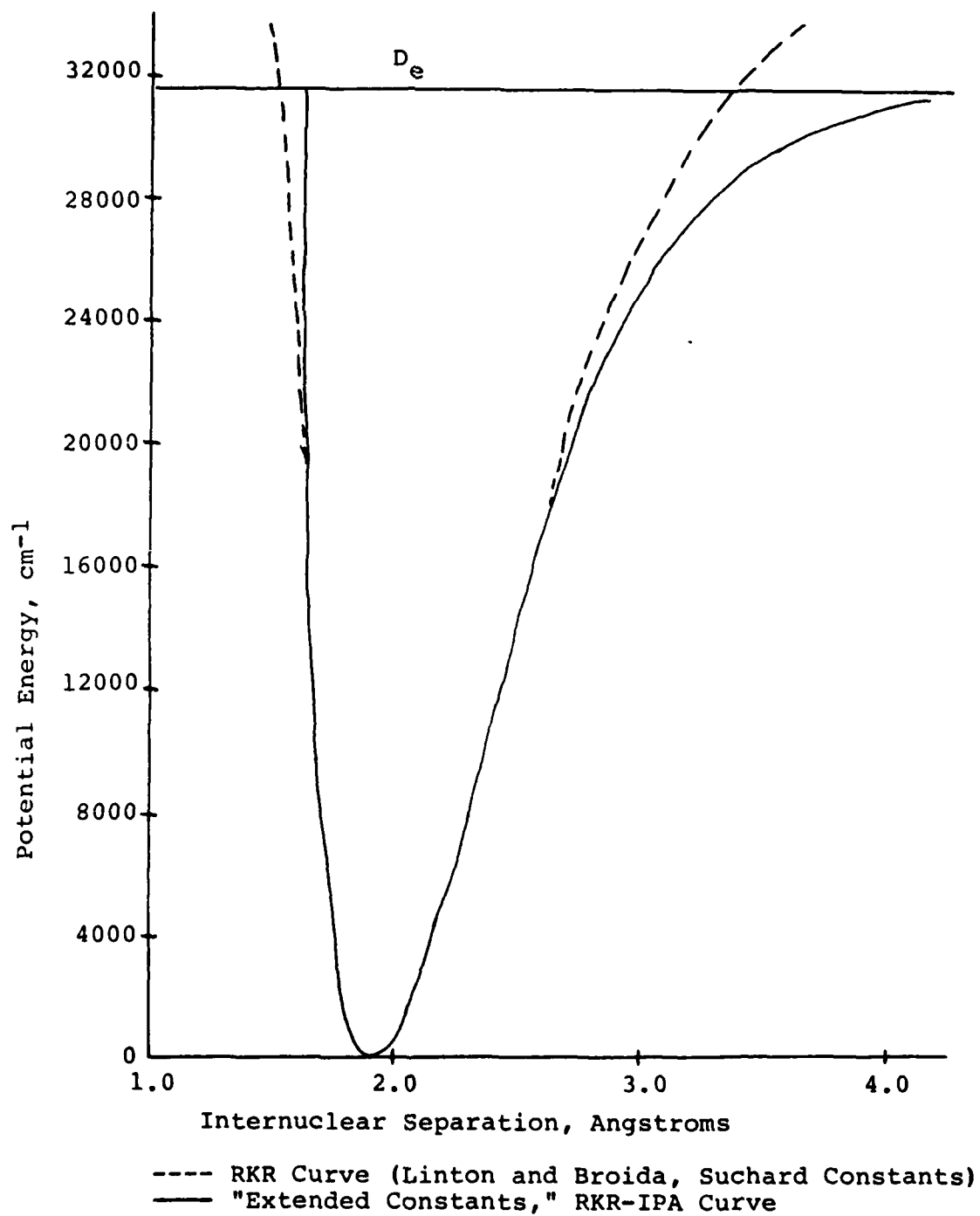


Fig IV-2. Lead-Oxide X-State Potential Energy Curves

limits. The creation of potential energy curves also requires the knowledge of rotational constants. The rotational constants were selected from Suchard (Ref 45). Table IV-12 contains the original constants and the final set of constants used in extending the curve to the dissociation limit.

The method prescribed by Leroy was used. Linton and Broida's constants were used to generate a set of $G(v)$'s according to Eq (87) for $v=0$ to 15. A trial value was selected for Y_{40} and the other constants, Y_{30} , Y_{20} , and Y_{10} were solved for by performing a least-squares fit to the value obtained from Eq (98). Program DUNCON was modified to perform the fit. The process was repeated until the criterion of " $\Delta Gv + \frac{1}{2} = 0$ " at D_e was satisfied.

Suchard's constants were used to generate a set of B_v 's for $v=0$ to 15 according to Eq (93). A trial Y_{21} was selected and new Y_{01} and Y_{11} constants were obtained from a least squares fit to the values calculated by Eq (99).

The new vibrational constants and rotational constants were used as the inputs for the RKR-IPA program. The process of adjusting the rotational constants was repeated until the criteria expressed in Eqs (95'), (96), and (97) were satisfied.

The last set of constants calculated are presented in Table IV-12 as the extended constants. The complete numerical results of the IPA-RKR routine are presented in Appendix B. The "Final Set of Turning Points," as output by the IPA routine was used to create the potential curve (solid line)

TABLE IV-12

Constants Used to Extend the Lead-Oxide X-State
Potential Energy Curve to the
Dissociation Limit, D_e

Constants	Original Values	Extended Values
Y_{10}	720.97(0.36)	721.062849
Y_{20}	- 3.536	- 3.57101904
Y_{30}		$3.85076374 \times 10^{-3}$
Y_{40}		- 1.29×10^{-4}
Y_{01}	0.307519	0.30726775
Y_{11}	- 1.9167×10^{-3}	- 1.7667×10^{-3}
Y_{21}		- 1.5×10^{-5}
Y_{02}	0.22×10^{-6}	0.22×10^{-6}
$D_e = 31570 \pm 410. \text{ cm}^{-1}$		

in Fig IV-2 which satisfies the dissociation criteria. The dashed line in Fig IV-2 is the RKR curve, as defined by the original constants of Linton and Broida, and Suchard. It should be noted that the constants, as presented in Table IV-12, will only produce the curve in Fig IV-2 when input into an RKR-IPA routine. Examination of the "Final Set of Turning Points" yields a minimum inner turning radius of about 1.62 angstroms for vibrational quantum numbers from $v=33$ to $v=69$. Examination of the turning points for the initial "Potential Generated by RKR," listed at the beginning of the RKR-IPA program output in Appendix B, shows RMIN turning points as small as 1.54 angstroms for $v=74$. For $v=69$, the last vibrational quantum number investigated by the IPA routine, the RKR program returned an RMIN of 1.59 angstroms. This decreasing value in RMIN indicates that the left branch of the curve would diverge just as shown by the dashed line on the left-hand side in Fig IV-2. The turning points of the RKR potential were of sufficient quality that the IPA program was able to correct the potential to yield the solid curve of Fig IV-2. In this work, the procedure described above, was the final one used; however, continued refinements are possible by the use of the RKR-IPA program. The next step should be to take the $G(v)$ $[U(R)]$ and $B(v)$ $[BV \times 100]$ values as output by the IPA program and perform a least-squares fit to obtain a new set of Y_{n0} and Y_{n1} constants. These, in turn, would be used as input for the

constants from the experimental data and calculating the higher $Y_{n+,n+}$ constants.

The convergence of the IPA routine became very sensitive as the "sought for value" of the last vibrational constant was approached. For the example, the IPA routine would not converge when values of $Y_{21} = -1.25 \times 10^{-5}$ or $Y = 1.75 \times 10^{-5}$ were used. The program would converge for values of Y_{21} larger and smaller than these, but the shape of the resulting curve diverged from the desired shape. An indication of the convergence of the IPA routine may be obtained by looking at the next to the last output of the IPA-RKR program, "The Summary of Errors of the Inverted Perturbation Approach."

Due to the fact that the "Final Set of Turning Points" fluctuates about 1.62 angstroms and the potential is increasing asymptotically along 1.62 angstroms, multiple potential energies are presented for the same RMIN turning point value. Thus, when searches are performed using a turning point radius value [XXX] as in DO-loop 55 of POTTAB, and PLYNN called from this loop, the routine stops at the first value satisfying the requirement $[XXX] < X(J)$ (Subroutine PLYNN). The end result is that potential energies corresponding to turning points of magnitude of less than about 1.62 angstroms in the "Final Potential" should not be accepted as valid without close inspection. Improved constants and successive iterations of the RKR-IPA routine may remove this discrepancy.

V. Summary and Recommendations

The programs and techniques necessary to transform molecular spectra for diatomic molecules into potential energy curves have been presented and described in detail. The program DUNCON performs least-squares fits to separate data sets and then merges them in a weighted-correlated manner based upon the variances of the separate fits to yield spectroscopic constants. The RKR-IPA program presented first calculates "semi-classical" turning points based upon spectroscopic constants. It then adjusts the resulting RKR potential through an inverted perturbation technique to yield a potential energy curve whose energy eigenvalues are in best agreement with the model of a vibrating-rotating diatomic molecule as specified by the Schroedinger wave equation and with the experimentally observed data. The routing also calculates the wave functions for the potential energy curve.

Techniques were presented for extending potential energy curves to their dissociation limit when experimental data does not permit such an extension by straightforward application of the RKR technique.

Using DUNCON, constants for the a-X, A-X, B-X, and D-X transitions were calculated from experimental data. The results are presented in Tables IV-1, IV-2, and IV-3. The calculated values agree well with published values for these states.

A new set of assignments was made for b-X transitions. The new constants calculated for the b-state are presented in Table IV-6, and the new assignments are in Table IV-7. The new assignments and constants produced a fit with a standard error of 10.49 cm^{-1} versus 47.9 cm^{-1} for the previous published assignments.

Recommendations

1. The use of Leroy's technique for extending a curve to its dissociation limit in conjunction with the RKR-IPA routine should be tested upon a potential energy curve whose shape is known and for which experimental data is available all the way up to the dissociation energy. If the technique produces a curve and energy eigenvalues consistent with a curve based upon experimental data then, the validity of the method will be confirmed.

2. This technique for extending curves might be further verified by applying it to two different states; for example, a- and b-states of lead-oxide, whose dissociation energies are the same. The coincidence of their potential energy curves at large separations should serve to verify both the extension technique and the quality of the constants used in construction of the curves.

3. A complete investigation of all published data using DUNCON should produce a better set of constants for lead-oxide. This is particularly true for cases where two

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NUMERICAL METHODS FOR THE PREPARATION OF POTENTIAL
ENERGY CURVES OF DIATO..(U) AIR FORCE INST OF TECH
WRIGHT-PATTERSON AFB OH SCHOOL OF SYST.. L L RUTGER

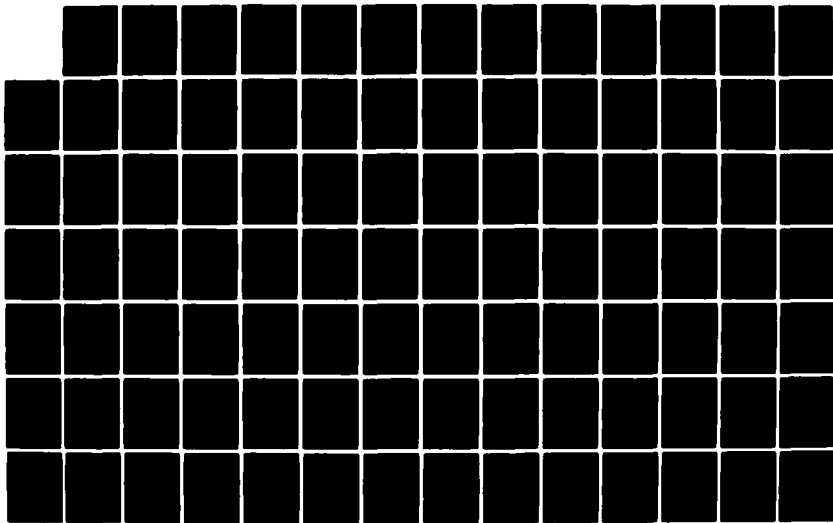
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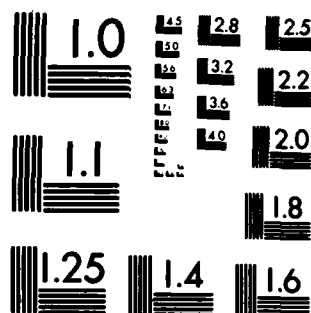
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

investigators have given different energy levels for the same transition. The judgment as to which data is the more accurate should be based upon the constants produced by DUNCON.

4. Constants obtained from a least-squares fit should be reported as a group. If not, care should be taken to report how the constants were obtained.

5. The reassignments made for the b-X transitions should be evaluated by an investigator with access to data specifying the relative intensities of the experimental data. These were not available for the assignments made in this work.

Also, the b-state constants should be reevaluated using a more accurate set of X-state constants as opposed to those obtained from the least-squares fit of the b-X data. By fixing the value of the X-state constants, it may be possible to obtain a positive $w_e x_e$ for the b-state. Having a positive $w_e x_e$, then Eq (102) and Tellinghuisen's method for constructing a potential energy curve might be used. Alternatively, Eq (101) might be applied. From the potential energy curve, it might be possible to determine what transitions are more probable. Some information along these lines can be obtained by assuming a similarity between the a-state potential and estimating the position of the b-state curve relative to the a-state curve.

6. Vidal made use of the RKR-IPA routine to improve RKR curves for low energies and then used these improved

curves to extend the curves in small increments to higher energy levels. This technique has not been pursued and warrants further investigation. The RKR-IPA routine could even be used to improve constants for low energy levels, i.e., small "v", prior to using them in the previously described extension technique. Both techniques warrant further investigation.

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Appendix A

Program DUNCON

The following section contains the program DUNCON. The program has provisions for obtaining separate least-squares fits to separate data sets and then merging the resulting constants in a weighted-correlated fashion based upon the variances and covariances of the original separate fits.

Presented first is a written description of the program and instructions on how to use the program. Following that is a listing of the program with a sample output.

Merged Least-Squares Spectroscopic Constants Program

Program DUNCON is structured so the user can generate a least-squares fit to several different groups of data which have different standard errors and then merge the fits to obtain a weighted, correlated linear-least squares fit as described in the previous discussion on least-squares fits (Refs 2 and 3). DUNCON is written in Fortran V. A copy of DUNCON follows in this appendix.

The user must set up the model which will be used to fit his spectroscopic data, input the data, dimension the arrays used in his program, and call the subroutines WAVNUM, CONST, MATEQ, VECEQ, MATINV, and MERCN to obtain a merged least-squares fit. In turn, these routines call on a package of matrix manipulating routines (Ref 13) contained in the subroutine MATMULT.

Program DUNCON

The user has complete freedom in structuring this portion of the program. To perform a least-squares fit, the user must choose a model to represent his data. For data representing transitions between electronic states, the following is a typical model using Dunham coefficients (Ref 18):

$$\nu = T_e' + Y_{10}' + Y_{20}' - Y_{10}'' - Y_{20}'' \quad (117)$$

where ν is the frequency of the transition expressed in units of cm^{-1} . As previously described, a series of transitions

(v) may be represented in matrix notation as:

$$v_k = X_{k k} B_k + \epsilon_k \quad k = 1, 2, 3 \quad (118)$$

where v is a column matrix made of experimentally determined wavelengths or wavenumbers:

$$v = \begin{bmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{bmatrix} \quad (119)$$

The X matrix is made up of the $v'_i+1/2$, $(v'_i+1/2)^2$, $v''_i+1/2$, and $(v''_i+1/2)^2$ terms:

$$X = \begin{bmatrix} 1 & v'_1+1/2 & (v'_1+1/2)^2 & v''_1+1/2 & (v''_1+1/2)^2 \\ 1 & v'_2+1/2 & (v'_2+1/2)^2 & v''_2+1/2 & (v''_2+1/2)^2 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & v'_n+1/2 & (v'_n+1/2)^2 & v''_n+1/2 & (v''_n+1/2)^2 \end{bmatrix} \quad (120)$$

This X matrix is calculated in lines 18-28 of the subroutine CONST. As the specific model chosen to represent spectroscopic data may vary, the user must define this section of CONST.

The β column matrix (vector) will contain the constants of the least-squares fits.

$$\beta = \begin{bmatrix} Te' \\ Y_{10}' \\ Y_{20}' \\ Y_{10}'' \\ Y_{20}'' \end{bmatrix} \quad (121)$$

To operate the program, the user must input the following data:

1. $\underline{v}$ --the experimentally determined energy of transition expressed in either angstroms (A) or wavenumbers (cm^{-1}). In the sample program in this appendix, v is called ANUx, where the small "x" represents the additional characters necessary to identify a specific group of data. This convention is continued throughout the discussion in this section.

2. $\underline{v}'$ --the vibrational quantum number associated with the upper state and referred to as QV1x in the program. It should be entered as a decimal.

3. $\underline{v}''$ --the vibrational quantum number associated with the lower state and referred to as QV2x in the program. It should be entered as a decimal.

NOTE: the values of ANUx, QV1x, and QV2x for each observed transition must be associated with each other by subscripts. (The subscript is placed in parenthesis and the subscript must start with "0".) For example:

ANUX(0),QV1x(0),QV2x(0)

ANUX(1),QV1x(1),QV2x(1)

ANUX(2),QV1x(2),QV2x(2)

etc.

4. N--the number of constants minus one to be calculated in the initial least-squares fit. For the model in Eq (117), N should be defined as follows: $N = 5 - 1 = 4$.

5. Mx--corresponds to the number of experimental values to be included initially in a data set for least-squares fitting prior to the merging step.

6. MM--corresponds to the total number of constants minus one which are generated in the initial least-squares fits for each of the independent data sets. For example, if the calculation is for two different transitions, i.e., A-X, B-X, and, as in Eq (1), five constants are to be calculated then $MM = 2*5 - 1 = 9$.

7. NM--the number of constants to be obtained in the merged least-squares fit.

8. XM(0:MM,0:NM)--the coefficient matrix which relates the redundant variables obtained from independent least-squares fits to the desired final set of variables. It controls the merging of the constants obtained in the separate least-squares fits to yield the merged weighted, correlated least-squares constants by the following formula:

$$\beta^M = (X^T \Theta I^{-1} X)^{-1} X^T \Theta I^{-1} Y \quad (122)$$

For a problem involving five constants for each of two electronic transitions, the XM matrix would be of size 14x5 and contain the elements as follows:

		<u>State</u>								Merged Constant
		<u>A</u>			<u>B</u>			<u>X</u>		
		Te	Y ₁₀ '	Y ₂₀ '	Te	Y ₁₀ '	Y ₂₀ '	Y ₁₀ ''	Y ₂₀ ''	
XM =	Te	1	0	0	0	0	0	0	0	Elements Pertaining to AX Transitions Elements Pertaining to B-X Transitions
	Y ₁₀ '	0	1	0	0	0	0	0	0	
	Y ₂₀ '	0	0	1	0	0	0	0	0	
	Y ₁₀ ''	0	0	0	0	0	0	1	0	
	Y ₂₀ ''	0	0	0	0	0	0	0	1	
	Te	0	0	0	1	0	0	0	0	
	Y ₁₀ '	0	0	0	0	1	0	0	0	
	Y ₂₀ '	0	0	0	0	0	1	0	0	
	Y ₁₀ ''	0	0	0	0	0	0	1	0	
	Y ₂₀ ''	0	0	0	0	0	0	0	1	
↓										
Constants from Independent Least-Squares Fit										

Fig A-1. Coefficient Matrix XM

9. THETAI(0:MM,0:MM)--this matrix is made by merging the variance-covariance matrices obtained from each of the independent least-squares fits. The details of its construction will be provided in the discussion of the subroutine MATEQ. The user must initially fill the matrix with zeros. The matrix has $(MM+1)^2$ elements. For example, if $MM=9$, then the statement, DATA THETAI (100*0D0) will initialize the matrix.

This concludes the data input required of the user. The only tasks remaining are the assembly of dimension statements and construction of statements in the main portion of the program to execute the least-squares and merging routines.

The sequence of statements required to perform a least-squares fit for each set of data are as follows:

```
CALL WAVNUM
CALL CONST
CALL MATEQ
CALL VECEQ
```

In the following section, the statement names and their arguments are listed along with a brief description of the routine.

WAVNUM(ANUX,Mx)

This subroutine converts data contained in the array ANUX(0:Mx) from angstroms to wavenumbers invacuo (cm^{-1}) by means of a correction for the index of refraction of air (Refs 7 and 21). ANUX is, as described above, an array of

the Mx experimental values for one group of data. NOTE: If ANUX is entered as wavenumbers, this statement is omitted.

CONST (ANUX,QV1x,QV2x,BETx,THETx,Xx,Xtx,XTXx,XTXXTx,XBx,
ANUXBx,CVRCx,Mx,N)

This routine does the work of obtaining minimum variance least-squares constants. It solves the matrix equation as outlined below:

$$v = X\beta + \epsilon \quad (124)$$

$$\beta = (X^T X)^{-1} X^T v \quad (125)$$

$$\sigma^2 = (v - X\beta)^T (v - X\beta) / fm \quad (126)$$

$$\theta = \sigma^2 (X^T X)^{-1} \quad (127)$$

The correspondence between the arguments for CONST and these equations are as follows including the dimensions required for the arrays: ANUX(0:Mx) = v

QV1x(0:Mx) and QV2x(0:Mx): These entries are the quantum mechanical vibration numbers which are for the upper (v') and lower (v'') states respectively, and are used to generate the Xx matrix as previously described.

Xx(0:Mx,0:N) = X: This matrix is generated by CONST in lines 18-28, as dictated by the user and by the model chosen to represent the data.

$XTx(0:N,0:Mx) = X^T$: This matrix is the transpose of matrix X and is generated by the subroutine TRNSPZ called from CONST.

$XTXx = \text{first}(X^T X)$, then $(X^T X)^{-1}$: This matrix is the product of X^T and X formed by the subroutine MATMLT. The matrix is then replaced by its inverse by the routine MATINV.

$XTXXTx(0;n,0:M) = (X^T X)^{-1} X^T$: This matrix is the product of the inverse of the first matrix times the transpose of the second.

$BETx(0:N) = (X^T X)^{-1} X^T v$: This column matrix (vector) contains the least-squares estimate of the constants in Eq (1). It is formed by multiplying the matrix $XTXXTx$ times the vector, v , using the routine MATVEC.

$XBx(0:Mx) = X\beta$: This column matrix is the product obtained from the subroutine VECVEC. It is the calculated estimate of the original experimental values based upon the constants obtained from the least-squares fit of the experimental data.

$ANUBx(0:Mx) = (v - X\beta)$: This column matrix (vector) contains the differences between the measured and calculated values of wavelength for a given data set. The calculation is performed by the routine VECSUB.

$VARINZ = \sigma^2 = (v - X\beta)^T (v - X\beta) / f_m$: VARINZ is a scalar and is the estimated variance of the least-squares fit.

The variance is given in the output of the program. f_m is the degree of freedom, $Mx - N$. VARINZ is calculated in the routine CONST.

$THETx(0:N,0:N) = \theta = \sigma^2 (X^T X)^{-1}$: THETx is the variance-covariance matrix for the calculated constants. Estimates of the variance for the constants are contained on the diagonal with off diagonal elements being the covariances. The matrix is obtained from the product of the scalar, σ^2 , and the matrix, $(X^T X)^{-1}$, using the routine SCAMAT.

$CVRCx(0:N,0:N)$: This matrix is generated by CVRCOR which is called from CONST. It contains three types of data.

1. Above its diagonal it contains the same covariances of the constants as in THETx.

2. The diagonal contains the estimate of the standard error of each of the constants.

3. The elements below the diagonal are the correlation coefficients associated with the constants. The coefficients are calculated by the following formula:

$$C = \theta_{ij} / (\theta_{ii} \theta_{jj})^{1/2} \quad (129)$$

where θ_{ij} are the elements of the matrix θ . Since the matrix is symmetric, the procedure of reporting variances for the top half and covariances for the bottom half is sufficient. The results are printed in the program output.

This completes the description of the arrays required for the least-squares fit of one group of data. If it is

necessary to perform a least-squares fit on several sets of data and merge them to obtain a correlated, weighted, least-squares estimate of the constants, then the MATEQ and VECEQ routines are used.

The merged least-squares calculation is based upon:

$$y = X\beta^M + \epsilon \quad (130)$$

where the known values obtained from the previous least-squares fits of the experimental data are the y and X matrices and

$$y = \begin{bmatrix} Te \\ Y'_{10} \\ Y'_{20} \\ Y''_{10} \\ Y''_{20} \\ Te \\ Y'_{10} \\ Y'_{20} \\ Y''_{10} \\ Y''_{20} \\ \text{etc.} \end{bmatrix} \quad (131)$$

and X is the XM matrix as defined in the input data section. It relates the redundant values of y to the corresponding members of β^M (Ref 3). β^M is the best estimate of the constants obtained from the formula

$$\beta^M = (X^T \theta I^{-1} X)^{-1} X^T \theta^{-1} y \quad (132)$$

where θI is of the form

$$\theta I = \begin{bmatrix} \theta_1 & 0 & 0 \\ 0 & \theta_2 & 0 \\ 0 & 0 & \theta_3 \end{bmatrix} \quad (133)$$

MATEQ(THETx, THETAI, N, N, MM, MM, x, x)

This routine inserts the variance-covariance matrices, the THETx's from each least-squares fit, into the matrix THETAI.

THETx(0:N, 0:N) : As previously defined.

THETAI(0:MM, 0:MM) = I : As previously defined.

The last two arguments for MATEQ, "x,x", determine where the smaller matrices are inserted into THETAI. The user must input these values (as integers). For the first group of data, "x,x" should be "0,0". If the number of constants determined in each of the separate least-squares fits is "N+1", then "x,x" for the second THETx inserted into THETAI is "2*(N+1), 2*(N+1)"; third, "3*(N+1), 3*(N+1)", etc. The end result is the placement of the THETx matrices into THETAI as depicted by Eq (133).

CALL VECEQ(BETx, YM, N, MM, x)

VECEQ performs a similar insertion of the constants BETx obtained in the separate least-squares fits into the

column matrix (vector) YM (y in Eqs (131) and (132)). The dimensions of these two parameters are BETx(0:N), and YM(0:MM).

The "x" value is again an integer and entered by the user. It corresponds to and is equal to the value used in the MATEQ statement. In this manner, the estimated constants and their variances are placed within the THETAI and YM matrices so their correspondence is retained in the merging calculations.

After the CALL WAVNUM through VECEQ statements have been executed for each of the separate groups of experimental data and the YM and THETAI matrices are loaded, the merging of the spectroscopic constants can be carried out. To accomplish this, the user must have constructed the XM matrix as previously described. Then the following statements will accomplish the merging:

```
IPV = 0
```

```
CALL MATINV
```

```
CALL MERCN
```

```
CALL MATINV (THETAI,MM,MM,IPV)
```

This routine inverts the THETAI matrix. The routine was obtained from the computer program by C. R. Vidal contained in Appendix B.

```
CALL MERCN (XM,THETAI,YM,XTM,XTHM,XTHMX,XTXXTH,BETAM,XBM,YXBM,  
YXTH,THETAM,CVRCM,MM,NM)
```

This routine performs the calculations outlined in Eq (132) to yield a set of merged least-squared constants. MERCN estimates by the following formula, the variance to be obtained using the merged constants:

$$\sigma_m^2 = (y - X\beta^M)^T \theta I^{-1} (y - X\beta^M) / f_m \quad (134)$$

It then calculates the variance-covariance matrix, θ^M , for the merged constants according to the following formula:

$$\theta^M = (X^T \theta I^{-1} X)^{-1} \quad (135)$$

Listed next are the arguments of MERCN and their correspondence to the equations presented in other sections of the report.

XM(0:MM,0:MM) = X : In Eqs (130), (132), (134), and (135).

THETAI(0:MM,0:MM) = θI : Eqs (133), (134), and (135).

YM(0:MM) = y : Eqs (130), (131), (132), and (134).

XTM(0:NM,0:MM) = X^T : Eqs (132) and (135).

XTHM(0:NM,0:MM) = $X^T \theta I$: Eqs (132) and (135).

XTHMX(0:NM,0:NM) = first $(X^T \theta I^{-1} X)$ then $(X^T \theta I^{-1} X)^{-1}$: Eqs (132) and (135).

XTXXTH(0:NM,0:MM) = $(X^T \theta I^{-1} X)^{-1} X^T \theta I^{-1}$: Eq (132).

BETAM(0:NM) = β^M : Eqs (130), (132), and (134).

XBM(0:MM) = $X\beta^M$: Eq (134).

YXBM(0:MM) = $y - X\beta^M$: Eq (134).

$$YXTH(0:MM) = (y - X\beta^M)^T \theta I^{-1} : \text{Eq (134)}.$$

$$THETAM(0:NM,0:NM) = \sigma^2 (X^T \theta I^{-1} X)^{-1} : \text{Eq (134)}.$$

This is the variance-covariance matrix for the merged constants.

CVRCM(0:NM,0:NM): CVRCM is the matrix containing the covariances, standard errors, and the correlation coefficients of the merged constants with the structure the same as described for the separate least-squares fits.

Calculations are performed in the subroutines CONST and MERCN using a group of matrix and vector manipulation routines (Ref 13).

The output of the program consists of the following for each separate set of data.

1. A listing of the experimental input values v , v' and v'' with the calculated value $X\beta$.
2. The variance of the fit.
3. The complete variance-covariance matrix.
4. The matrix containing the covariances, standard errors and correlation coefficients.
5. The constants for the upper and lower levels.

For the merged data, the merged constants, the variance of the fit and variance, covariance, standard errors, and correlation coefficients of the merged constants are printed.

```

1      PROGRAM DUNCO,
2
3      C      QUN319, QUN317, QUN324, 10 DEC 82
4      C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
5      C      DIMENSIONING STATEMENTS FOR SNYDER-GLESSNER SMALL H-X
6      C      LEAD-OXIDE DATA
7      C      DIMENSION ANUA(0:9),QVA1(0:9),QVA2(0:9)
8      C      DIMENSION AHETA(0:4),THETA(0:4,0:4),XA(0:9,0:4),XTA(0:4,0:9)
9      C      DIMENSION XTXXTA(0:4,0:9),XHA(0:9),XTXA(0:4,0:4),ANUXBA(0:9)
10     C      DIMENSION CVCA(0:4,0:4)
11     C      DIMENSION STATEMENTS FOR OLDENBERG, DICKSON, AND ZARE
12     C      DIMENSION ANUB(0:5),QVH1(0:5),QVH2(0:5)
13     C      DIMENSION ABETH(0:4),THETH(0:4,0:4),XRC(0:5,0:4),XTR(0:4,0:5)
14     C      DIMENSION XTXXTH(0:4,0:5),XBH(0:5),XTXB(0:4,0:4),ANUXBB(0:5)
15     C      DIMENSION CVCH(0:4,0:4)
16     C      DIMENSION STATEMENTS FOR DATA OF KURYLO, ET AL.
17     C      DIMENSION ANUC(0:15),QVC1(0:15),QVC2(0:15)
18     C      DIMENSION ABETC(0:4),THETC(0:4,0:4),XC(0:15,0:4),XTC(0:4,0:15)
19     C      DIMENSION XTXXTC(0:4,0:15),XBC(0:15),XTXC(0:4,0:4),ANUXBC(0:15)
20     C      DIMENSION CVCC(0:4,0:4)
21     C      ARRAYS FOR MERGING 3 SEPARATE FITS
22     C      DIMENSION XM(0:9,0:4),THETA(0:9,0:4),YM(0:9)
23     C      DIMENSION XTH(0:4,0:5),XTHM(0:4,0:9),XTHMX(0:4,0:4)
24     C      DIMENSION YXTH(0:4),THETAM(0:4,0:4),CVCH(0:4,0:4)
25     C      DIMENSION XTXXTH(0:4,0:9),BETAM(0:4),XBM(0:9),YXBM(0:9)
26     C      DATA FOR SNYDER-GLESSNER
27     C      DATA ANUA/5716.500,6406.500,7050.200,7476.900,6222.300,
28     C      +541.900,7621.300,2036.300,352.700,5031.400/
29     C      DATA QVA1/300.300,400.000,300.900,100.100,300.100/
30     C      DATA QVA2/600.400,800.400,200.700,500.600,300.100/
31     C      DATA FOR OLDENBERG
32     C      AND
33     C      DATA FOR KURYLO
34     C      DATA IN INVERSE CENTIMETERS
35     C      DATA ANUC/2164300,2120000,1551500,
36     C      +1721200,1710000,1703300,1691500,1677300,
37     C      +1661400,1647400,1643400,1629700,1621500,1577300,
38     C      +1562300,1536300/
39     C      DATA QVC1/1400,1300,700,400,700,200,500,300,
40     C      +100,400,700,1700,1400,1300,200,300/
41     C      DATA QVC2/100,100,100,100,300,000,200,100,000,
42     C      +200,400,1100,900,900,200,300/
43     C      INITIALIZING MERGING MATRICES
44     C      DATA XM/100,4400,100,5000,
45     C      +100,4400,100,5000,
46     C      +100,4400,100,5000,
47     C      +100,4400,100,5000,
48     C      DATA THETA/100,000/
49
50
51     N=4
52     NA=9
53     NB=5
54     NC=15
55     NM=5
56
57     M=4
58     C      CALCULATION OF CONSTANTS FOR SNYDEPS DATA
59     C      CALL MATHUM(ANUA,NA)
60     C      CALL CONST (ANUA,QVA1,QVA2,AHETA,THETA,XA,XTA,XTHA,XTXXTA,
61     C      +XHA,ANUXHA,CVCA,NA,1)
62     C      CALL MATHQ(THETA,THETA1,NA,MM,MM,0.1)
63     C      CALL VECEQ(AHETA,YM,NA,MM,0)
64     C      CALCULATION OF CONSTANTS FOR KURYLOS DATA
65     C      CALL CONST(ANUC,QVC1,QVC2,ABETC,THETC,XC,XTC,XTXC,XTXXTC,
66     C      +XRC,ANUXRC,CVCC,NC,1)
67     C      CALL MATHM(THETC,THETA1,NA,N,MM,MM,5.5)
68     C      CALL VECEQ(ABETC,YM,N,MM,5)
69     C      IPV=1
70     C      CALL MATHM(THETA1,MM,MM,IPV)
71     C      CALL MERCH(XM,THETA1,YM,XTH,XTHM,XTHMX,XTXXTH,
72     C      +BETAM,XBM,YXBM,YXTH,THETAM,CVCH,MM,NM)
73     C      END

```

```

1      SUBROUTINE MATINV(A,N,IPV)
2      C      REFERENCES: OBTAINED FROM PROGRAM PREPARED BY C.R. VIDAL
3      C      MATRIX INVERSION
4      C      IPV.EQ.1: NO SEARCH FOR PIVOT.  IPV.NE.1: SEARCH FOR PIVOT
5      C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
6      C      DIMENSION IPIVOT(1:63),INDEXR(1:63),INDEXC(1:63)
7      C      DIMENSION A(1:N,1:N)
8      C      .....INITIALIZATION
9      C
10     DO 20 J=0,N
11     20  IPIVOT(J) = 1
12     DO 500 I=0,N
13     IF (IPV.NE.1) GO TO 40
14     ICLM=I
15     GO TO 260
16     C      .....SEARCH FOR PIVOT ELEMENT
17     40  AMAX=0.D
18     DO 105 J=0,N
19     IF (IPIVOT(J).EQ.1) GO TO 105
20     C      FOR UNSYMMETRIC MATRIX: A(I,J).NE.A(J,I)
21     DO 100 K=0,N
22     C      FOR SYMMETRIC MATRIX: A(I,J).EQ.A(J,I)
23     C      DO K=J,N
24     IF (IPIVOT(K).EQ.1) GO TO 100
25     IF (ABS(AMAX).GE.ABS(A(J,K))) GO TO 100
26     IROW=J
27     ICLM=K
28     AMAX=A(J,K)
29     100  CONTINUE
30     105  CONTINUE
31     IPIVOT(ICLM)=IPIVOT(ICLM) + 1
32     INDEXR(I) = IROW
33     INDEXC(I) = ICLM
34     C      .....INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
35     IF (IROW.EQ.ICLM) GO TO 260
36     C
37     DO 200 L=0,N
38     SWAP = A(IROW,L)
39     A(IROW,L)=A(ICLM,L)
40     A(ICLM,L) = SWAP
41     C
42     C
43     C
44     C
45     C
46     200  PIVOT = A(ICLM,ICLM)
47     IF (N.GT.10) GO TO 330
48     C
49     C      .....DIVIDE PIVOT ROW BY PIVOT ELEMENT
50     310  A(ICLM,ICLM) = 1.D
51     DO 320 L = 0,N
52     320  A(ICLM,L)=A(ICLM,L)/PIVOT
53     C
54     C
55     C

```

```

56      C .....REDUCE NON-PIVOT ROWS
57      300 DO 550 L1 = 0,N
58          IF (L1.EQ.ICLM) GO TO 550
59          T = A(L1,ICLM)
60          A(L1,ICLM) = 0.
61          DO 450 L = 0,N
62      450  A(L1,L) = A(L1,L) - A(ICLM,L)*T
63      .
64      .
65      .
66      550 CONTINUE
67      IF (IPV.EQ.1) RETURN
68      C .....INTERCHANGE COLUMNS
69      DO 710 I = 0,N
70          L = I-I
71          IROW = INDEXP(L)
72          ICLM = INDEXC(L)
73          IF (IROW.EQ.ICLM) GO TO 710
74          DO 705 K = 0,N
75      705  SWAP=A(K,IROW)
76      .
77          A(K,IROW) = A(K,ICLM)
78      705  A(K,ICLM) = SWAP
79      710 CONTINUE
80      RETURN
81      END

```

SUBROUTINE MATMLT 74/74 OPT=0, FOUNDE= A/ S/ M/-0,-0 FTM 5.1+554
 DB=-LONG/-CT,APG=-COMMON/-FIXED,CS= USER/-FIXED,DB= TB/ SH/ SL/ EP/-ID/ PMO/-ST,PL
 FTM5,DB. J000.50

```

1      C   THE FOLLOWING ROUTINES PERFORM STANDARD MATRIX OPERATIONS
2      C   AND VECTOR OPERATIONS
3      *
4      *
5      SUBROUTINE MATMLT(A,U,T,M,N,P)
6      IMPLICIT DOUBLE PRECISION (A-M,O-Z)
7      DIMENSION A(0:M,0:N),U(0:N,0:P),T(0:M,0:P),R(0:M,0:N)
8      DIMENSION D(0:P1,0:P2)
9      DIMENSION X(0:N),Y(0:N),Z(0:M),V(0:N,0:M),Z1(0:N)
10     INTEGER I,J,M,N,C,P
11     INTEGER P1,P2
12     *
13     DO 1 I=0,M
14     DO 1 J=0,P
15       1   T(I,J)=0D+0
16     DO 2 I=0,M
17     DO 2 J=0,P
18     DO 2 K=0,N
19     *
20     2   T(I,J)= A(I,K)*U(K,J) + T(I,J)
21     RETURN
22     *
23     ENTRY VEC SUB(X,Y,Z1,N)
24     C   THIS ROUTINE SUBTRACTS TWO VECTORS
25     DO 3 I=0,N
26     Z1(I)=X(I)-Y(I)
27     CONTINUE
28     RETURN
29     *
30     ENTRY MATVEC (A,X,Z,M,N)
31     *THIS ROUTINE MULTIPLIES A MATRIX TIMES A VECTOR YEILDING A VECTOR
32     DO 5 I=0,M
33     Z(I)=0D+0
34     DO 6 I=0,M
35     DO 6 J=0,N
36     6   Z(I)=A(I,J)*X(J) + Z(I)
37     RETURN
38     *
39     ENTRY SCAVEC (S,X,Y,N)
40     * THIS ROUTINE MULTIPLIES A SCALAR TIMES A VECTOR TO YEILD A VECTOR.
41     DO 7 I=0,N
42     Y(I)=S*X(I)
43     RETURN
44     *
45     ENTRY SCMAT (S,A,B,M,N)
46     * ROUTINE MULTIPLIES A SCALAR TIMES A MATRIX
47     DO 8 I=0,M
48     DO 8 J=0,N
49     B(I,J)=S*A(I,J)
50     RETURN
51     *
52     ENTRY VECVEC (X,Y,S,N)
53     * THIS ROUTINE MULTIPLIES TWO VECTORS TOGETHER YEILDING A SCALAR
54     S=0D+0
55     DO 9 I=0,N

```

```

54      S= S + X(I)*Y(I)
55      RETURN
56
57      ENTRY VECMAT (Z,A,X,M,N)
58      C THIS ROUTINE MULTIPLIES A VECTOR TIMES A MATRIX TO YIELD A VECTOR
59      DO 10 J=0,N
60      X(J)= 0.0
61      DO 10 K=0,M
62      X(J)=X(J) + Z(K)*A(K,J)
63      RETURN
64
65      ENTRY TRASPZ (A,V,M,N)
66      C THIS ROUTINE TRANSPOSES A MATRIX
67      DO 14 I=0,M
68      DO 14 J=0,N
69      V(J,I)=A(I,J)
70      RETURN
71
72      ENTRY CURCOR(A,T,M,N,P)
73      C THIS ROUTINE CREATES A MATRIX FOR PRINT OUT OF
74      C STANDARD ERRORS, COVARIANCES, AND CORRELATION COEFFICIENTS OF
75      C THE "CUMULAN COEFFICIENTS".
76
77      DO 15 I=0,M
78      DO 15 J=0,M
79      IF (I.LT.J) THEN
80      C(I,J)=A(I,J)
81      ELSE IF (I.EQ.J) THEN
82      C(I,J)=DSQRT(A(I,J))
83      ELSE IF (I.GT.J) THEN
84      C(I,J)=A(I,J)/(DSQRT(A(I,I))*DSQRT(A(J,J)))
85      END IF
86      CONTINUE
87      RETURN
88
89      ENTRY WAVNUM(X,N)
90      C THIS ROUTINE CONVERTS WAVELENGTHS IN ANGSTROMS TO
91      C WAVE NUMBERS (INVERSE CENTIMETERS).
92      C WITH CORRECTION FOR INDEX OF REFRACTION OF AIR
93      C REFERENCE: S.T. BIRGE, PHYSICAL REVIEW, VOL. 60, 766-785(1941).
94      DO 16 I=0,N
95      WL = X(I)/1000.000
96      XREF = 272.5*100 + 1.545300/WL**200 + 0.021600/WL**400
97      XREF = 100 + XREF/106
98      X(I) = 105/(WL*XREF)
99      RETURN
100
101      ENTRY MATEO(A,C,M,N,P1,P2,K1,K2)
102      C THIS ROUTINE TRANSFERS MATRIX A(M,N) INTO MATRIX C
103      C STARTING AT POSITION X(K1,K2)
104      P2=K1+M
105      K2=K2+N
106      DO 17 I=K1,K2
107      DO 17 J=K2,N+1
108      C(I,J)=A(I-K1,J-K2)
109      CONTINUE
110      CONTINUE
111      RETURN
112
113      ENTRY VECEQ(X,Z,N,M,P1)
114      C THIS ROUTINE TRANSFERS MATRIX X(N) INTO VECTOR Z(M)
115      C STARTING AT POSITION Z(P1)
116      M2=I,P1
117      DO 18 I=P1,N+1
118      Z(I)=X(I2)
119      CONTINUE
120      RETURN
121      END

```

SUBROUTINE CACT 74/74 OPT=0,ROUND= A/ S/ M/-D,-DS FTH 5.1+554
 DO=-LONG/-LT,AFGE=COMMON/-FIXED,CS= USER/-FIXED,DB= TB/ SB/ SL/ E/-ID/ P40/-ST,1
 FTNS,DR. J00039

```

1      SUBROUTINE CACT(ANU,QV1,QV2,RETA,THETA,X,XT
2      *,XTX,XTXT,XH,ANUXB,CVRC,M,N)
3      C      THIS ROUTINE PERFORMS THE ACTUAL CALCULATION OF THE
4      C      "DUNHAM MOLECULAR CONSTANTS."
5      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
6      DIMENSION ANU(0:M),QV1(0:M),QV2(0:M)
7      DIMENSION RETA(0:M),THETA(0:M,0:M)
8      DIMENSION X(0:M,0:M),XC(0:M,0:M),XTX(0:M,0:M),XTXT(0:M,0:M)
9      DIMENSION XH(0:M),ANUXB(0:M),CVRC(0:M,0:M)
10     DOUBLE PRECISION L1
11     N2=N/2
12     N3=N2+1
13     C      THIS SECTION CALCULATES THE X MATRIX WHICH IS MADE UP
14     C      OF THE VIBRATIONAL AND/OR ROTATIONAL QUANTUM NUMBERS
15     C      WITH "V+1/2" AND "J*(J+1)" RAISED TO POWERS MAKING UP
16     C      THE X(I,J) TERMS.
17     *
18     DO 2001 I = 0,N
19     DO 2000 L = 0,N2
20     L1=L
21     L2 = L + 1/2 + 1
22     X(I,L1)=(QV1(I)+0.500)**L1
23     CONTINUE
24     DO 2002 L=N3,N
25     L1=L-N2
26     X(I,L2)=-(QV2(I)+0.500)**L1
27     CONTINUE
28     2001 CONTINUE
29     C      CALCULATION OF CONSTANTS
30     CALL TRNSFZ(X,XT,M,N)
31     CALL MATMLT(XT,X,XTX,N,M,N)
32     IPV=0
33     CALL MATINV(XTX,N,N,IPV)
34     CALL MATMLT(XTX,XT,XTXT,N,N,M)
35     CALL MATVEC(XTXT,ANU,RETA,N,M)
36     C      CALCULATION OF VARIANCE OF ENERGY LEVEL. OF IS DEGREES
37     C      OF FREEDOM.
38     DF=1.00+0.70HLE(M-N)
39     CALL MATVEC(X,RETA,XH,M,N)
40     CALL VECSUB(ANU,XH,ANUXB,M)
41     PRINT*,* QV1 QV2 OBSERVED
42     DO 996 I=0,M
43     PRINT 55 ,QV1(I),QV2(I),ANU(I),XH(I)
44     999 FORMAT (2X,F3.0,2X,F3.0,2X,F19.7,2X,F19.7)
45     996 CONTINUE
46     CALL VECVEC(ANUXB,ANUXB,STEMP,M,M)
47     VARINZ=STEMP*DF
48     PRINT*,* *,* VARIANCE *,VARINZ
49     PRINT*,* *,* VARIANCE COVARIANCE MATRIX ELEMENTS*
50     CALL SCAMAT(VARINZ,XTX,THETA,N,N)
51     DO 123 I=0,N
52     DO 123 J=0,N
53     PRINT*,* *,J,THETA(I,J)
54     123 CONTINUE
55     C

```

SUBROUTINE CONS

74/74 CP7ED, POUND= A/ 5/ M/-D,-DS

FTL 5.1+554

```

54      C      THIS SECTION PLACES THE COVARIANCES ABOVE THE DIAGONAL
55      C      OF THE MATRIX "CVRC." IT PLACES THE STANDARD ERROR
56      C      FOR THE CONSTANTS ON THE DIAGONAL. ITS CALCULATES THE
57      C      CORRELATION COEFFICIENTS AND PLACES THEM BELOW THE DIAGONAL.
58      C      CALL CVRCCR(THETA,CVRC,P,N)
59      C      PRINT *, "STANDARD ERROR(I=J), CORRELCOFF(I>J), COVARIANCE(I<J)"
60      DO 615 I=0,N
61      DO 614 J=0,N
62      614 PRINT *, " ", I, J, CVRC(I, J)
63      615 CONTINUE
64      C      PRINT OUT THE CONSTANTS FOR THE TWO ELECTRONIC STATES
65      C      PRINT *, " "
66      PRINT *, " ", "VIBRATIONAL CONSTANTS FOR UPPER LEVEL"
67      DO 2010 I=0,N-2
68      2010 PRINT *, " ", I, BETA(I)
69      PRINT *, " "
70      PRINT *, " ", "VIBRATIONAL CONSTANTS FOR LOWER STATE"
71      DO 2020 I=0,N-1
72      2020 PRINT *, " ", I, BETA(I)
73      PRINT *, " "
74      PRINT *, " "
75      END

```

SUBROUTINE MERCH 74/74 OPTED, ROUNDED A/ S/ M/-D, -DC FTX 5.1564
 DO=-LONG/-CT, ARG=-COMMON/-FIXED, CSE= USER/-FIXED, DB= TH/ SB/ SL/ FR/-ID/ PWD/-S*, PL=
 FTX5, DB. 100010

```

1      SUBROUTINE MERCH(XM, THETA1, YM, XTH, XTHM, XTHMX, XTXXTH,
2      *RETAM, XBM, YXBM, YXTH, THETAM, CVPCM, M, N)
3      C      THIS ROUTINE MERGES RESULTS TO OBTAIN A BEST ESTIMATE
4      C      OF THE SPECTROGRAPHIC CONSTANTS
5      C      IMPLICIT DOUBLE PRECISION (A-H, Q-Z)
6      DIMENSION XM(0:M, 0:N), THETA1(0:M, 0:N), YM(0:M)
7      DIMENSION XTH(0:N, 0:M), XTHM(0:N, 0:M), XTHMX(0:N, 0:M), XTXXTH(0:N, 0:M)
8      *
9      DIMENSION BETAM(0:N), XBM(0:M), YXTH(0:M), THETAM(0:N, 0:N)
10     DIMENSION YXBM(0:M)
11     DIMENSION CVPCM(0:N, 0:N)
12     C      CALCULATE DEGREES OF FREEDOM AND DIVIDE INTO 1
13     DF=100/(M-1)
14     C      CALCULATE MERGED CONSTANTS
15     CALL TRNSFZ(XP, XTH, M, N)
16     CALL MATMLT(XTH, THETA1, XTHM, N, M, M)
17     CALL MATMLT(XTHM, XM, XTHMX, N, M, M)
18     IPV=0
19     CALL MATINVT(XTHMX, N, N, IPV)
20     CALL MATMLT(XTHMX, XTHM, XTXXTH, N, N, M)
21     CALL MATVEC(XTXXTH, YM, BETAM, N, M)
22     PRINT*, 'Merged constants'
23     DO 2500 I=0, N
24     2500 PRINT*, 'I, BETAM(I)'
25     C      CALCULATE ESTIMATED VARIANCE OF MERGED FIT
26     CALL MATVEC(XM, THETAM, XBM, M, N)
27     CALL VECSTH(YM, XBM, YXBM, M)
28     CALL VECMAT(YXBM, THETA1, YXTH, M, M)
29     CALL VECVEC(YXTH, YXBM, TEMP, M)
30     VARH=DF*TEMP
31     PRINT*, 'ESTIMATED VARIANCE OF MERGED FIT'
32     PRINT*, 'VARH'
33     C      CALCULATE VARIANCE-COVARIANCE MATRIX
34     CALL SCAMAT(VARM, XTHMX, THETAM, N, N)
35     PRINT*, 'VARIANCE-COVARIANCE MATRIX'
36     DO 2510 I=0, N
37     DO 2520 J=0, N
38     2520 PRINT*, 'I, J, THETAM(I, J)'
39     2510 CONTINUE
40     C      CALCULATE MATRIX CONTAINING STANDARD ERRORS, COVARIANCES,
41     C      AND CORRELATION COEFFICIENTS.
42     PRINT*, 'STANDARD ERROR(I, J), COVARIANCE(I, J), CORRELATION'
43     PRINT*, 'COEFFICIENTS(I, J)'
44     CALL CVRCOR(THETAM, CVPCM, N, N, N)
45     DO 2530 I=0, N
46     DO 2540 J=0, N
47     2540 PRINT*, 'I, J, CVPCM(I, J)'
48     2530 CONTINUE
49     END

```

QV1	QV2	OBSERVED	CALCULATED
3.	0.	17460.4535277	17427.5335259
3.	4.	14687.8345667	14682.6419301
8.	4.	14180.1271055	14175.5752521
0.	4.	13367.3042301	13367.6583264
3.	2.	16766.0475222	16372.9523207
9.	7.	15281.9124564	15287.3239519
1.	5.	13117.5451259	13118.5212743
1.	6.	12440.1452036	12437.5603409
3.	8.	11964.9138577	11771.2336055
		13077.7755115	13220.1576109

VARIANCE 27.151-53047332.6595945146-6
 VARIANCE COVARIANCE MATRIX ELEMENTS
 0 1 10.94377354765 41250353510.
 0 1 -24.823005275304619886537406
 0 2 1.4554406327130195362941617
 0 3 29.72831467202226536150594
 0 4 -3.03942206996610594556146726
 1 0 -24.823005275304619886537406
 1 1 4.55501144214124147-50547072
 1 2 -5.93722950795163151594637059
 1 3 -5.33970877953061435484753739
 1 4 .590342278664380529499535251
 2 0 1.4554406327130195362941615
 2 1 -6.93722950795163151594637059
 2 2 .057672348522568070895234-11
 2 3 .342319216616244845298540695
 2 4 -.0423319804895164476142194149
 3 0 29.728314672022265361505985
 3 1 -5.33970877953061435484753745
 3 2 .342319216616244845298540701
 3 3 10.8103680779663898694347119
 3 4 -1.12878957131627880276969448
 4 0 -3.03942206996610594556146727
 4 1 .590342278664380529499535254
 4 2 -.0423019804895164476142194155
 4 3 -1.12878957131627880276969448
 4 4 .122137633221571353-67305532
 STANDARD ERROR(I=J), CORRELCOEF(I>J), COVARIANCE(I<J)
 0 0 10.34136250524647603521 1765
 0 1 -24.823005275304619886537406
 0 2 1.4554406327130195362941617
 0 3 29.728314672022265361505984
 0 4 -3.03942206996610594556146726
 1 0 -.815910954530275794487410141
 1 1 2.94194014938123477429646276
 1 2 -5.93722950795163151594637059
 1 3 -5.33970877953061435484753739
 1 4 .590342278664380529499535251
 2 0 .747127709011346315065481603
 2 1 -.981902610730813605940460774
 2 2 .249150679474901355242424536
 2 3 .342319216616244845298590695
 2 4 -.0423019804895164476142194149
 3 0 .874323771734515617085590476
 3 1 -.552031034636677914637007376
 3 2 .494196469797379890867983241
 3 3 3.29791241944651072674435463
 3 4 -1.12878957131627880276969448
 4 0 -.440985278667382339124252159
 4 1 .574176214296088263911799752
 4 2 -.504024737192267731212117987
 4 3 -.982353713159175053120706129
 4 4 .349482035620675435408365922

1
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 0 16312.026857255934565462443
 1 436.758636992113042914614P53
 2 .342474361766086446615621136

0
 VIBRATIONAL CONSTANTS FOR LOWER STATE
 3 716.16716167627412431577451
 4 -2.95885234656566905415542633

QV1	QV2	OBSERVED	CALCULATED
14.	1.	21643.000000	21645.509775

7.	1.	14515.0000000	15517.1503100
4.	1.	17212.0000000	17159.6506564
7.	3.	17107.0000000	17114.7119709
2.	0.	17033.0000000	17041.7052010
5.	2.	16515.0000000	16532.2802129
3.	1.	16773.0000000	16763.6231663
1.	0.	16614.0000000	16608.7402350
4.	2.	1644.0000000	16454.6631321
7.	4.	16434.0000000	16424.8376563
17.	11.	16277.0000000	16300.2472034
14.	9.	16215.0000000	16217.5145372
13.	9.	15773.0000000	15765.9517442
2.	2.	15623.0000000	15624.0777412
3.	3.	15363.0000000	15361.1448271

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VARIANCE COVARIANCE MATRIX ELEMENTS

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0 4	.125530805840288421747521572	
1 0	-14.3193687032877357317447143	
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1 3	13.0926491601496321953140174	
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2 4	.0799805775413012916145822767
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3 4	-2.2876362343280972966800286
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VIBRATIONAL CONSTANTS FOR LOWER STATE
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MERGED CONSTANTS
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3 721.406462578490950565385459
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0 4 -3.10748812164627308613720658
1 0 -14.8847784025539974174710745
1 1 6.08785529072724516123847419
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1 3 .931640599155044541753524962
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2 3 -.185417894407544335325907409
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4 0 -3.10748812164627308613720658
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4 2 .02312710472257424115737883-1
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STANDARD ERROR (I=J), COVARIANCE (I<J), CORRELATION
COEFFICIENTS (I>J)
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```

Appendix B

RKR-IPA Program

The following section contains the RKR-IPA program as provided by C. R. Vidal.

Presented first is a written description of the program and instructions on the use of the program. Next, the original introductory comments by C. R. Vidal on the use of the program are presented.

Then a complete listing of the program and a sample output is presented.

Program Main (RKR-IPA Control)

Presented in the following section is a discussion of the RKR-IPA program provided by C. R. Vidal (Ref 41). The program MAIN contains a routine to perform RKR calculations and a routine to perform IPA calculations starting with the potential obtained from the RKR program. The program was originally written in Fortran IV to run on a CRAY-1 computer at the Max-Planck Institut fur Extraterrestrische Physik, Garching, Germany. It has been modified slightly to run on the CDC 6600 computer at the Air Force Institute of Technology, Wright-Patterson AFB, Ohio. The program, as presented in this appendix, is written in Fortran V. Comments provided by Vidal at the front of his program are included. PUNCH statements included by Vidal have been changed to comment cards. Many of the formatting statements have been changed from Hollerith editing to apostrophe editing formats.

Due to memory size constraints, 370 K octal, several arrays were reduced in size. Arrays now sized (2403) were originally sized (3601) in Vidal's program. Arrays sized (11,2403) were originally (24,3601) in size.

As sized, the program required a field length of 211,600 octal to run. A core memory size of 360 K was used. Maximum run times used for the RKR routine were less than 20 seconds. This involved the calculation of turning points (RMIN, RMAX) for 128 different energy levels.

Run time for the combined RKR-IPA routine ranged from 160 seconds for the calculation of parameters covering the following ranges:

v, vibrational quantum energy levels; v = 0 to 69

J, rotational quantum energy levels; J = 1

Iterations of IPA routine; n = 4

Array sizes; 1001 of 2403 maximum

to a maximum run time of 1150 seconds for:

v = 0 to 70

J = 2,6,10,14,17,20,21,23,28,30

n = 4

Array sizes; 1001 of 2403 maximum

One change has been made in the logic of Vidal's program. In the function subroutine FUNC, line 37, the third line after statement label 70, was changed from:

IF (XX.GT.RAA) RETURN

to

IF (KK.EQ.1) RETURN

The consequences of and reasons for suggesting this change are presented in the discussion of FUNC.

The discussion of Vidal's program is divided into two subsections: first, the discussion of the RKR portions of his program and, then, a discussion of the IPA portion. Within each section, the discussion is started with the inputs required of the user. Then the logic of the program is

traced with explanations of the calculations and the sub-routines used.

Numerical RKR Calculations

This section starts with the inputs required to perform the RKR calculations. The card number, the name of the input and the format of the input is given. The word CARD is used if only one card is required. CARDSET is used if more than one card (line of data) may be required.

CARD 1

NAME: ITEST

FORMAT: Integer.

ITEST should be placed in column 1. If ITEST = 0, the program stops. If ITEST = 1, the program is executed.

CARD 2 and 3

NAME: IHEAD

FORMAT: Lines 1-72 of these two cards.

These two cards contain the title to be printed at the top of the output. Relevant information that is suggested for the title includes the name of the molecule with the isotopes involved, the electronic state for which the calculations is performed, date, etc.

CARD 4

NAME: IIMS, ZMAS1, ZMAS2, ICODE

FORMAT: I4,2D16.9,32X,A4

IIMS must be 1 if the masses of the atoms are expressed in AMU's based upon the Carbon-12 scale and 2 if they are based upon the Oxygen-16 scale. ZMAS1 and ZMAS2 are the masses of the two atoms expressed in atomic mass units (AMU). The reduced mass of the two atoms may be entered in place of ZMAS1. If the reduced mass is used, ZMAS2 is left blank.

ICODE is the alphanumeric code used to describe the electronic state under investigation.

CARD 5

NAME: NDUN, JM(1), JM(2)...JM(NDUN)

FORMAT: 14I5

NDUN and JM specify the number of Dunham coefficients YDH and the order in which they will be read into the program.

CARDSET 6

NAME: YDH(1,1), YDH(2,1)...YDH(JM(2),1)

YDH(1,2), YDH(2,2)...YDH(JM(2),2)

.
.
.
YDH(1,NDUN), YDH(2,NDUN)...

YDN(JM(NDUN),NDUN)

FORMAT: 4D18.9

These cards contain the Dunham coefficients required as input for the RKR routine. The READ statement is structured so that JM(I) values of YDH(JM(I),I) are read in for each value of I with I ranging from 1 through NDUN. For each new value of I, the 1 through JM(I) values of YDH should be started on a new card. This means that the JM(1) coefficients Y(1,n) are read in, then the JM(2) YDH(2,n) coefficients, etc.

CARD 7

NAME: DE, TE

FORMAT: 2D15.8

DE is the dissociation energy and TE is the electronic term energy of the electronic state. Both are expressed in reciprocal centimeters. DE is the difference between the minimum in the potential of the electronic state and the dissociation energy. TE is

the energy separation between the minimum of the potential curve and the minimum potential on the ground state of the molecule. If the ground state is being investigated, TE is omitted.

CARD 8

NAME: VFIN, VINC

FORMAT: 2F6.2

VFIN is the largest vibrational quantum number, v , for which the RKR routine calculates the classical turning points r minimum (RMIN) and r maximum (RMAX). The turning points are calculated starting with value of $v = -0.25$ and for each value of v from 0 to VFIN in increments of VINC. It is not necessary that either VINC or VFIN be whole numbers. That is, both may be decimal fractions. The quantity VFIN/VINC must not exceed 398.

CARD 9

NAME: IOPG

FORMAT: I1

IOPFG is the Klein action integral. "I" (see Eqs (32) and (81)), print switch.

All iterations are printed if IOPFG=1.

If IOPFG=0, these values are not printed.

CARD 10

NAME: RLIM1, RLIM2, NEXT

FORMAT: 2F6.2,I2

FLIM1 and FLIM2 are the inner and outer limits of r , respectively to which the RKR curve will be extended. The curves will be extended by fitting formulas to points making the inner and outer portions of the curves plus any extra radius-potential energy pairs input as data to guide this fit. FLIM1 and RLIM2 also determine the range over which the final IPA curve will be expressed. RLIM1 and RLIM2 should be sized to contain any inner and outer radii generated by the RKR and IPA programs.

NEXT is the number of extra data points which will be used to guide the extension of the curve. NEXT must be less than 25 and may be 0 if no extra data points are to be added.

These data points must be obtained in one manner or another. The program does not

specify how. But if these points are available, this card makes provision for entering them into the program.

CARDSET 11

NAME: $R_1(I), PE_1(I)$, where $I = 1$ to NEXT

FORMAT: (4X,1PD16.9,7X,D16.9/)

If NEXT = 0, these cards are omitted.

$R_1(I)$ and $PE_1(I)$ are the radius and potential energy pairs which will be used to guide the extension of the RKR curve which will be adjusted by the IPA program.

$R_1(I)$ should be in angstroms. $PE_1(I)$ should be in reciprocal centimeters.

These NEXT points, along with a given number of points from the inner and outer ends of the RKR curve, will be used to obtain a fit to formulas as described below to extend the original RKR curve to the RLIM1 and RLIM2 limits.

CARD 12

NAME: $KFIT(1), KFIT(2), KOUT(1), KOUT(2),$
 $KOUT(3), KOUT(4)$

FORMAT: 6I5

$KFIT(1)$ is the number of constants (A_n) used in fitting a formula to the inner

portion of the RKR curves. The formula is of the form:

$$V(r) = 10^{A_1 + A_2 * X + A_3 * X^2 \dots} \quad (136)$$

where

$$x = \frac{r_e - r}{r_e}$$

KFIT(1)+2 is the number of data points taken from the inner portion of the RKR potential. These points, along with any extension data contained in CARDSET 11 for the inner portion of the curve, will be used to guide the extension of the curve to RLIM1. KFIT(2) is the number of constants (terms) used in the formula to extend the outer portion of the curve to RLIM2. The formula is of the form:

$$V(r) = A_1 \left(\frac{1}{r} \right)^{KOUT(1)} + A_2 \left(\frac{1}{r} \right)^{KOUT(2)} + A_3 \left(\frac{1}{r} \right)^{KOUT(3)} + \dots \quad (137)$$

KOUT(I), as shown above, is the power to which each 1/r term is raised.

KFIT(2)+4 of the outermost turning points of the original RKR potential plus any

outer turning points included in CARDSET
11 are used in extending the curve to
RLIIM2.

If CARD 12 is blank the default values for
KFIT(1) through KOUT(4) are "2,4,0,6,8,
and 10" respectively.

CARD 13

NAME: IPNRKR,IPNIPA

FORMAT: 2I2

These two values in Vidal's original program
controlled the punching of an output deck
for the RKR and IPA programs. As the
PUNCH statements have been changed to
comment cards, these two inputs should be
0 until the program in the appendix is
modified. In the original program, if
IPNRKR and IPNIPA equaled 1, the card
decks were punched.

CARD 14

NAME: LTEST

FORMAT: I1

If LTEST = 0, the IPA routine is skipped
and the program proceeds to read in the
next set of data starting with the quantity
ITEST. See CARD 1.

This completes the input required to run the RKR portion of the program. Input required for the IPA portion of the program will be presented with the discussion of the IPA calculations.

The following section discusses the functions of each of the major routines of the RKR program in the order which they are used. The headings used are the titles of the subroutines. Sections of the program which have a physical significance and are helpful in understanding the flow of the program are highlighted. Numerical techniques which perform the RKR calculations are discussed in more detail to aid the reader in understanding the technique. Calculations which are straightforward and not necessary to understanding the program are not described.

The line numbers in parenthesis refer to lines in the program in this appendix. In this development, program symbols corresponding to the mathematical symbols defined for the RKR calculation are given immediately following the mathematical symbols to which they correspond. The symbols are placed in brackets.

PROGRAM MAIN

PROGRAM MAIN acts as a controller directing the major objectives of the whole program, the calculation of an RKR curve and its adjustment by the IPA routine.

MAIN starts by insuring that mass units of the atoms are expressed in terms of the Carbon-12 system making conversions as directed by input data in IIMS (lines 12,23,24,28). The reduced mass, ZMU, is calculated in AMU's (line 27).

The Dunham constants, YDH, as specified by CARDSET 6, are read as a result of the statement CALL YDHP11 (line 30). The Dunham constant Y_{01} is assigned to "BE" the normal name of that spectroscopic constant as shown in Table I (line 31). Then using BE, the internuclear equilibrium distance, r_e , is calculated in angstroms according to the following formula:

$$r_e = \frac{FAC}{(BE)^{1/2}} = \left(\frac{h N_A}{4\pi c \mu Be} \right) \times 10^8 \quad (138)$$

Then Y_{00} is calculated according to Eq (6) (lines 35 and 36).

SUBROUTINE RKR

This routine is called from line 70 of PROGRAM MAIN.

First a calculation is performed to determine the number of $G(v)$ energy levels which will be evaluated in the RKR routine. This number is assigned to the variable "M" (lines 34-39). Then values of the vibrational quantum number, v , for the $G(v)$ energy levels are calculated (lines 44 and 45). In the program, the term "TEMP" corresponds to "v" and the term "U" to $G(V)$. The function POLY performs

the calculation of U [Gv] according to Eq (87) (line 46, statement label 110).

The program calculates, by an iterative technique, the value of " v_0 " corresponding to Eq (90) (lines 51-62). It uses the Newton-Raphson method to find the value of " v_0 " at which $Gv+Y=0$ (Eq 89)). The program uses " $v^* = Y_{00}/Y_{10}$ " as its first estimate of " v_0 " (line 55). From Eq (90), it can be determined that " v_0^* " is approximately "1/2" quantum units larger than the true value. Next, the value " $G(v_0^*)+Y_{00}$ " is calculated (line 56). The Newton-Raphson method is used to converge to the value of " v_0 " which satisfies " $G(v_0)+Y_{00}=0$ " (lines 57-62, between statement labels 120 and 130).

For illustrative purposes, the Newton-Raphson method may be formulated as:

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)} \quad (139)$$

By the definition of $f'(x)$:

$$f'(x) = \frac{f(x_1) - f(x_2)}{x_1 - x_2} \quad (140)$$

Hence:

$$x_2 = x_1 - f(x_1) \left[\frac{x_1 - x_2}{f(x_1) - f(x_2)} \right] \quad (141)$$

which corresponds directly to format of line 58. In Eq (141) $f(x)$ corresponds to " $G(v_0)+Y_{00}$ ". Loop 120 is repeated until a value of " v_0 " is obtained such that " $G(v_0)+Y_{00}$ " is close to 0 (line 57, statement label 120).

The remaining portion of the RKR routine, from statement label 130 to the end of the program, performs the integration required to solve Eqs (88) and (93) for "f" and "g". These, in turn, provide the classical turning points RMIN and RMAX of Eq (94). RMIN and RMAX values are obtained for each value of "v" [TEMP(I)] and corresponding "G(v)" [U(I)] as selected by inputs VFIN and VINC.

The solutions of the integrals for "f" and "g" contain a singularity. When " $G(v') = G(v)$ ", the denominator [DENQ] of Eqs (88) and (93) go to 0 (lines 82,83,102, and 110). This singularity handled by assigning an "artificial" upper limit "v" [BS] to the integrals which is smaller than the true upper limit of the integral, TEMP(I), for the energy level "G(v)" [U(I)] involved. The artificial upper limit, BS, is allowed to approach the true value of "v" [TEMP(I)] in increasingly smaller steps until the solution of the integrals for two consecutive values of BS meet certain criteria. As BS is changed, the dv [d(BS)] contribution to the integrals is calculated and added to the sum for the integrals of "f" and "g". The rate at which BS approaches TEMP(I) is calculated in lines 72 and 130.

The criteria used for determining whether the solutions to the integrals are close enough to their true solution are given in lines 120-124 (statement labels 250-260). FEG is the value of the integral "f" for a given value of BS_n (line 120). FEG2 is the value by which the integral for

"f" is increased for the new value of BS_{n+} . Thus, if the ratio of the change in the value of the integral (FEG2) to the previous value for the integral (FEG) is less than 0.5×10^{-7} , the accuracy to which "f" has been determined is considered to be satisfactory. GEG2 and GEG in line 121 are tested in the same manner. In line 122, a ratio of changes (FEG2/FEG1) in the value of the integral "f" (FEG) for two consecutive calculations greater than 0.9 indicates that the accuracy of the integration is reaching a limit and should be halted. First, a ratio greater than 0.9 could indicate that the convergence to the true value is slower than desirable. Second, stopping the integration at this point is justified if the FEG1, FEG2 values are small. It is assumed that they are small. Similar arguments are given for GEG2 and GEG1.

The RKR program contains two integration routines. For the first three adjustments of BS, the upper limit of integration for "f" and "g", a Simpson rule integration is used. Lines 77-92 perform the integration of the functions for "f" and "g" over a range from VMIN (v) to BS on the first cycle. On the second cycle, VMIN is equated to BS, the lower limit of integration and a new upper limit BS is established as previously explained. In line 77-92, UV corresponds first to the v' and then to the $(G(v)-G(v'))$ of Eqs (88) and (93). And, expressed in the notation of the computer program, EV is the $G(v')$ and BI is the $B(v')$ of Eqs (88) and (93).

For the fourth through the twentieth adjustments of BS, a Gaussian integration routine is used to provide a higher degree of accuracy. The routine is contained in lines 93-113 (from statement label 180 through label 240). The abscissas [XGAUS] and weight factors [AGAUS] are listed at the start of the RKR routine for a Gaussian integration of moments where $K=0$ and $N=4,6$, or 8 depending upon the success of the iteration. The formula for the integration is (Ref 1:931):

$$\int x^k f(x) dx \approx \sum_{i=1}^n w_i f(x_i) \quad (142)$$

Where

x_i = abscissas

w_i = weight factors

Finally, RMIN and RMAX for each v , [TEMP] and G_v , [U], are calculated in lines 139 and 140 per formula (95).

After all turning points have been calculated, control is transferred back to the program MAIN where CALL YDHP11(0) causes the input Dunham coefficients plus Y_{00} to be printed.

Routines EXTEND, GLSQ, FUNC, and EXTEND

The subroutine EXTEND, in conjunction with the above routines, performs a least-squares fit to the inner and outer portions of the RKR and extend them to RLIM1 and RLIM2 respectively. The fits are performed according to Eqs (117) and (118). Eq (117) expressed in the notation used in lines 16-31 of GLSQ and 31-39 of FUNC becomes:

$$\text{Log}_{10}U(I) = Z(I) = B_1[X(I)]^0 + B_2[X(I)]^1 + B_3[X(I)]^2 + \dots \quad (143)$$

$Z(1)$ is calculated in EXTEND and, as expressed, is the log to base ten of the energy. The inner turning radii, RMIN, are transferred into the $X(I)$ array, and then the function FUNC (called from line 18 of GLSQ) transforms the variable X to the form given in Eq (117), i.e.,:

$$X = \frac{r_e - r_{\min}}{r_e} \quad (144)$$

Expressing Eq (124) in the notation of GLSQ yields a matrix equation of the form:

$$\begin{bmatrix} n & \Sigma x_i & \Sigma x_i^2 & \Sigma x_i^3 \\ \Sigma x_i & \Sigma x_i^2 & \Sigma x_i^3 & \Sigma x_i^4 \\ \vdots & & \vdots & \\ \Sigma x_i^3 & & \Sigma x_i^6 & \end{bmatrix} \begin{matrix} B \\ B \\ \vdots \\ B \end{matrix} = \begin{matrix} Z \\ Z \\ \vdots \\ Z \end{matrix} \quad (145)$$

or

$$A(J,K) * B(J) = BB(J)$$

where $A(J,K)$ is formed in line 22 of GLSQ. $BB(J)$ is formed in line 20. In line 23, the routine MATINV solves Eq (126) by inverting $A(I,J)$, multiplying it times $BB(J)$ and returns the B vector in place of the BB vector. The operation performed by MATINV may be expressed as follows:

$$B(J) = A(J,K)^{-1} BB(J) \quad (146)$$

A similar pattern is followed for the outer portion of the curve except that formula (118) is used instead of (117).

After the fits have been performed, EXTEND calculates 20 additional points between the inner limit of the RKR curve and RLIM1, and 99 additional points between the outer end of the RKR curve and RLIM2. The points are calculated using fitting Eqs (117) and (118).

The change made in line 37 of FUNC affects the manner in which the curve fit is performed for values of r between the inner limit of the RKR curve and RLIM2. The difference occurs only if the extension data input in CARDSET 11 has an r , $[R1(I)]$, between RLIM1 and the inner limit of the RKR curve. When FUNC is called from GLSQ which, in turn, has been called from EXTEND with an argument of "1" (CALL GLSQ(1)), the inner turning points are to be fit according to Eq (117). As written in Vidal's original program, line 37, "IF (XX.GT.AAA) RETURN", permitted the routine to continue on to the next statement when extra extension data was added with a radius less than the inner limit of the RKR curve [RAA]. This resulted in the returning of the energy $[U(i)]$ of Eq (143) instead of the log of the energy, $[Z(I)]$. Then when the energy and the log of the energies are mixed in the fitting process, the fit is incorrect. By changing line 37 to "IF(KK.EQ.1) RETURN", the fit for the inner turning points is performed correctly. The variable "KK" is always "1" when the fit to

the inner portion of the RKR curve is performed (line 31 of EXTEND). This change does not affect the operation of the program when FUNC is called from other routines. When FUNC is called from line 56 of FIPA, "KK" is equal to "0". Hence, the radius [XX] is the controlling factor in lines 7 and 8 of FUNC. Then when the potential energy for the extension points are being calculated, the routine proceeds through line 37 as it should.

This concludes the discussion of the RKR calculations.

Subroutine FIPA

Control of the program is transferred from MAIN to FIPA by line 83. This routine controls the IPA portion of the program. In the following section, the inputs required to run the FIPA routine are described.

FIPA Input

CARD 14

NAME: LTEST

FORMAT: I1

This input description is repeated from the RKR section. If LTEST is not equal to "0", the IPA calculation is continued and an IPA data deck is required as described below.

CARD 15

NAME: NI,NS,IPSIQ,MAXITT,EPSC

FORMAT: 4I4,D10.0

If NI=1, data from each SCHR iteration is printed.

If NI=0, the iterations are not printed.

If NS=1, the wavenumbers are printed at every IPSIQ points.

If NS=0, the wavenumbers are not printed.

EPSC is the convergence criterion for the solution of the Schroedinger wave equation for its energy eigenvalues, E_{vJ} . An EPSC of 0.001 wavenumbers is suggested as a good starting value.

MAXITT is the maximum number of times SCHR will attempt to satisfy the convergence criterion.

CARD 16

NAME: RMIN, RMAX, M NRPTT, NPL, MCH, LSW

FORMAT: 2F10.0,5I5

RMIN and RMAX are the minimum and maximum values over which the potential is evaluated by the IPA procedure. M is the number of points at which the potential will be evaluated. The maximum M should be 2401, for the program as written in the appendix.

Memory size limitations may dictate that fewer points be calculated.

NRPTT is the number of iterations performed in the IPA routine. On the last iteration, the rotationless potentials are calculated to obtain G_v and B_v .

NPL is the number of terms in the Legendre polynomial used to represent the correction, ΔV , to the energy potential.

MCH is the control used to punch a deck of the G_v and B_v values. As stated, all PUNCH cards have been changed to comment cards. If PUNCH statements are reactivated and MCH=1, the decks will be punched. Note that PUNCH is not a legitimate Fortran V statement.

If LSW=0, the first and last iterations of the IPA program are printed.

If LSW=1, all iterations are printed.

CARDSET 17

NAME: (MTRMIN(I),MTRIAL(I),BJTT(I),I=1,11)

FORMAT: (6(I2,I3,F7.0)/5(I2,I3,F7.0))

MTRMIN and MTRIAL defines the range of vibrational quantum numbers, v , which are investigated in the Schroedinger calculations.

These variables are input as "v+1" values. Hence, an input of "1" corresponds to the vibrational quantum number "0", etc. BJTT determines the "J(J+1)" values for which the corresponding MTRMIN-MTRIAL range is calculated. The number of BJTT values is limited to 11. The last BJTT value must be "0" so that the rotationless potentials may be calculated.

This completes the input required for the RKR-IPA program.

The IPA routine uses the Numerov-Cooley method to find numerical solutions to the Schroedinger equation (Refs 11:363; 14:1872). The routine presented here provides a method for finding solutions for bound states. Vidal also mentions methods for solving unbound states (Ref 43:7). They will not be presented here.

Terms initialized at the start of FIPA are described here. AZERO is the Bohr radius as measured in angstroms. Lines 47-49 repeat the calculation of " r_e ", [RRE], the inter-nuclear equilibrium separation according to Eq (119). Line 50 converts " r_e " [CRE] from angstroms to units of Bohr Radii.

Lines 51 and 52 insure that the limits of the extended RKR curve are beyond the RMIN-RMAX limits specified by the IPA input CARD 16. If not, the RMIN-RMAX limits are redefined to conform to the limits of the extended RKR curve.

Line 53 defines the step size of r [RH] for which the potential curve is calculated.

DO-loop 140 calculates the radius-potential energy pairs $[P(J)$ and $V(J)]$ which will be used in the IPA routine. The line of statement label 140 calls on the function FUNC to generate potential energies for each value of r . FUNC obtains the potential energies, $V(r)$, for each value of r by performing a Lagrangian interpolation on the radius potential-energy pairs of the extended RKR curve. The Lagrangian technique may be expressed as follows (Ref 16):

$$V(r) = \sum_{i=0}^n \prod_{j=0}^n \frac{r-r_j}{r_i-r_j} \quad (147)$$

where r is the value for which $V(r)$ is to be calculated. In FUNC, four points on both sides of r are used for the interpolation of each point. In this manner, the $V(r)$ values are obtained for evenly spaced values of r from the unevenly spaced potentials of the RKR routine.

The section of FIPA following the comment "SEARCH FOR CENTRIFUGAL BARRIER," finds the maximum energy which a molecular system can have for a given rotational energy level, J , for a bound state. Expressed in the notation of the computer program, the effective potential energy, SX , is calculated by the formula:

$$SX = V(I) + ABE * \left[\frac{RE}{P(I)} \right]^2 * AJTT \quad (148)$$

In lines 65-72, SX is calculated for rotationless potential energy and radius pairs, [V(I) and P(I)]. Hence, SX is the effective potential energy for a given radius and rotational quantum level, J . Fig B-1 shows the behavior of the potential for increasing J values.

The program first finds the minimum of the potential curve and assigns it to ASX. Once the minimum has been found, the potential increases with r . Each successive larger value of SX is assigned to TX. At the same time, ASX is equated to SX. This process is continued until the effective potential energy curves reaches a maximum as in Fig B-1. This maximum value of SX is retained in TX and is the sought for centrifugal barrier.

Having found the largest permissible value of SX (TX) for a given J value, the routine BETRL (line 73 of FIPA) finds the E_{vJ} [ETRIAL] which is just smaller than the centrifugal barrier, TX, and the corresponding rotational quantum number plus one (v+1). The "v+1" value is returned as NTRIAL to the FIPA routine. NTRIAL is then compared with input MTRIAL(KI) and the smaller value retained in the variable MTRIAL(KI) (lines 74-76). The ETRIAL corresponding to the retained MTRIAL(KI) is stored in the array variable ER(KI) (line 77).

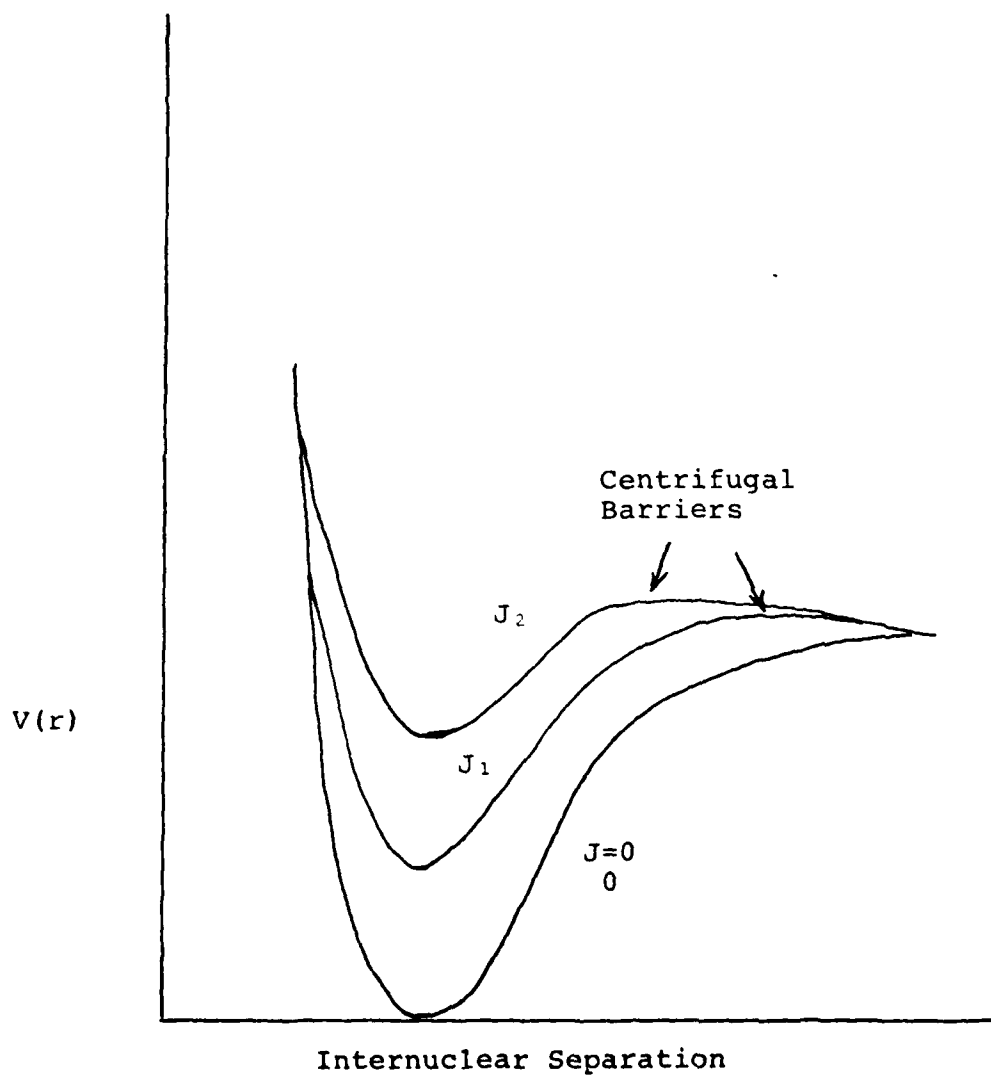


Fig B-1. Effective Potential Energy Curves for
Three Rotational Energy Levels,
 J_1 , J_2 , and J_0

In addition to calculating the effective potential energy, the routine BETRL also calculates the values for B_V [BTRIAL], where J does not equal 0. The variable B_V is determined according to the following relationship:

$$B_V|_J = \frac{\partial E_{VJ}}{\partial J(J+1)} = \frac{\partial E_{TRIAL}}{\partial J(J+1)} \quad (149)$$

The next step is to determine the range of internuclear separations, r , which is to be considered in the IPA routine. This range is predetermined by the MTRIAL(J) and BJTT(J) values. This range is assigned to the variables RMII and RMAA.

DO-loop 200 performs the first step in identifying the RMII and RMAA values. The third line of the loop finds the first energy level, $V(I)$, on the inner portion of the RKR curve which is smaller than or equal to the $ER(KI)$ value being investigated. The value of the subscript for that $V(I)$ is retained in N3AA. Line 88 finds the first energy level, $V(I)$, on the outer portion of the RKR curve which is just larger or equal to the $ER(KI)$ value being investigated. The subscript of that $V(I)$ is retained in N3BB. The process is repeated for each $ER(KI)$, and the smallest value of N3AA is retained as N3A (line 92, statement label 220). The largest value of N3BB is retained as N3B. The values N3A and N3B are the subscripts of the array $P(I)$ which provide:

$$RMII = P(N3A) \quad (150)$$

$$RMAA = P(N3B) \quad (151)$$

In this manner, the limits of r over which the IPA routine and Schroedinger equation are to be investigated have been established so that they are consistent with the specified values BJTT(I) and MTRIAL(I) and the centrifugal barrier. The values MTRMIN(KI) along with the MTRIAL(KI) values which have been adjusted to be consistent with the centrifugal barrier, determine the range of vibrational quantum numbers, v , over which the RKR curve is evaluated for each value of BJTT(KI). This is true for all iterations of the IPA routine except the last iteration.

The range of vibrational quantum numbers, v , which are considered in the last iteration for each BJTT(KI) value may be different from that range specified by NTRMIN(KI) and MTRIAL(KI). The investigation of potential energy ranges specified by RMII and RMAA may uniquely define energy levels, E_{vJ} , for a specific BJTT(KI) value not included in the input NTRMIN(KI)-MTRIAL(KI) values. For the last IPA iteration, MTRIAL(KI) is replaced by LTRIAL(KI).

If the radius of the centrifugal barrier is greater than RMAA and, thus, outside the region investigated by previous iterations of the IPA routine, the maximum energy level to be investigated for a given value of BJTT is the smaller of the two following values:

$$TX = V(N3B) + ABE(RRE/RMAA) * AJTT \text{ (line 99)} \quad (152)$$

$$SX = V(N3A) + ABE * (RRE/RMII) AJTT \text{ (line 101)} \quad (153)$$

where $V(N3A)$ is the potential energy corresponding to RMAA, and $V(N3A)$ is the energy corresponding to RMII.

If the radius of the centrifugal barrier is smaller than RMAA, then the energy of the centrifugal barrier, $YMAX(KI)$, for a given $BJTT(KI)$ is compared with the value in Eq (152) and the smaller value retained for investigation and assigned to the variable. $BETRL(TX)$ then identifies the first quantum vibrational-rotational energy level below TX for a given $BJTT(KI)$. Then "v+1" is assigned to the $LTRIAL(KI)$ variable.

Subroutine PLEGEN

Subroutine PLEGEN and lines 109-119 perform the calculations necessary to give a numerical value to the function $f(r)$ which will be used to perform the calculations of Eqs (113), (114) and (115).

First, all the radii measurements are converted to units of Bohr radii.

Kosman and Hinze chose Legendre polynomials $P_i(x)$ to represent the $f_i(r)$ functions (Ref 23). Vidal found that attempting to extend calculations beyond RMII and RMAA, as specified by E_{vJ} , produced large oscillations. He finally settled upon a combination of Legendre polynomials and an exponential function to dampen the oscillations. This combination improved the convergence of the IPA method. The expression Vidal used is as follows (Ref 41:50):

$$\Delta V_0(r) = \sum_i c_i P_i(x) \exp(-x^{2n}) \quad (154)$$

where the typical range for "n" is $1 < n < 5$. The Gaussian part of Eq (154) provides a smooth cutoff avoiding unphysical oscillations. The Legendre polynomials are calculated using the standard recursion relations (Ref 6:424):

$$(n+1)P_{n+1}(x) = (2n+1)XP_n(x) - nP_{n-1}(x) \quad (155)$$

where $P_1 = 1$ and $P_2 = X$.

Kosman and Hinze used a linear relationship between r and X such that $X=1$ for $r=r_{\max}$ and $X=-1$ for $r=r_{\min}$. Vidal found this relationship to provide poor convergence when dealing with vibrational levels all the way to the dissociation limit and when dealing with anharmonic potentials. He stated that the reason for the poor convergence in the case of a highly anharmonic potential is that a linear interpolation tends to optimize only the outer turning points of the rotationless potential. To avoid this, Vidal chose a nonlinear interpolation given by:

$$X = \frac{(r-r_e)(r_{\max}-r_{\min})}{(r_{\max}+r_{\min})(r_e+r)-2r_{\max}r_{\min}-2r_er} \quad (155')$$

This relation assumes $X=1$, for $r=r_e$, and $X=0$, for $r=r_{\max}$ and $X=1$, for $r=r_{\min}$. The interpolation becomes linear for:

$$r_e = \frac{r_{\max} + r_{\min}}{2} \quad (155)$$

This formulation treats the inner and outer turning points with comparable weight and reduces the number of Legendre polynomials in Eq (154).

Using these formulas, PLEGEN and DO-loop 270 calculate a Legendre polynomial $F(J,I)$ with "NPL" terms (i.e., $J=1$ to NPL) for each of the turning points $P(I)$ on the RKR potential where $I=1$ to M .

The section of FIPA from statement label 180 through the second line after statement label 780, contains the statements necessary to solve the Schroedinger wave equation (SWE) for its eigenvalues, E_{vJ}^0 , and radial wave functions, ψ_{vJ}^0 . It also calculates the correction to the potential, $\Delta v_0(r)$, necessary to make the eigenvalues obtained from the SWE consistent with those observed experimentally. The program returns to statement label 180 until all the "NRPTT" iterations have been completed. On the last iteration ($NREP=NRPTT$), lines 123-125 specify that $NT3=NT1$. The term "NTT" is equal to the number of BJTT values which are greater than "0".

As noted, the first use of the perturbation technique to adjust approximate potential energy curves is attributed to Hinze and Kosman (Ref 23). The technique used in this program to solve the Schroedinger equation is the Numerov-Cooley method (Refs 11; 14). The Numerov-Cooley method of

solving the SWE was used by J. K. Cashion to test the validity of approximate eigenvalue equations developed by Pekeris for a rotating Morse oscillator (Ref 11).

The routine presented in this paper solves the SWE for bound states. Vidal discusses techniques for handling quasibound states. The techniques for evaluating quasibound states are not part of the present program but are here briefly discussed. One approach, Vidal used for quasibound states involved starting the integration of the SWE at small internuclear distances and looking for the maximum of the internal amplitude inside the centrifugal barrier as well as the phase shift of the partial wave outside the centrifugal barrier using a Breit-Wigner parametrization (Ref 12). Vidal also used a second approach in the same work (Ref 43). For quasibound states, he introduced an artificial barrier at large internuclear distances permitting the use of the Numerov-Cooley method. The eigenvalues he found in this manner were slightly higher than the energy eigenvalues derived from the maximum of the internal amplitude. Proper choice of the barrier kept the differences within the standard errors of the measurement. Using this technique, Vidal stated the same numerical method can be used for both quasibound and bound states.

Continuing with the program, as presented in this paper, it is necessary to transform the energy used in the SWE to units which are consistent with the units of length

being used, Bohr radii. Thus far, energy has been expressed in terms of inverse centimeters, wavenumbers. To convert wavenumbers to energy units consistent with Bohr radii, it is necessary to divide by this factor (Ref 11:1873).

$$\frac{\hbar N_A}{4\pi c a_0 \mu_A} = \frac{60.19972628}{\mu_A} \text{ wavenumbers} \quad (156)$$

where $a = 0.52197706$ and $N_A =$ Avogadro's number. The inverse of this quantity is assigned to the variable ZEIN.

The effective potential energies (given according to Eq (148)) for the first BJTT value, for the whole range of the RKR curve, is calculated in DO-loop 340. The energy reference frame is shifted so that the dissociation energy [DE] is the zero energy level.

The lines between statement labels 340 and 360, establish the values of $J(J+1)$ [BJTT(KI)] and the range of vibrational quantum numbers, NTRMIN through NTRIAL which will be considered for the experimental energy eigenvalue $V(I)$ of statement label 340. Loop 660 also starts here.

If it is the last iteration of the IPA routine (NREP=NRPTT), the range of vibrational quantum numbers starts at "v+1=1" and extends through LTRIAL(KI) for each corresponding value of BJTT(KI). This range is specified by lines 140 and 141.

The value of $J(J=1)$, to be investigated on a cycle of loop 660, is assigned to the variable AJTT in statement label 360.

CALL BETRL(TX) this time calculates all the term values, E_{vJ} [ETRIAL], for all values of "v+1" from 1 to NTRIAL with J specified by J(J+1) [AJTT]. B_v [BTRIAL] is also calculated over the same range. The rotational quantum number J corresponding to J(J+1) is assigned to the variable LJT in line 142.

The Schroedinger loop which calculates the radial wave functions [P(J)], B_{vJ} [BCALC], and E_{vJ}^0 [ECALC] starts with line 152. The SWE loop (loop 600) starts by specifying the "v+1" values will be investigated, MTRMIN through MTRIAL. These variables were assigned their values in lines 137-141. Variables MA and MB are initiated to zero prior to entering the SWE routine.

Integer Function SCHR

The SCHR routine solves the Schroedinger equation by the Numerov-Cooley method. The routine is called by line 158 of FIPA. Using this method, each of the experimental term values is adjusted to be consistent with the whole RKR curve. Hence, all term values which were used to produce the RKR curve are indirectly used to adjust each eigenvalue, E_{vJ} , solution found by the SCHR routine.

Numerov-Cooley Method for Solving the SWE

The Numerov-Cooley method for solving the SWE is outlined here. Using Cooley's notation, the SWE may be expressed as follows:

$$P^2(r) = [U(R) - E]P(R) \quad (157)$$

$$P^{(n)} = \frac{d^n P}{d R^n}$$

where $P(R)$ is the radial wavefunction and E are the eigenvalues of the SWE. Cooley defines the potential energy $U(R)$:

$$U(R) = [J(J+1) - \Lambda^2]R^{-2} - Z_a Z_b R^{-1} + E_{e1}(R) \quad (158)$$

In this paper, the contribution of the Λ quantum number, the z-component, due to the electronic angular momentum, is ignored. The electrostatic Coloumb repulsion energy of the nuclei, $Z_a Z_b R^{-1}$, and the electronic energy, $E_{e1}(R)$, make up the vibrational $(v+1/2)$ term of the E_{vJ} 's as expressed by Eq (2). The boundary conditions used are:

$$P(0) = 0, \text{ and } P(R) \text{ bounded} \quad (158')$$

The following definitions are used to convert Eq (157) to a finite difference equation:

$$\begin{aligned} R_i &= h & i &= 0, 1, 2 \dots n+1 \\ P_i &= P(R_i) \\ U_i &= U(R_i) \end{aligned} \quad (159)$$

By dropping fourth order and higher terms in the series:

$$P_{i+1} + P_{i-1} = \sum_{k=0}^{\infty} \frac{2h^{2k}}{(2k)!} P_i^{2k} \quad (160)$$

and by using the different equation to replace P_i^2 , Cooley obtained the integration formula:

$$P_{i+1} + P_{i-1} - 2P_i = h^2 (U_i - E) P_i \quad (161)$$

The error involved in Eq (161) is approximately $\frac{h^4}{12} P_i^{(4)}$. He then presented a higher order integration formula, developed by Numerov, which does not involve the calculation of additional P_i 's. The formula is obtained by subtracting the product of $\frac{h^2}{12}$ times the following series:

$$P_{i+1}^{(2)} + P_{i-1}^{(2)} = \sum_{k=0}^{\infty} \frac{2h}{(2k)} P_i^{(2k+2)} \quad (162)$$

from Eq (160). Then dropping sixth and higher order terms in h , gives the differencing scheme used in Vidal's program:

$$Y_{i+1} + Y_{i-1} - 2Y_i = h^2 (U_i - E) P_i \quad (163)$$

where:

$$Y_i = P_i - (h^2/12) P_i^{(2)} = [1 - (h^2/12) (U_i - E)] P_i \quad (164)$$

The error for this formula is approximately $-\frac{h^6}{240} P_i^{(6)}$.

For all unbound states, $E > U(\infty)$, solutions exist for all E and, according to Cooley, may be approximated by using Eqs (161) or (163) to integrate outward starting with boundary values:

$$P = 0, P = a \text{ small arbitrary number} \quad (165)$$

For bound states, $E < U(\infty)$, only discrete eigenvalues, E , exist. The boundary conditions for solution to Eq (163) are:

$$P(0) = 0 \quad (166)$$

and for $P(R)$ bounded:

$$P_{n+1} = \text{a small arbitrary number} \quad (167)$$

$$P_n = P_{n+1} \exp \left(R_{n+1} \sqrt{U_{n+1} - E} - R_n \sqrt{U_n - E} \right) \quad (167')$$

The second condition results from the assumption that at R_n , $U(R)$ is slowly approaching a constant value.

The method of solution involves starting with some E (i.e., the experimentally obtained term values) and with the boundary conditions specified by Eq (166) integrate outward to some point R_M using Eq (163). Then the wavefunctions P_i to P_m are normalized to P_m :

$$P_i^{\text{out}} = P_i / P_m \quad i = 1, 2, 3, \dots, m \quad (168)$$

Then the same procedure is followed starting at P_{n+1} and integrating inward to P_m . Again, the P_i values are normalized, this time, using the P_m^{in} value obtained in the inward integration. Hence, $P_m^{\text{out}} = P_m^{\text{in}} = 1$. At this point, a correction for E is determined from the difference in slopes of the two portions of the curve ($R < R_m$ and $R > R_m$). The inward-outward, E correction cycle is repeated until the value for E on successive iterations differs by some established limit, ϵ [EPS]. When this occurs, a satisfactory eigenvalue E has been obtained.

The correction formula is expressed as follows:

$$D(E) = (P'_{\text{out}} - P'_{\text{in}}) / \int_0^{\infty} [P(R)] dR \quad (169)$$

where the P' terms are derivatives of the wavefunctions at R_m resulting from the inward and outward integration. Expressed as a difference equation which is consistent with Eq (163) $D(E)$ is:

$$D(E) = [(-Y_{m-1} + 2Y_m - Y_{m+1})h^{-2} + (U_m - E)P_m] / \sum_{i=1}^n P_i^2 \quad (170)$$

Convergence difficulties with this approach may be encountered. Cooley describes the convergence of the technique and how to recognize what types of difficulties can be encountered. These will not be covered here.

Problems with convergence will be encountered if a $P(R)$ is selected so that the magnitude of radial wavefunction at R_m is "0". Recalling that the procedure calls for normalizing the radial wavefunction $P(R)$ at the point P_m , it is clear that dividing by a number close to "0" into larger numbers can introduce significant errors.

Cooley's program used the Numerov method to solve the SWE. His program was structured so that $D(E)$ must be decreasing in magnitude from one iteration to the next; then, the $D(E) < \epsilon$ convergence criterion is applied.

The problem of stopping at a radius R_m when $P_m(R)$ is zero, is handled rather nicely from the knowledge that for

the anharmonic motion of a diatomic molecule, the wavefunction $P(R)$ reaches a maximum at a radius near the outer portion of the potential. Thus, Cooley started his inward integration and stopped at the value of R_m such that P_m had stopped increasing, i.e., it had reached its maximum. This method finds the largest P and, hence, keeps the correction technique from becoming accidentally unstable due to a poor choice of P_m . This value of R_m is retained and the outward integration is then performed. This concludes the discussion of Cooley's article. His article includes a derivation of $D(E)$ and further discussion of the convergence of the method.

The discussion of the SCHR routine is now continued. As in previous sections, the notation in Vidal's program will be placed in brackets following the notation of Cooley when use of both is desirable.

The routine SCHR starts by initializing the values H [H], h^2 [$H2$], and $h^2/12$ [HV] of difference Eqs (159), (163) and (164). The value "NN" corresponds to the "M" of input CARD 16. Line 13 sets E_{vJ} [E] equal to the value of $ETRIAL(I)$ where "I" corresponds to a "V+1" vibrational quantum number. The "I" value is specified by FIPA, DO-loop 600.

The rotational quantum number J being considered corresponds to the $J(J+1)$ [$AJTT$] specified by statement label 360 of FIPA. The E_{vJ} [$ETRIAL(I)$] was calculated by $CALL\ BETRL(TX)$, line 144 of FIPA.

Next, DO-loop 10 finds the value on the potential curve which is just greater than $E_{vJ}[E]$ and identifies it temporarily by the subscript of $V(LCRIT)$. If the inner potential $V(IPP)$ does not extend above $E_{vJ}[E]$, then an error message is printed indicating the failure of the integration routine with $KERR=1$. The loop 16 decreases the starting subscript of the potential to either $V(1)$ or until " $WCRIT>20.0$ " is satisfied. It is assumed that this criterion is sized so that for the minimum value of R considered, the magnitude of the wavefunction $P(R)$ will be sufficiently small to satisfy the assumed boundary conditions, Eqs (166) and (167).

This assumption may be checked in the printout. Values for the inner and outer wavefunctions $P(R_{min})$ [$S(MA)$] and $P(R_{max})$ [$S(MB)$] are printed. In the introductory comments to his program, Vidal states that $S(MA)$ and $S(MB)$ should typically be of a magnitude of 1×10^{-10} , if the $RMIN$ and $RMAX$ limits are wide enough. This implies that the " $WCRIT>20.0$ " will produce $S(MA)$ and $S(MB)$ of similar magnitude.

The process is repeated to find the first value greater than $E_{vJ}[E]$ at the outer end of the potential. The routine then extends the potential to sufficient magnitude of R so that the value of the outer wavefunction $S(MB)$ will be sufficiently small. Again, an error message is printed with " $KERR=2$ " if the outer portion of the potential does not extend above $E_{vJ}[E]$.

The values of NL1 and NL2 are assigned such that V(NL1) is the second value on the inner portion of the curve less than $E_{vJ}[E]$ and V(NL2) is the first value greater than $E_{vJ}[E]$ (lines 23 and 130). These values will be used as the limits S(NL1) and S(NL2) between which the number of codes (i.e., the number of times P(R) [S(R)] becomes zero) associated with each E are counted. This count is the determination of the vibrational quantum number v[KV] associated with that eigenvalue E_{vJ} (lines 120-123, DO-loop 70). These values are printed out in the program listing.

Following Cooley's method, the inward integration is started first. The outer numerical value for the wavefunction P_{n+1} [S(MB)] is assigned an arbitrary value of 1×10^{-10} (Eq (117)). The next point P_n [S(MB-1)] is evaluated according to Eq (167').

The lines between statement labels 36 and 40 perform the inward integration until P(R) [S(I)] stops increasing. The largest value of the wavefunction, P_m , is assigned to the variable PM. The correspondence between Eq (163) and the program is as follows:

$$Y_{i+1} + Y_{i-1} - 2Y_i = h^2 (U_i - E) P_i \quad (163)$$

$$YA + YC - 2YB = H2*(GI)*S(M+1) \quad \text{Line 66}$$

$$Y_i = [1 - h^2/12 (U_i - E)] P_i \quad (164)$$

$$YC = [1.D0 - HV*GI] (SM) \quad \text{Line 68}$$

The portion of the wavefunction obtained from the inward integration is normalized by PM_{in} .

If $S(I)$ goes negative on the inward integration, an error message indicating the failure of the SCHR routing is printed with "KERR=3" indicating the source of the failure.

The process is repeated starting at the inner portion of the potential curve and integration continued out to the radius corresponding to the previously identified PM, the point at which the wavefunction first reached a maximum for the inward integration. This wavefunction from $S(MA)$ to PM is normalized with PM_{out} . The variable DF corresponds to the denominator EP_i^2 of Eq (170) (statement label 53). The variable F corresponds to numerator and the correction to $E_{vJ}[E]$ is DE. This DE should not be confused with the DE of the rest of the program which is the dissociation energy.

The convergence criterion, as outlined by Cooley, is satisfied by the lines between statement labels 56 and 60. Restating that criterion, $DE [DE=ABS(E_{new}-E_{old})]$ must be less than some ϵ [EPS] with the stipulation that E is converging on consecutive iterations. A converging E requires that DE be getting smaller and smaller. Vidal's program handles these requirements in the following manner. TEST is assigned a value of "-1". If the SCHR routine converges on every iteration, i.e., DE gets smaller on every iteration, TEST is assigned a positive value. Then line 112 is never applied. On the other hand, if DE increases, the

ε [EPS] criterion is never applied because TEST will remain negative. Hence, DE must get smaller which results in TEST being assigned a positive value before the convergence criterion is checked. This prevents the routine from accidentally satisfying the convergence criterion without true convergence being obtained. This still does not prevent the program from jumping from a solution for one vibrational quantum number v to an eigenvalue associated with a different v . This error can be detected in the printout by observing that a proper ordering of $v[KV]$ is not maintained.

DO-loop 70 counts the number of times the wavefunction $P(R) [S(J)]$ becomes "0". This number, as noted, corresponds to the vibrational quantum number v for eigenvalue $E_{vJ}[E]$.

The last computation is the normalization of the wavefunction $P(R) [S(J)]$ so that

$$\int_{J=MA}^{MB} S(J) * S(J) dH = 1 \quad (171)$$

The remainder of the SCHR routine is concerned with the option of printing the solution of the routine. This option is controlled by the "NS" input of CARD 15.

FIPA (Continued)

At this point, control is returned to FIPA. If the SCHR routine has been successful, a wavefunction ranging from

S(MA) to S(MB) is returned along with a new eigenvalue E_{vJ} [ECALC]. In this case, "SCHR=0" and the programs proceed to statement label 420.

When "SCHR=1", this indicates that the SCHR routine was converging towards the limit ϵ [DE], but that the limit was not achieved in the number of iterations permitted, MAXITT, specified by input CARD 15. In this case, the program proceeds to statement label 400, and LLK is incremented. The variable "LLK" is used to report the number of times the convergence criterion ϵ is not satisfied. This value is printed by the command in statement label 620.

If "SCHR=2" is returned from the routine SCHR, the routine has failed to converge for a specific E_{vJ} . The reason for the failure is specified by the value "KERR" specified in SCHR (lines 21, 37, or 69) and printed out by the command in statement label 83 of SCHR.

If SCHR fails, the program proceeds to statement label 300 and KLK is incremented. If the SCHR routine fails "KLIM" times (where KLIM is specified as "2" in line 147), the program is halted by CALL EXIT (line 163).

If SCHR has been successful at finding the wavefunction S(J) for a given eigenvalue ECALC, then control proceeds to label 420 where the limits of the Schroedinger loop are, if necessary, adjusted to be consistent with MA and MB. The expectation values of $\left(\frac{1}{r}\right)^2$ are calculated for a specific

of v and J by lines 169 through 173. Simpson's rule is used to perform the required integration:

$$B_v = \frac{\hbar}{4\pi\mu c} \left\langle \psi_{vJ} \left| \frac{1}{r^2} \right| \psi_{vJ} \right\rangle \quad (172)$$

where ψ_{vJ} is the numerical wavefunction $S(MA)$ to $S(MB)$ returned from SCHR.

The eigenvalue ECALC is converted to the proper units and the reference changed so the bottom of the potential well is zero by adding the dissociation energy DE to the potential (line 157).

The experimentally determined eigenvalue, ETRIAL(I), (calculated from the Dunham coefficients by the routine PETRL), is also returned to the reference frame where the bottom of the potential well is zero (line 175). The difference [DIFF] between the experimental eigenvalue (ETRIAL) and the eigenvalue (ECALC) is then calculated. The variable DIFF is the ΔE_{vJ} of Eq (109).

Line 177 directs the program to advance to statement label 540, if the program is in the last iteration of the IPA routine as specified by NRPTT. This skips several calculations necessary to obtain the ΔV of Eq (113). These are not necessary because the last values calculated by the program will be printed and the routines necessary to calculate Eq (113) will be skipped.

If the program is not on the last iteration of the IPA routine, it calculates (Eq (114)) the expectation values

[FPL(k)] of the f(r)'s [FX(K,J)] of Eq (113) where the f(r)'s are expressed in terms of Legendre polynomials as expressed in Eqs (154), (155), and (155'). The polynomials for f(r) were calculated in DO-loop 270 FIPA (lines 180-186).

The reason for the statistical weight EWG in line 189 has not been determined at this time. It might be used to reflect the different uncertainties in the determination of ΔE_{vJ} for different positions on the potential curve.

Next I shall discuss the solving of Eq (115) for the coefficients c_i [COEFF(K)]. The equation is manipulated and constants calculated in the normal least-squares fashion according to Eqs (12-16).

The least-squares fit is performed according to the general formula:

$$B = (X^T X)^{-1} X^T \quad (13)$$

where X^T corresponds to:

$$BL(K) = \sum_{k=1}^{NPL} DIFF * FPL(K) \quad (172)$$

as defined by DO-loop 520. And $(X^T X)$ in notation of the computer program is:

$$AL(K,J) = \sum_{k=1}^{NPL} \sum_{j=1}^{NPL} FPL(j) * FPL(k) \quad (173)$$

The errors associated with the calculations are tabulated in several ways. The sum of the errors, $\sum \Delta E_{vJ}$

[DIFF] are calculated for each value of AJTT. This sum of differences expressed in the notation of the computer program is:

$$\text{GVDF} = \sum_{v = \text{MTRMIN}(KI)}^{\text{MTRIAL}} \text{DIFF} \quad (174)$$

The average difference is calculated in line (219) as the variable GVDA. The root mean square error, GVDF2, is calculated in lines 199 and 217 according to the formula:

$$\text{GVDF2} = \left[\frac{\sum \text{DIFF}}{\text{APLTST}} \right]^{\frac{1}{2}} \quad (175)$$

where APLTST is as defined in line 216.

The difference DIFB between B_v as calculated by Eq (172), and B_v as calculated by Eq (91) is obtained in line 202. This quantity is multiplied by 1000 and 1000*DIFB is the value printed in the output of the program.

The variable "NL" of lines 197 and 133 is a count of the total number of "v,J" combinations for which calculations are performed for one iteration of the FIPA. DO-loops 640 and 650 adjust the potential V(I) to reflect a new J(J+1) value for the next solution of the Schroedinger wave equation.

The average variance and the standard error of the fit used to obtain the "NPL" coefficients of the Legendre polynomials (Eqs (113) and (115)) for the "NL" combinations of "v,J" are calculated in lines 228 and 229.

On the first iteration, line 230 transfers the program to statement label 700 where the coefficients of the Legendre

polynomials of Eq (115) are calculated. The routine MATINV called by line 242 inverts the matrix $AL(K,J)$ which then corresponds to the $(X^T X)$ of Eq (13) and returns the inverted value in the same matrix. The MATINV routine, using the inverted $AL(K,J)$ matrix and $BL(K)$ calculates the coefficients of the Legendre polynomials of Eq (115), and returns the coefficients in the $BL(K)$ array. DO-loop 720 then assigns the $BL(K)$ coefficients to the array $COEFF(K)$. DO-loops 740 and 760, then use the coefficients $c_i[BL(k)]$ and the expectation value $FX(K,I)$ to calculate the correction potential $\Delta V(r)$ of Eq (113). Then in the same line, a new corrected potential is obtained (Eq (110)).

The minimum of the potential curve is found (VMIN) and a new Y_{00} [YDH(1,1)] Dunham coefficient is calculated (line 253).

At this point, program control returns to statement label 253 for the "NREP"th iteration of the inverse perturbation routine.

On the second and following iterations, the program continues on from line 230. The standard error of E_{vJ} for all combinations of "v,J" is assigned to GVT. Using the coefficients $COEFF(K)$ and the "error" $ERROR(K)$ of the previous cycle (see DO-loop 720, DO-loop 680 prints the constants [DBAA] of the Legendre polynomials used to calculate ΔV , the standard error of that constant $T\frac{1}{2}$ (line 236), and the ratio of the error to the constant, i.e., $T/DBAA$.

After the last iteration, iteration number "NRPTT", line 241 transfers the program out of the loop which performs the IPA calculations. DO-loops 820 and 840 calculate the correlation coefficients for the Legendre polynomials (Eq (16)).

The routine POTTAB (called from line 264 of FIPA) then takes the potential energy curve generated by the IPA routine and produces the final set of turning points for the eigenvalues E_{vJ} of the routine and a second potential arranged in order of increasing "r" from P(I) minimum to P(I) maximum.

POTTAB starts by finding the minimum potential V(I) and assigns that value of "I" to IMIN. Next, starting with the inner portion of the adjusted IPA potential, from V(1) to V(IMIN), CALL PLYNN finds the inner turning radii (AINN(I) for each of the eigenvalues E_{vJ} [EEE(I)] which were defined in line 203 of FIPA. PLYNN obtains the turning points by doing a Lagrangian interpolation to the IPA potential. The process is repeated from V(IMIN) to V(M) for each EEE(I) to obtain the turning points on the outer portion of the IPA potential. The vibrational quantum numbers, $v[IA]$, the energy eigenvalues [EEE(I)], the inner and outer turning points [AINN(I) and AOUT(I)], and the corresponding B_v [BBB(I)] values are printed.

POTTAB then using the new IPA potential, P(I) and V(I), where $I=I,M$, and the original RKR curve XI(I) and Yi(I) where $I=1,N$, determines an "IPA" potential energy for

each RKR turning point, $XI(I)$, by interpolation of the IPA curve. The difference in RKR and IPA energies for that radius is calculated.

Next POTTAB estimates the standard error of the potential for each value of "r" [$XI(I)$]. This standard error is based upon Eq (110):

$$V(r) = V(r) + \Delta V_0(r) \quad (110)$$

The validity of the calculation used, is based upon the assumption that the routine has converged within some acceptable error limits to some $V(r)$. Any error in $V(r)$ is then associated with calculation of $\Delta V(r)$. The correction ΔV to the energy potential has been obtained using the Legendre polynomials of Eq (154). From the errors of the coefficients " c_i " used to calculate the correction potential, the error of the correction can be estimated. DO-loop 99 calculates the estimated standard error of the potential and prints it, the potential, the turning point, the difference between the RKR and IPA potential and the standard error of the potential.

Control of the program is returned from POTTAB to FIPA. FIPA prints out a summary of the sum of the differences for each value of $J(J+1)$ calculated on each IPA iteration. It also prints out the average errors for all values of $J(J+1)$ for each iteration. The program last of all prints

out the original Dunham coefficients with the new Y_{00} which has been calculated to set the minimum of the potential energy curve to zero.

This completes the description of the RKR-IPA program for one of set data. Control is then passed back to MAIN. If new data is provided, the RKR-IPA calculations are repeated for the new data.

To avoid any loss of information, Vida's original comments on input and output are included in this appendix with the revised program.

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1      1. PROGRAM MAIN
2      C AMJS: GCRJLHND
3      C MAIN PROGRAM: RIPA SYSTEM
4      C
5      C THIS PROGRAM IS A UNIFICATION OF THE RKR AND IPA PROGRAMS WHERE
6      C THE RKR POTENTIAL IS USED AS AN INITIAL POTENTIAL IN THE IPA
7      C PROCEDURE.
8      C
9      C RIPA CONSTRUCTS A POTENTIAL CURVE FOR AN ELECTRONIC STATE OF A
10     C ROTATIONLESS DIATOMIC MOLECULE -- I.E., PAIRS OF INNER AND OUTER
11     C CLASSICAL TURNING POINTS AND ASSOCIATED ENERGY LEVELS -- FROM
12     C DUNHAM EXPANSION COEFFICIENTS  $D_n$  USING THE RYDBERG-KLEIN-REES
13     C METHOD. IT THEN PERFORMS AN EXTRAPOLATION OF THE INNER AND OUTER
14     C TURNING POINTS. FINALLY, RIPA PERFORMS AN INVERTED PERTURBATION
15     C APPROACH WHERE THE MEASURED TERM VALUES ARE FITTED TO THE QUANTUM
16     C MECHANICAL ENERGY EIGENVALUES OF A ROTATING VIBRATOR BY MEANS OF
17     C A LEAST SQUARES FIT USING A VARIATIONAL METHOD.
18     C
19     C THE INPUT CARD DECK OF THE PROGRAM RIPA MUST BE AS FOLLOWS.
20     C
21     C THE FIRST CARD HAS ITEST IN COLUMN 1. IF ITEST = 0, THE
22     C PROGRAM WILL STOP. IF ITEST = 1, THE PROGRAM WILL START A
23     C COMPLETE CALCULATION SEQUENCE, AND THE DATA DECK MUST BE AS
24     C FOLLOWS.
25     C
26     C THE NEXT TWO CARDS HAVE THE OUTPUT PAGE TITLE IN COLUMNS 1
27     C THROUGH 72.
28     C
29     C THE NEXT CARD HAS IIMS, THE VALUES OF THE MASSES OF THE TWO ATOMS
30     C AND THE IDENTIFICATION CODE OF THE ELECTRONIC STATE UNDER STUDY
31     C IN FORMAT 14,2D16.9,32X,A4. THE VALUES OF THE MASSES SHOULD BE
32     C EXPRESSED IN ATOMIC UNITS. IIMS MUST BE 1 IF THE CARBON SCALE
33     C IS USED AND MUST BE 2 IF THE OXYGEN SCALE IS USED. THERE IS AN
34     C OPTIONAL WAY OF USING THIS MASS CARD. INSTEAD OF LISTING THE
35     C MASSES OF THE TWO ATOMS SEPARATELY, THE REDUCED MASS OF THE
36     C MOLECULE (IN ATOMIC UNITS) MAY BE ENTERED IN THE FIRST MASS FIELD.
37     C THE SECOND MASS FIELD MUST THEN BE LEFT BLANK. THE CHOICE OF
38     C CARBON OR OXYGEN SCALE MUST, OF COURSE, STILL BE ENTERED.
39     C
40     C THE NEXT CARD READS NDUM,(JH(I),I=1,NDUM) IN FORMAT 11I5. THE
41     C NDUM VALUES OF JH: N1, N2, N3, .... SPECIFY THE NUMBER OF DUNHAM
42     C COEFFICIENTS Y(I,1), Y(I,2), Y(I,3), ....
43     C THE NEXT CARDS CONTAIN THE DUNHAM COEFFICIENTS Y(I,K) WHICH ARE
44     C READ IN GOING FROM I=1 TO NDUM: (Y(I,1),I=1,N1), (Y(I,2),I=1,N2),
45     C (Y(I,3),I=1,N3),..... IN FORMAT (4D18.9).
46     C
47     C THE NEXT CARD CONTAINS THE DISSOCIATION ENERGY DE AND THE ELEC-
48     C TRONIC TERM TE IN FORMAT 2D15.8 AND EXPRESSED IN RECIPROCAL
49     C CENTIMETERS. DE IS THE ENERGY SEPARATION BETWEEN THE POTENTIAL
50     C MINIMUM OF THE ELECTRONIC STATE UNDER STUDY AND ITS DISSOCIATION
51     C LIMIT. TE IS THE ENERGY SEPARATION BETWEEN THE POTENTIAL MINIMA
52     C OF THE ELECTRONIC STATE UNDER STUDY AND OF THE GROUND ELECTRONIC
53     C STATE OF THE MOLECULE. IF THE ELECTRONIC STATE UNDER STUDY IS
54     C ITSELF THE GROUND STATE, THIS CARD MUST BE BLANK.
55     C
56     C THE NEXT CARD CONTAINS VFIN, AND VINC IN FORMAT 2F10.2. RIPA CAL-
57     C CULATES INNER AND OUTER TURNING POINTS FOR  $V = -0.25$  AND FOR
58     C EACH VALUE OF V FROM ZERO TO VFIN IN STEPS OF VINC. IT IS NOT

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59 C NECESSARY THAT V_{FIN} , AND/OR V_{INC} BE INTEGRAL. THE QUANTITY
 60 C V_{FIN}/V_{INC} MUST NOT EXCEED 39%.
 61 C
 62 C THE NEXT CARD IS THE KLEIN ACTION INTEGRAL PRINT SWITCH AND
 63 C CONTAINS IOPFG IN FORMAT I1. IT IS USED IN GENERATING THE
 64 C INITIAL RKR POTENTIAL. IF IOPFG=1, THE VALUES OF THE KLEIN ACTION
 65 C INTEGRALS ARE PRINTED FOR ALL OF THE ITERATIONS ASSOCIATED WITH
 66 C EACH OF THE VALUES OF V FOR WHICH PAIRS OF TURNING POINTS ARE
 67 C CALCULATED. IF IOPFG=0, THESE VALUES ARE NOT PRINTED.
 68 C
 69 C THE NEXT CARD CONTAINS RLIM1, RLIM2, AND NEXT IN FORMAT 2F6.2,I2.
 70 C RLIM1 AND RLIM2 ARE THE INNER AND OUTER LIMITS, RESPECTIVELY,
 71 C TO WHICH EXTENSIONS OF THE RYDBERG-KLEIN-REES TURNING POINTS
 72 C WILL BE ESTIMATED, IN A FASHION TO BE DESCRIBED BELOW. THE
 73 C INPUT QUANTITY NEXT IS THE NUMBER OF EXTRA EXTENSION DATA
 74 C POINTS TO FOLLOW. NEXT MAY NOT EXCEED 25 AND MAY BE ZERO, IF
 75 C NO EXTRA DATA POINTS ARE TO BE ADDED.
 76 C
 77 C THE NEXT NEXT CARDS EACH CONTAIN R1(I) AND PE1(I) IN FORMAT
 78 C 2D15.9. THE R1(I) AND PE1(I) ARE R AND POTENTIAL ENERGY PAIRS
 79 C WHICH MAY BE USED TO GUIDE THE EXTENSION TO THE RYDBERG-
 80 C KLEIN-REES TURNING POINTS, AS DESCRIBED BELOW. THE UNITS OF
 81 C THE R1(I) AND PE1(I) SHOULD BE ANGSTROMS AND RECIPROCAL
 82 C CENTIMETERS, RESPECTIVELY. NOTE....IF NEXT IS ZERO, THESE
 83 C CARDS MUST BE OMITTED FROM THE INPUT DECK.
 84 C
 85 C THE NEXT CARD CONTAINS THE FITTING PARAMETERS KFIT(I), I=1,2 AND
 86 C KINT(I), I=1,4 IN FORMAT 6I5. IF THE CARD IS BLANK THE PROGRAM
 87 C TAKES THE DEFAULT VALUES 2, 4, 0, 6, 5, 10. FOR EXTRAPOLATING THE
 88 C INNER TURNING POINTS KFIT(1) CONSTANTS INSIDE AN EXP-FUNCTION
 89 C OF THE FORM $\exp(A(1)+A(2)*x+...)$ ARE USED WHICH ARE DETERMINED
 90 C BY A LEAST SQUARES FIT OF THE KFIT(1)+2 INNERMOST RKR TURNING
 91 C POINTS. FOR EXTRAPOLATING THE OUTER TURNING POINTS KFIT(2) CON-
 92 C STANTS ARE USED IN A FUNCTION OF THE FORM $\sum(A(K)*R^{K+KINT(K)})$
 93 C WHERE KINT SPECIFIES THE INVERSE POWERS OF THE INTERNUCLEAR DIS-
 94 C TANCE R IN THE LONG RANGE INTERACTION FUNCTION. THE CONSTANTS ARE
 95 C DETERMINED BY A LEAST SQUARES FIT OF THE KFIT(2)+4 OUTERMOST RKR
 96 C TURNING POINTS.
 97 C
 98 C THE NEXT DATA CARD IS THE PUNCH CONTROL CARD AND CONTAINS IPNRKR
 99 C AND IPNIPA IN FORMAT 2I2. IF IPNRKR=1, AN OUTPUT DATA DECK (RKR)
 100 C IS PUNCHED. IF IPNIPA=1, AN OUTPUT DATA DECK (IPA) IS PUNCHED.
 101 C
 102 C THE NEXT CARD HAS LTEST IN COLUMN 1. IF LTEST=0, THE VARIATIONAL
 103 C PROCEDURE IS SKIPPED AND THE PROGRAM RETURNS TO THE BEGINNING TO
 104 C RESUME THE NEXT PROBLEM BY READING ITEST (SEE ABOVE).
 105 C
 106 C IF LTEST=1, THE FOLLOWING ADDITIONAL CONTROL CARDS ARE NEEDED TO
 107 C RUN THE INVERTED PERTURBATION APPROACH.
 108 C
 109 C THE NEXT CARD CONTAINS CONTROL VARIABLES FOR SCHP AS FOLLOWS--
 110 C NI, NS, IPSIQ, MAXIT, AND EPS IN FORMAT 4I4,D10.0.
 111 C IF NI = 1 DATA FROM EACH ITERATION IS PRINTED.
 112 C IF NI = 0 THE ITERATIONS ARE NOT PRINTED.
 113 C IF NS = 1 THE WAVE FUNCTIONS ARE PRINTED AT EVERY IPSIQ POINTS.
 114 C IF NS = 0 THE WAVE FUNCTIONS ARE NOT PRINTED.
 115 C EPS IS THE CONVERGENCE CRITERION. A GOOD WAVELENGTHS IS A GOOD
 116 C STARTING VALUE.

117 C MAXIT IS THE MAXIMUM NUMBER OF TIMES SCHR WILL ATTEMPT TO SATISFY
 118 C THE CONVERGENCE CRITERION. TEN IS A GOOD STARTING VALUE.
 119 C
 120 C THE NEXT CARDS CONTAIN RMIN, RMAX, M, NRPT, NPL, MCH, LSW
 121 C AND MTRMIN(I), MTRIAL(I), RJTT(I), I=1,11)
 122 C IN FORMAT 2(I,1),5(I5/5(12,13,F5.3)/3(12,13,F5.0)).
 123 C RMIN AND RMAX ARE THE LOWER AND UPPER LIMITS OVER WHICH THE
 124 C POTENTIAL CURVE IS TO BE CONSIDERED IN THE IPA PROCEDURE.
 125 C M IS THE NUMBER OF POINTS TO BE USED IN THE INTERPOLATED WELL
 126 C MAXIMUM M IS 2401
 127 C NRPT DEFINES THE NUMBER OF ITERATIONS FOR THE INVERTED PERTURBA-
 128 C TION APPROACH, WHERE THE LAST ITERATION CALCULATES THE ROTATION-
 129 C LESS POTENTIAL FOR THE DEFINITION OF THE GV AND BV.
 130 C NPL IS THE ORDER OF THE CORRECTION FUNCTION OF THE POTENTIAL
 131 C WHICH IS DESCRIBED BY A SUM OF LEGENDRE POLYNOMIALS.
 132 C MTRMIN AND MTRIAL ARE THE MINIMUM AND MAXIMUM VALUE OF V+1 FOR
 133 C WHICH TRIAL VALUES ARE GENERATED (USING THE DUNHAM COEFFICIENTS)
 134 C FOR CALCULATING THE SCHRÖDINGER EQUATION. THE PROGRAM STOPS
 135 C AUTOMATICALLY AT THE LAST BOUND STATE.
 136 C RJTT ARE THE VALUES OF J(J+1) FOR WHICH THE POTENTIAL IS CALCU-
 137 C LATED.
 138 C FOR MCH=1 THE PROGRAM PUNCHES A DECK OF ALL THE GV AND BV VALUES
 139 C CALCULATED IN THE LAST ITERATION.
 140 C FOR LSW=2 THE PROGRAM PRINTS THE FIRST AND LAST ITERATION OF THE
 141 C INVERTED PERTURBATION APPROACH. FOR LSW=1 ALL ITERATIONS ARE
 142 C PRINTED.
 143 C
 144 C THIS COMPLETES THE INPUT DATA DECK FOR ONE ELECTRONIC STATE.
 145 C THERE ARE NOW TWO OPTIONS. IF NO OTHER POTENTIAL CURVES ARE TO
 146 C BE CALCULATED, A BLANK CARD MUST BE AT THE END OF THE DATA DECK,
 147 C I.E., ITEST=0. IF A SECOND INPUT DATA DECK IS TO FOLLOW FOR
 148 C ANOTHER ELECTRONIC STATE, THE ABOVE INSTRUCTIONS SHOULD BE
 149 C REPEATED, I.E., ITEST=1.
 150 C
 151 C THE FOLLOWING COMMENTS APPLY TO THE PRINTED OUTPUT OF RIPA.
 152 C
 153 C THE FIRST LISTING STARTS WITH THE TITLE AND THE IDENTIFICATION
 154 C NUMBER OF THE ELECTRONIC STATE. THE VALUES OF THE ATOMIC MASSES
 155 C (OR THE VALUE OF THE REDUCED MASS OF THE MOLECULE) ARE ALSO
 156 C PRINTED AND THE CHOICE OF CARBON OR OXYGEN SCALE IS NOTED. THE
 157 C LISTING ALSO CONTAINS THE RESULTS OF THE RKR CALCULATIONS. FOR
 158 C EACH VALUE OF V IN STEPS OF VINI UP TO VFIN, THE POTENTIAL AND
 159 C INERTIAL ENERGIES, THE INNER AND OUTER TURNING POINTS, AND THE
 160 C FINAL VALUES OF THE KLEIN ACTION INTEGRALS ARE LISTED. THE
 161 C POTENTIAL ENERGY IS THE EXPANSION FOR GV + Y(J,0) EVALUATED AT
 162 C V. THE INERTIAL ENERGY IS THE EXPANSION FOR BV EVALUATED AT V.
 163 C BOTH ARE EXPRESSED IN RECIPROCAL CENTIMETERS. THE TWO TURNING
 164 C POINTS ARE EXPRESSED IN ANGSTROMS. THIS LISTING WILL ALSO
 165 C INCLUDE THE INTERMEDIATE VALUES OF THE KLEIN INTEGRALS IF
 166 C IJPG=1.
 167 C
 168 C THE SECOND LISTING CONTAINS THE PARAMETERS THAT PERTAIN TO THE
 169 C FIT OF THE INNER AND OUTER EXTENSIONS OF THE RKR POTENTIAL.
 170 C FOR THE FUNCTIONS INDICATED ABOVE THE LISTING GIVES THE CONSTANTS
 171 C AND THEIR STANDARD ERRORS AND THE TOTAL STANDARD ERROR. IT SHOWS
 172 C THE FIT FOR THE EXTENSION OF THE INNER AND OUTER TURNING POINTS.
 173 C FINALLY, IF EXTRA EXTENSION DATA POINTS ARE USED, THE DIFFERENCES
 174 C BETWEEN THESE AND THE FIT FUNCTION ARE GIVEN FOR EACH OF THE

175 C INPUT R(1).
 176 C FURTHERMORE, THE DUNHAM COEFFICIENTS ARE LISTED WITH THE CALCULATED VALUE $Y(0,0)$.
 177 C
 178 C
 179 C THE FOLLOWING PRINTOUT EXCEPT FOR THE DUNHAM COEFFICIENTS DOES NOT APPEAR IF LTFST=0.
 180 C
 181 C
 182 C THE FOLLOWING LIST PRESENTS THE PARAMETERS OF THE INVERTED PERTURBATION APPROACH.
 183 C
 184 C
 185 C THE PROGRAM THEN GENERATES A PRINTOUT OF THE FIRST AND LAST ITERATION OF THE INVERTED PERTURBATION APPROACH AND A PRINTOUT OF THE INTERMEDIATE ITERATIONS IF LS4 = 1. FOR EVERY VALUE OF BJST IT GENERATES A TABLE WHICH CONTAINS FOR ALL VALUES OF V SPECIFIED BY MTRMIN AND MTRMAX, THE QUANTUM MECHANICAL ENERGY EIGENVALUE, THE MEASURED TERM VALUE, THE DIFFERENCE, THE CALCULATED RV VALUE, THE DIFFERENCE TO THE MEASURED VALUE AND THE VALUES OF THE WAVE FUNCTIONS FOR THE INNERMOST AND OUTERMOST MEMBERS OF THE ARRAY S. MA AND MB ARE DETERMINED BY THE SCHRÖDINGER ROUTINE SUCH THAT S(MA) AND S(MB) ARE TYPICALLY 1.0-1.0 IF THE LIMITS RMIN AND RMAX ARE MADE WIDE ENOUGH.
 196 C FOR THE LAST ITERATION THE TABLE CONTAINS VIBRATIONAL LEVELS ABOVE THE UPPER DASHED LINE AND BELOW THE LOWER DASHED LINE WHICH WERE NOT SPECIFIED BY THE DATA FIELD ABOVE, BUT WHICH ARE UNIQUELY SPECIFIED BY THE RANGE OF INTERNUCLEAR DISTANCES WHICH HAD TO BE ADJUSTED IN THE INVERTED PERTURBATION APPROACH.
 200 C THE MEASURED VALUES ARE THOSE DEFINED BY THE DUNHAM COEFFICIENTS. EVERY TABLE IS CLOSED WITH THE AVERAGE DEVIATION AND THE STANDARD ERROR IN CM*(C-1).
 204 C
 205 C AFTER EVERY ITERATION THE PROGRAM PRINTS THE COEFFICIENTS OF THE LINEAR COMBINATION OF LEGENDRE POLYNOMIALS OBTAINED IN THE INVERTED PERTURBATION APPROACH. IT ALSO LISTS THE STANDARD ERROR AND THE RELATIVE STANDARD ERROR. IF THE LATTER QUANTITY IS LARGER OR COMPARABLE TO 1 AFTER THE FIRST ITERATION, NPL CAN BE LOWERED IN THE NEXT RUN OF THE PROGRAM. THE LAST SET OF COEFFICIENTS IS FOLLOWED BY THE CORRESPONDING CORRELATION MATRIX.
 212 C
 213 C THE NEXT LISTING GIVES THE INTERPOLATED INNER AND OUTER TURNING POINTS AND THE BV VALUES FOR THE CALCULATED QUANTUM MECHANICAL ENERGY EIGENVALUES OF THE ROTATIONLESS MOLECULE AS OBTAINED AFTER THE LAST ITERATION.
 216 C
 217 C
 218 C THE FINAL LISTING CONTAINS A TABULATION OF THE ENTIRE POTENTIAL WELL. THESE DATA ARE (1) THE TURNING POINTS AND ENERGIES FROM THE LAST IPA ITERATION, (2) THE DIFFERENCE TO THE INITIAL RKR POTENTIAL AND (3) THE CORRESPONDING STANDARD ERROR OF THE POTENTIAL. IN ADDITION, IT CONTAINS THE 20 INNER AND 99 OUTER EXTENSION POINTS FROM THE EXTRAPOLATION METHOD DESCRIBED ABOVE. THE 20 INNER EXTENSION POINTS ARE EQUALLY SPACED IN R BETWEEN RMIN1 AND THE INNERMOST RKR TURNING POINT, AND THE 99 OUTER EXTENSION POINTS ARE EQUALLY SPACED IN R BETWEEN THE OUTERMOST RKR TURNING POINT AND RMIN2. ALL UNITS ARE ANGSTROMS AND RECIPROCAL CENTIMETERS.
 229 C
 230 C THE PRINT OUT CLOSSES WITH A RECOMMENDED SET OF INTEGRATION LIMITS RMIN AND RMAX AS OBTAINED IN THE IPA PROCEDURE. THEY SHOULD BE USED IN THE FOLLOWING RUNS. IT IS FOLLOWED BY A SUMMARY OF THE

233 C STANDARD ERRORS OF ALL ITERATIONS AND A TABLE OF THE DUNHAM COEFFICIENTS WITH A CORRECTED VALUE OF $Y(0,0)$ SUCH THAT THE POTENTIAL MINIMUM DEFINES ZERO ENERGY.

234 C

235 C

236 C

237 C THIS COMPLETES THE PRINTED OUTPUT FOR ONE ELECTRONIC STATE. IF

238 C DATA FOR MORE THAN ONE STATE ARE INCLUDED IN THE INPUT DECK, THE

239 C ABOVE OUTPUT IS REPEATED.

240 C

241 C THE FOLLOWING COMMENTS APPLY TO THE PUNCHED OUTPUT OF RKR.

242 C

243 C IF IPURKR=1 AND/OR IPNIPA=1, A DECK IS PUNCHED WHICH IS TAILORED

244 C TO SERVE AS INPUT TO OTHER PROGRAMS. ALL UNITS ARE ATOMIC MASS

245 C UNITS (CARBON SCALE), ANGSTROMS, OR RECIPROCAL CENTIMETERS.

246 C FOR IPURKR=1 ONE OBTAINS THE RKR-POTENTIAL.

247 C FOR IPNIPA=1 ONE OBTAINS THE IPA-POTENTIAL.

248 C

249 C THE FIRST CARD CONTAINS THE REDUCED MASS OF THE MOLECULE

250 C (AND EXPRESSED IN ATOMIC MASS UNITS, CARBON SCALE) AND ICODE IN

251 C FORMAT 36X,D16.9,16X,A4.

252 C THE NEXT CARD READS NOUN,(JN(I),I=1,10) IN FORMAT 11I5. THE NOUN

253 C VALUES OF JN: N1, N2, N3, ... SPECIFY THE NUMBER OF DUNHAM

254 C COEFFICIENTS $Y(1,1)$, $Y(1,2)$, $Y(1,3)$, ... (AS EXPLAINED ABOVE)

255 C

256 C THE NEXT CARD CONTAINS DE AND TDE IN FORMAT 2D15.8. DE IS THE

257 C ENERGY SEPARATION BETWEEN THE BOTTOM OF THE ROTATIONLESS

258 C POTENTIAL WELL OF THE ELECTRONIC STATE UNDER STUDY AND ITS

259 C DISSOCIATION LIMIT. TDE IS THE ENERGY SEPARATION BETWEEN THE

260 C BOTTOM OF THE ROTATIONLESS POTENTIAL WELL OF THE NEUTRAL OR IONIC

261 C ELECTRONIC STATE UNDER STUDY AND THE $V=0$, $J=0$ LEVEL OF THE

262 C GROUND ELECTRONIC STATE OF THE NEUTRAL MOLECULE. NOTE.... IF

263 C ELECTRONIC STATE UNDER STUDY IS ITSELF THE GROUND STATE OF THE

264 C NEUTRAL MOLECULE, THEN TDE=-TCH,0).

265 C

266 C THE NEXT CARD CONTAINS N IN FORMAT I3, WHICH IS THE NUMBER OF R

267 C AND POTENTIAL ENERGY PAIRS TO FOLLOW.

268 C

269 C THE NEXT N CARDS CONTAIN THE R AND POTENTIAL ENERGY PAIRS WITH

270 C TWO PAIRS PER CARD IN FORMAT 2D16.9,4X,2D16.9. THE DATA ON THESE

271 C CARDS IS THAT TABULATED IN THE FIRST TWO COLUMNS OF THE THIRD

272 C OUTPUT LISTING.

273 C

274 C THIS COMPLETES THE PUNCHED OUTPUT FOR ONE ELECTRONIC STATE. IF

275 C DATA FOR MORE THAN ONE STATE ARE INCLUDED IN THE INPUT DECK, THE

276 C ABOVE OUTPUT IS REPEATED.

277 2. DIMENSION KINS(2),ZIMS(2),HFT(2),LJUT(4),THEAD(36)

278 3. COMMON/RP4/R1(25),PE1(25),NEXT

279 4. COMMON/YD/YDH(20,10),I4(10)

280 5. COMMON/FC/FC(11),JC(11),KE,RAA,ROB,KFIT(2),KUOT(4)

281 6. COMMON/EX/EV(921),UV(921),M

282 7. DATA KIMS/4MC=12,4HD=16/

283 8. DATA HFT/ 2, 4/

284 9. DATA LJUT/ 0, 6, 8, 10/

285 10. DATA ZIMS/ 1.0, 3.997622165/

286 C RKR USES THE FOLLOWING FACTORS FOR CONVERTING BETWEEN MASS SCALES

287 C AND DIFFERENT PHYSICAL UNITS.

288 C ZIMS(2) IS 15.99491664/16, WHICH IS THE MASS OF OXYGEN ON THE

289 C CARBON SCALE DIVIDED BY THE MASS OF OXYGEN ON THE OXYGEN SCALE.

290 C FACTOR=SQRT(M-BAR*AV*GADRJS NUMBER/(6*PI*C))*10**8

PRCCFAM MAIN 74/74 OPT=L,ACUM=D A/ 0/ M/-0,=0 F11 0.1+00
DO=-LONG/-CT,AFG=-COMMON/-FIXED,CS= USER/-FIXED,DB= TB/ CH/ CL/ FF/-TD/ -MD/-CT,PL
FTAS,DB.

```

1      PRCCFAM MAIN
2      C      RK=1H,1 0, 10 D/C 19-2
3      DIMENSION ZIMS(2),NFT(2),LCUT(4),IHEAD(36)
4      COMMON/PPW/P1(25),PE1(25),NEXT
5      COMMON/YD/YDH(20,10),IY(10)
6      COMMON/FC/FC(11),H(11),RE,FAA,PHH,KFIT(2),KOUT(4)
7      COMMON/EX/EX(521),LV(521),M
8      CHARACTER KIMS(2)*4
9      DATA (KIMS(I),I=1,2)/'C=12','C=16'/
10     DATA NFT/ 2, 4/
11     DATA LCUT/ 0, 6, 8,10/
12     DATA ZIMS/ 1.0, 0.9946+2165/
13     C      RKR USES THE FOLLOWING FACTORS FOR CONVERTING BETWEEN
14     C      MASS SCALES AND DIFFERENT PHYSICAL UNITS. ZIMS(2) IS
15     C      15.99491464/16, WHICH IS THE MASS OF OXYGEN ON THE CARBON SCALE
16     C      DIVIDED BY THE MASS OF OXYGEN ON THE OXYGEN SCALE.
17     C      FACNUM=SQRT(H-B*AVCGADPCS*NUMBER/(4*PI*C))*10**8
18     FACNUM=4.105404548
19     C      .....READ IN INPUT DATA
20     10 READ 109,ITEST
21     IF(ITEST.EQ.0) STOP
22     READ 110,IHEAD
23     READ 111,IIMC,ZMAS1,ZMAS2,ICODE
24     IF((IIMS.NE.1).AND.(IIMS.NE.2)) IIMC=1
25     C      .....PUT REDUCED MASS INTO ZMU
26     ZMU=ZMAS1
27     IF(ZMAS2.GT.0) ZMU=ZMAS1+ZMAS2/(ZMAS1+ZMAS2)
28     ZPL=ZMU*ZIMS(IIMC)
29     FAC=FACNUM/SGRT(ZMU)
30     CALL YDHF11(3)
31     HE = YDH(1,2)
32     RE=FAC/SGRT(HE)
33     READ 112,DE, E
34     C      .....CALCULATE YCO
35     A2=-YCH(2,2)*YDH(2,1)/(12.0D+0*H)
36     YCH(1,1)=(BE+YDH(3,1))/4.0D+0+A2+A2*A2/BF
37     READ 113,VFA,VINC
38     READ 109,ICFFG
39     READ 113,RLM1,PLM2,NEXT
40     C      .....READ EXTRA EXTENSION DATA IF NECESSARY
41     IF (NEXT.LE.25) GO TO 20
42     PRINT 103
43     STOP
44     20 IF (NEXT.LT.1) GO TO 40
45     GO 30 I=1,NEXT
46     30 READ 104,R1(I),PE1(I)
47     40 READ 116,(KFIT(I),I=1,2),(KOUT(I),I=1,4)
48     GO 50 I=1,2
49     IF(KFIT(I).EQ.0) KFIT(I)=NFT(I)
50     IF(KFIT(I).GT.11) KFIT(I)=11
51     50 CONTINUE
52     GO 60 I=1,4
53     IF(KOUT(I).EQ.0) KOUT(I)=LCUT(I)
54     60 CONTINUE
55     READ 109,IPAPKR,IPNIFA

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```

56      C .....PRINT OUT THE INPUT DATA
57      PRINT 114, IHEAD
58      PRINT 115, ICODE
59      C .....PRINT THE MASSES AND THEIR UNITS
60      IF (ZMAS2.LT.0.0) GO TO 70
61      PRINT 116, KIMS(IIMS), ZMAS1, ZMAS2
62      GO TO 80
63      70 PRINT 117, KIMS(IIMS), ZMAS1
64      80 PRINT 105, DE, TE
65      PRINT 106, RLPM1, RLPM2, VFIL, VINC, ICPFG, IPARKP, IPNIPA
66      C .....PRINT EXTRA EXTENSION DATA IF NECESSARY
67      IF (NEXT.LT.1) GO TO 90
68      PRINT 107
69      PRINT 109, (F1(I), F2(I), I=1, NEXT)
70      90 CALL MKP(VFIL, VINC, ICPFG, FAC)
71      CALL YDHP11(1)
72      PRINT 114, IHEAD
73      C .....EXTRAPOLATE FOR END POINTS OF POTENTIAL FUNCTION
74      CALL EXTEND(FLM1, FLM2)
75      P=2**120
76      IF (IPARKP.NE.1) GO TO 95
77      PUNCH 102, IIMS, ZMAS1, ZMAS2, ZMU, ICODE
78      C CALL YDHP11(IPARKP)
79      C PUNCH 112, DE, TE
80      C PUNCH 119, M
81      C PUNCH 120, (EV(I), UV(I), I=1, M)
82      95 PRINT 121
83      CALL FIPA(ZMU, DE)
84      CALL YDHP11(2)
85      IF (IPNIPA.NE.1) GO TO 10
86      C PUNCH 102, IIMS, ZMAS1, ZMAS2, ZMU, ICODE
87      CALL YDHP11(IPNIPA)
88      C PUNCH 112, DE, TE
89      C PUNCH 119, M
90      C PUNCH 120, (EV(I), UV(I), I=1, M)
91      GO TO 10
92      102 FORMAT(14,3D16.5,1EX,A4)
93      103 FORMAT(37HOTCO MANY EXTRA EXTENSION DATA POINTS)
94      104 FORMAT(2D16.5)
95      105 FORMAT(//6H DE = ,D15.7,10X,6H TE = ,D15.7//)
96      106 FORMAT(2X,10H LIM1 = ,F9.4,10X LIM2 = ,F9.4,10X VFIL = ,F7.2,
97      * VINC = ,F7.2// ICPFG = ,I1,10X IPARKP = ,I1,
98      * IPNIPA = ,I1//)
99      107 FORMAT(// THE FOLLOWING DATA WERE INCLUDED IN THE LEAST-SQUARE
100      * FIT THAT DETERMINED THE COEFFICIENTS OF THE WKB-//
101      * SICK FUNCTION TO THE PKA TURNING POINTS.//
102      * 10X,15X,POTENTIAL ENERGY //)
103      108 FORMAT(4X,1FD16.9,7X,D16.9//)
104      109 FORMAT(2I2)
105      110 FORMAT(15A4)
106      111 FORMAT(14,2D16.9,32X,A4)
107      112 FORMAT(2D15.5)
108      113 FORMAT(2F6.2,I2)
109      114 FORMAT(2X,15A4/2X,18A4)
110      115 FORMAT(// THE CODE NUMBER FOR THIS STATE IS ,A4)
111      116 FORMAT(// THE MASSES OF THE TWO ATOMS,// BASED ON ,A4, A F ,
112      * 1PD16.9, AND ,D16.3//)

113      117 FORMAT(// THE REDUCED MASS OF THE TWO ATOMS, BASED ON ,A4,
114      * IS ,1FD16.9)
115      118 FORMAT(10I5)
116      119 FORMAT(13)
117      120 FORMAT(2D16.9,4X,2D16.9,4X)
118      121 FORMAT(// BEGINNING OF INVERTED PERTURBATION APPROACH //)
119      END

```

SUBROUTINE RKF 74/74 CPT=0, HCON= A/ 5/ M/-0, -02 FTA=5.14 12
 DC=-LJAG/-CT, ARG=-COMMON/-FIXED, CS= USEF/-FIXED, DE= TW/ CB/ CL/ 55/-CD/ 1MP/-77, FL= 13317
 FTA5,08.

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1 SUBROUTINE RKF(VFIN,VINC,IOPFG,FAC)
2   C   RKF PROCEDURE
3   DIMENSION HI(101),TEMP(400),DF(0(0)),M2(3),I7(3),XC(4),YC(4)
4   DOUBLE PRECISION AGAUS(3,4),XGAUS(3,4)
5   COMMON/YD/YDH(20,10),IP(10)
6   COMMON/EX/EV(521),UV(421),M
7   COMMON/RX/RMIN(400),RMAX(400),U(400)
8   .....INTEGRATION CONSTANTS(AH,OMCH,ITZ,P,521)
9   C   THE XGAUS ARE THE AMPHICISAS AND AGAUS ARE THE WEIGHTING FACTORS
10  C   FOR A GAUSSIAN INTEGRATION OF MOMENTS WHERE MEO ARE THE
11  C   4,6, OR 8 DEPEND. ON THE DEGREE OF SUCCESS OF THE
12  C   ITERATION.
13  DATA XGAUS/0.01985507175123200,0.03376524265642400,0.53411440
14  +0297400,
15  +0.10166676129318600,0.16935530676666700,0.3370054780775700,
16  +0.23723379504183600,0.3765040675540200,0.669990052175242800,
17  +0.40828267675217500,0.61930459304159700,0.93156155707200,
18  +0.5917173212472500,0.83060469323313200,0.000,0.7627668049516400,
19  +0.96623475710157600,0.000,0.898332370681400,0.000,0.000,0.930144
20  +02824876800,
21  +0.000,0.000/
22  DATA AGAUS/0.05061426814516800,0.08566224614559500,0.17327425007
23  +2700,
24  +0.11119051722668700,0.1803807865240700,0.32607057743107700,
25  +0.15685332253844400,0.23395696724634500,0.32607257743107700,
26  +0.181341891649100,0.23395696724634500,0.1732742500700,
27  +0.191341891649100,0.1803807865240700,0.000,0.15685332253844400,
28  +0.08566224614559500,0.000,0.11119051722668700,0.000,0.000,0.050614
29  +26614518800,
30  +0.000,0.000/
31  DATA M2/101,41,61/
32  DATA IZ/H,6,4/
33  C   ..CALCULATE TEMP(TEMP) AND U(TEMP) FOR EACH TURNING POINT
34  M=VFIN/VINC+0.500
35  M=M+2
36  IF(M.LE.400) GO TO 100
37  IVINC=100./(VFIN/3.5+1.)
38  VINC=1./FLOAT(IVINC)
39  M=VFIN/VINC + 2.5
40  PRINT 291,VINC
41  100 TEMP(1)=0.250+0
42  U(1)=POLYN(TEMP(1),1)
43  DO 110 I=2,M
44  TEMP=FLOAT(I-2)*VINC+0.500
45  TEMP(I)=TEMP
46  110 U(I)=POLYN(TEMP,I)
47  STEP=.900
48  PRINT 294
49  C   COMMENCE FINDING TURNING POINTS BY INTEGRATION AND
50  C   ITERATE TO A BUILT IN LIMIT OF PRECISION
51  SVTR=0.0
52  VTR=0.000
53  SETR=POLYN(VTR,1)
54  IF (ABS(SETR).LT.1.E-08) GO TO 130
55  VTR=-YDH(1,1)/YDH(2,1)

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56      ETR=POLYN(VT,1)
57      120 IF (ABS(ETR).LT.1.0D-8) GO TO 130
58      XTR=SVTR-(SFTR*(SVTR-VTP))/(SETA-ETP)
59      SVTR=VTR
60      VTR=XTR
61      SETP=ETP
62      ETR=POLYN(XTR,1)
63      GO TO 120
64      130 VMIN=VTR-0.5
65      DO 240 I=1,4
66      VMIN=VMIN+0.5
67      FEG=0.00
68      GEG=0.000
69      LT=1
70      TGD=0
71      TFC=0
72      140 HS=VMIN*(TEMP(I)-VMIN)*STEP
73      IF (LT.GT.3) GO TO 160
74      MQ=M7(LT)
75      KM=MQ-2
76      A=(HS-VMIN)/FLCAT(MQ-1)
77      DO 160 J=1,MQ
78      UV(J)=VMIN+FLCAT(J-1)*A
79      EV(J)=POLYN(UV(J),1)
80      IF (TGD.EQ.0) BI(J)=POLYN(UV(J),2)
81      DENG(I)=L(I)-EV(J)
82      UV(J)=1.00/SGRT(AES(DENG(I)))
83      160 EV(J)=BI(J)*UV(J)
84      FSLP=UV(1)+4.00*UV(MQ-1)+UV(MQ)
85      GSUM = EV(1) + 4.00*EV(MQ-1) + EV(MQ)
86      DO 170 J=2,MQ-2
87      FSLP=FSLP + 4.00*UV(J) + 2.00*UV(J+1)
88      170 GSUM = GSUM + 4.00*EV(J) + 2.00*EV(J+1)
89      FEG2=A*FSLP/3.00
90      GEG2=A*GSUM/3.00
91      IF (LT.GT.1) GO TO 250
92      GO TO 260
93      180 IZDO=(LT-1)/3
94      IF (IZDO.GT.3) IZDO=3
95      NGAS=IZ(IZDO)
96      DO 190 J=1,NGAS
97      XG(J)=(HS-VMIN)*XGALS(IZDO,J)+VMIN
98      190 LV(J)=XG(J)
99      EPSH = TEMP(I) - XG(NGAS)
100      IF (EPSH.LE.0.) GO TO 270
101      DO 200 K=1,NGAS
102      DENG(K)=POLYN(TEMP(I),1)-POLYN(XG(K),1)
103      IF (TGD.NE.0) GO TO 220
104      DO 210 J=1,NGAS
105      210 BI(J)=POLYN(LV(J),2)
106      220 FSUM=0.000
107      GSLP=0.000
108      DO 240 J=1,NGAS
109      IF (DENG(J).LE.0.) GO TO 270
110      XG(J)=AGALS(IZDO,J)/SGRT(DENG(J))
111      YG(J)=BI(J)*XG(J)
112      FSLP=FSLP+XG(J)

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113      240  GSUM=GSUM+YG(J)
114      HSN=HS-VFIN
115      FEG2=FCV-FSUM
116      GEG2=BSV+GSUM
117      C      CHECK IF ITERATION C-ITERION IS ME
118      C      IT MAY HAVE TO BE ADJUSTED IN STATEMENTS 250
119      C      FOR PROPER CONVERGENCE WHEN RUN ON OTHER MACHINE
120      250  IF ((FEG2/FEG).LE.5.D-7) IFD=1
121      IF ((GEG2/GEG).LE.5.D-7) IGD=1
122      IF (ABS(FEG2/FEG1).GT.0.9) IFD=1
123      IF (ABS(GEG2/GEG1).GT.0.9) IGD=1
124      260  LT=LT+1
125      FEG1=FEG2
126      GEG1=GEG2
127      IF (IFD.EQ.0) FEG = FEG + FEG2
128      IF (IGD.EQ.0) GEG = GEG + GEG2
129      IF ((IFD.NE.0).AND.(IGD.NE.0)) GO TO 270
130      VFIN=HS
131      C      IF INTERMEDIATE EVALUATIONS OF KLEIN ACTION INTEGRALS
132      C      ARE TO BE OUTPUT THEN WRITE OUT THE FEG AND GEG
133      IF (ICFEG.NE.0) PRINT 295,FEG,GEG
134      IF (LT.LE.20) GO TO 140
135      PRINT 297
136      RETURN
137      270  F=FEG*FAC
138      GF=GEG/FAC
139      RMAX(I)=SQRT(F+F*F/GF)*F
140      RMIN(I)=RMAX(I)-2.00*F
141      C      WRITE OUT THE TURNING POINTS AND THE
142      C      CORRESPONDING KLEIN ACTION INTEGRALS
143      TEPP(I)=TEMP(I)-0.5
144      PRINT 296,TEMP(I),UEI,RI(NGAS),RMIN(I),RMAX(I),F*GF
145      280  CONTINUE
146      C      .....END OF INTEGRATION AND ITERATION LOOP
147      RETURN
148      291  FORMAT(1X,'VFIN, AND VINC GIVE MORE THAN 400 TURNING POINT PAIR
149      *--INCREMENT HAS BEEN ADJUSTED TO VINC=',F5.2)
150      294  FORMAT(1X,'POTENTIAL GENERATED BY PKP IS AS FOLLOWS://1X,
151      *POTENTIAL',10X,'INERTIAL',5X,'KLEIN ACTION INTEGRALS'//1X,
152      *ENERGY',13X,'ENERGY',15X,'RMIN',1X,'RMAX',1X,'F*GF'//1X,
153      295  FORMAT(1X,'FEG = ',D16.4,', GEG = ',D16.4)
154      296  FORMAT(1X,F5.2,F15.4,D22.9,F16.5,F20.9,3X,D20.6)
155      297  FORMAT(' LT REACH MAXIMUM VALUE OF 20--PKP INTEGRATION ITT-A
156      *TION NOT LIKELY TO SUCCEED. ')
157      END

```

```

1      FUNCTION POLYN(X,N)
2      C      SUBROUTINE FOR PKP SYSTEM
3      C      SOLVES FOR ROOTS OF POLYNOMIAL FUNCTIONS OF TYPE
4      C      POLYN=CLM FOR I=1 TO IMAX OF Y(I),1+Y**((I+1))
5      COMMON/VD/Y(20,10),IM(10)
6      POLY=0.
7      J=IM(N)
8      IF (J.EQ.0) RETURN
9      =1.
10     DO 10 I=1,J
11     POLYN= POLYN +Y(I,N)*G
12     10  S=S*X
13     RETURN
14     END

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UNCLASSIFIED//FOR OFFICIAL USE ONLY

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1      SUBROUTINE EXTEND(PLM1,PLM2)
2      C      SUBROUTINE FOR RKR SYSTEM
3      C      PCUTINE FOR FINDING INNERMOST 20 POINTS AND OUTERMOST 20 POINTS
4      C      OF POTENTIAL FUNCTION BY EXTRAPOLATION. THIS ROUTINE ALSO
5      C      REORDERS THE POINTS DEFINING THE POTENTIAL FUNCTION IN ASCENDING
6      C      MAGNITUDE OF R (THE INTERNUCLEAR DISTANCE).
7      COMMON/GL/X(928),Z(828),L
8      COMMON/RPW/R1(25),PE1(25),NEXT
9      COMMON/FC/F(11),R(11),PE,RAA,PRB,NIN,NCUT,LCUT(4)
10     COMMON/EX/XO(921),YO(921),N
11     COMMON/RX/RMIN(400),RMAX(400),U(400)
12     DO 10 I=1,11
13     10  R(I) = 0.
14     C      .....SPECIFY LIMITS OF FIT FUNCTION
15     RAA=RMIN(N) - 1.0-R
16     PRB=RMAX(N) + 1.0-R
17     C      .....FIT OF THE INNER TURNING POINTS
18     L=NI + 2
19     DO 20 I = 1,L
20     X(I) = RMIN(N-I+1)
21     Z(I) = ALOG10(U(N-I+1))
22     IF (NEXT.EQ.0) GO TO 30
23     DO 25 I = 1,NEXT
24     IF (P1(I).GE.RAA) GO TO 25
25     L=L+1
26     X(L)=R1(I)
27     Z(L) = ALOG10(PE1(I))
28     25  CONTINUE
29     30  PRINT 92,RAA,NIN
30     PRINT 93
31     CALL GLSQ(1)
32     C      .....FIT OF THE OUTER TURNING POINTS
33     L=NCUT + 4
34     DO 40 I = 1,L
35     X(I) = RMAX(N-I+1)
36     Z(I) = U(N-I+1)
37     IF (NEXT.EQ.0) GO TO 60
38     DO 50 I = 1,NEXT
39     IF (P1(I).LE.PR) GO TO 50
40     L=L+1
41     X(L)=R1(I)
42     Z(L) = PE1(I)
43     50  CONTINUE
44     60  PRINT 94,PRB,NCUT
45     PRINT 95
46     CALL GLSQ(2)
47     C      .....FINAL FIT OF THE POTENTIAL
48     F6 = (RMIN(N) - PLM1)/20.
49     DO 70 I=1,20
50     XMC=PLM1+FLCAT(I-1)*F6
51     XO(I) =XMC
52     70  YO(I) = FUNC(0,XMC)
53     DO 80 I=1,N
54     J=N-I+1
55     K = 20+I

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```

56      Y0(K) = SPIN(J)
57      Y0(K) = U(J)
58      DO 85 I=1,N
59      K= N+I+21
60      X0(K)= RMAX(I)
61      Y0(K)= U(I)
62      K=N +21
63      X0(K)=RE
64      Y0(K)= 0.000
65      F6 = (RL*2 -RMAX(N))/99.
66      DO 90 I=1,99
67      K=2+I+1+21
68      XMC = RMAX(N) +FLOAT(I)*F6
69      X0(K) =XMC
70      Y0(K)=FUNC(0,XMC)
71      RETURN
72      92      FORMAT(' FIT OF INNERMOST TURNING POINTS FOR EXTRAPOLATING U(')
73      *WITH R LESS THAN ',1PD15.7,' USING '///'A FUNCTION OF THE FORM
74      *EXP(R(1)+R(2)*X+R(3)*X*X....+R(K)*X**(K-1)) WITH K=12')
75      93      FORMAT(12X,'*',15X,'LOG(L(P))',13X,'FCALC',15X,'DIFF'//)
76      94      FORMAT(' FIT OF OUTERMOST TURNING POINTS FOR EXTRAPOLATING U(')
77      *WITH R GREATER THAN ',1PD15.7,' USING '///'A FUNCTION OF THE FORM
78      *R(1)+R(2)*R**(-6)+R(3)*R**(-5)+....R(K)....WITH K=K012')
79      95      FORMAT(12X,'*',15X,'U(R)',15X,'FCALC',15X,'DIFF'//)
80      END

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AD-A127 315

NUMERICAL METHODS FOR THE PREPARATION OF POTENTIAL
ENERGY CURVES OF DIATO..(U) AIR FORCE INST OF TECH
WRIGHT-PATTERSON AFB OH SCHOOL OF SYST.. L L RUTGER

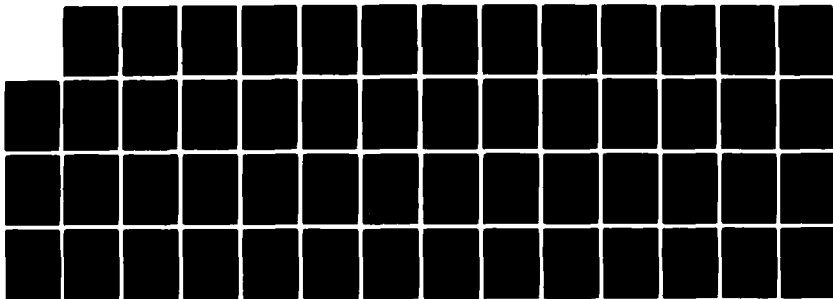
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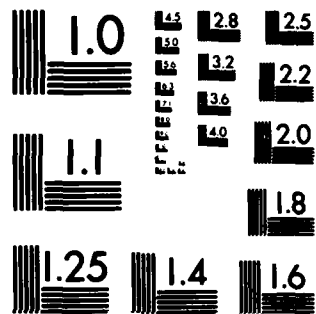
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DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

```

1      SUBROUTINE GLSQ(KK)
2      C      GENERAL LEAST SQUARES ROUTINE TO FIT A SET OF N DATA POINTS
3      C      KK=1: FIT RKP TURNING POINTS BY LEGENDRE POLYNOMIAL
4      C      KK=2: FIT INNER TURNING POINTS BY EXPONENTIAL FUNCTION
5      C      KK=3: FIT OF OUTER TURNING POINTS BY SUM OF C(1)*EXP(-N)
6      DIMENSION T(11)
7      COMMON/GL/X(420),Z(620),N
8      COMMON/FC/F(11),B(11),RE,RAA,RHB,NFI(2),LCUT(4)
9      COMMON/TM1/A(64,64),BB(64)
10     M=NFI(KK)
11     C      .....INITIALIZATION
12     DO 20 J=1,M
13     RR(J)=0.000
14     DO 20 K=1,M
15     A(J,K)=0.000
16     C      .....CALCULATION OF THE MATRIX
17     DO 30 I=1,N
18     DUMMY=FUNC(KK,X(I))
19     DO 30 J=1,M
20     RR(J)=RR(J)+Z(I)*F(J)
21     DO 30 K=1,M
22     A(J,K)=A(J,K)+F(J)*F(K)
23     CALL MATINV(DETERM,M,1.0)
24     DO 40 I=1,M
25     C=I
26     IF (KK.GT.1) NC=NFI(1) + I
27     B(NC) = BB(I)
28     C      .....CALCULATION OF FIT AND STANDARD ERROR
29     SIG=0.0
30     DO 50 I=1,N
31     XCRY=X(I)
32     DUMMY=FUNC(KK,XCRY)
33     DEL=Z(I) - DUMMY
34     PRINT 104,XCRY,Z(I),DUMMY,DEL
35     SIG=SIG+DEL*DEL
36     SIGMA=SQRT(SIG/FLCAT(N-M))
37     C      .....ITERATION TEST
38     IF (M.LE.2) GO TO 60
39     DRDH=ABS(SQRT(ABS(A(M,M)))/RR(M))-SIGMA
40     IF ((SIGMA.GT.1D-3).AND.(DRDH.LT.0.7)) GO TO 60
41     M=M-1
42     NFI(KK) = M
43     GO TO 10
44     C      .....PRINT OUT OF CONSTANTS AND ERROR
45     DO 70 I=1,M
46     T(I)=SQRT(ABS(A(I,I)))*SIGMA
47     DRDH=ABS(T(I)/BB(I))
48     PRINT 102,I,RR(I),T(I),DRDH
49     PRINT 103,N,SIGMA
50     PRINT 101,CONSTANTS OF FIT??
51     PRINT 102,RR(12,*)=0.015,0.04,0.005 ERROR = 0.015,0.04,0.005
52     PRINT 103,NUMBER OF ENTRIES : 0.13, STANDARD ERROR = 0.18014,5/1
53     PRINT 104,1F020.9,3D20.9)
54
55

```

SUBROUTINE GLSQ

74/74 OPT=0,-QUAD= A/ S/ M/-0,-NS

FTN 5.1+544

56
57

RETURN
END

B-64

```

1      SUBROUTINE MATINV(DETERM,N,M,IPV)
2      C      MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS
3      C      IPV.EQ.1: NO SEARCH FOR PIVOT,IPV.NE.1: SEARCH FOR PIVOT
4      C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
5      DIMENSION IPVCT(64),INDEXP(64),INDEXC(64)
6      COMMON/TH1/A(64,64),B(64,1)
7      C      .....INITIALIZATION
8      DETERM=1.0
9      DO 20 J=1,M
10     C      IPVOT(J) = 0
11     DO 550 I=1,N
12     IF (IPV.NE.1) GO TO 40
13     ICLM = I
14     GO TO 260
15     C      .....SEARCH FOR PIVOT ELEMENT
16     40     AMAX = 0.0
17     DO 105 J = 1,M
18     IF (IPVOT(J).EQ.1) GO TO 105
19     C      FOR UNSYMMETRIC MATRIX: A(I,J).NE.A(J,I)
20     C      DO 100 K=1,M
21     C      FOR SYMMETRIC MATRIX: A(I,J).EQ.A(J,I)
22     DO 100 K=J,M
23     IF (IPVOT(K).EQ.1) GO TO 100
24     IF (ABS(AMAX).GE.ABS(A(J,K))) GO TO 100
25     IROW = J
26     ICLM = K
27     AMAX=A(J,K)
28     100     CONTINUE
29     105     CONTINUE
30     IPVOT(ICLM) = IPVOT(ICLM) + 1
31     INDEXP(I) = IROW
32     INDEXC(I) = ICLM
33     C      .....INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
34     IF (IROW.EQ.ICLM) GO TO 260
35     DETERM = -DETERM
36     DO 200 L = 1,M
37     SWAP = A(IROW,L)
38     A(IROW,L) = A(ICLM,L)
39     200     A(ICLM,L) = SWAP
40     IF (M.LE.0) GO TO 260
41     DO 250 L=1,M
42     SWAP = B(IROW,L)
43     B(IROW,L)=B(ICLM,L)
44     250     B(ICLM,L) = SWAP
45     260     PIVOT = A(ICLM,ICLM)
46     IF (M.GT.10) GO TO 330
47     DETERM = DETERM*PIVOT
48     C      .....DIVIDE PIVOT ROW BY PIVOT ELEMENT
49     330     A(ICLM,ICLM) = 1.0
50     DO 350 L=1,M
51     350     A(ICLM,L) = A(ICLM,L)/PIVOT
52     IF (M.LE.0) GO TO 370
53     DO 370 L = 1,M
54     370     B(ICLM,L)=B(ICLM,L)/PIVOT
55     C      .....REDUCE NON-PIVOT ROWS

```

```

56      3=0 DO 550 L=1,N
57      IF (L1.EQ.ICLM) GO TO 550
58      A(L1,ICLM) =0.0
59      DO 450 L= 1,
60      450 A(L1,L) = A(L1,L)-A(ICLM,L)*
61      IF (M.LE.0) GO TO 550
62      DO 500 L=1,N
63      500 B(L1,L) = B(L1,L) - A(ICLM,L)*
64      550 CONTINUE
65      IF (IPV.EQ.1) RETURN
66      C .....INTERCHANGE COLUMNS
67      DO 710 J= 1,N
68      L= N+1-J
69      IROW = INDEX(L)
70      ICLM = INDEX(L)
71      IF (IROW.EQ.ICLM) GO TO 710
72      DO 705 K =1,N
73      SWAP= A(K,IROW)
74      A(K,IROW) = A(K,ICLM)
75      A(K,ICLM) =SWAP
76      705 A(K,ICLM) =SWAP
77      710 CONTINUE
78      RETURN
79      END

```

```

1      FUNCTION FU(C(KK,XX)
2
3      C      ROUTINE DEFINES THE LEGEND POLYNOMIALS FOR FITTING THE PK
4      C      POTENTIAL AND CONTAINS THE TWO EXTRAPOLATION FUNCTION HEREON
5      C      THE INNERMOST AND OUTERMOST TURNING POINTS, RESPECTIVELY.
6      COMMON/FC/F(11),B(11),RE,RAA,RRR,RIN,ROUT,LCUT(4)
7      COMMON/EX/XI(921),YI(921),N
8      IF((XX.LT.RAA).OR.(KK.EQ.1)) GO TO 50
9      IF ((XX.GT.RRR).OR.(KK.EQ.2)) GO TO 50
10     C      .....FUNCTION FOR RKR TURNING POINTS
11     NPOLY = 8
12     FUNC = 0.0
13     NM = (NPOLY + 1)/2
14     NM1 = NM + 1
15     NUP = N + NM1 - NPOLY
16     DO 20 J = NM1,NUP
17     IF (XX.LE.XI(J)) GO TO 30
18     CONTINUE
19     J=NUP
20     L=J-NM
21     LLL = L + NPOLY - 1
22     DO 50 K = L,LLL
23     TERM = 1.0
24     DO 40 M = L,LLL
25     IF (K.EQ.M) GO TO 40
26     TERM = TERM * (XX-XI(M))/(XI(K)-XI(M))
27     CONTINUE
28     TERM = YI(K)*TERM
29     FUNC = FUNC + TERM
30     RETURN
31     C      .....FUNCTION FOR INNER TURNING POINTS
32     X = (RE-XX)/RE
33     F(1) = 1.0
34     FUNC = F(1) * B(1)
35     DO 70 I = 2,NIN
36     F(I) = F(I-1)*X
37     FUNC = FUNC + F(I)*B(I)
38     IF (KK.EQ.1) RETURN
39     FUNC = 10.***FUNC
40     RETURN
41     C      .....FUNCTION FOR OUTER TURNING POINTS
42     X = 1./XX
43     FUNC = 0.0
44     DO 90 I = 1,ROUT
45     F(I) = X**LCUT(I)
46     FUNC = FUNC + F(I)*B(NIN+I)
47     RETURN
48     END

```

```

1      SUBROUTINE YDMF11(NSW)
2      C      PRINT,PUNCH AND READ SUBROUTINE OF DUNHAM COEFFICIENTS
3      C      (NSW.LE.1) PRINT, NSW=1;PRINT AND PUNCH, NSW=2; READ AND
4      C      PRINT, (NSW.GE.3);READ
5      COMMON/YD/YDM(20,10),JM(10)
6      IF (NSW.LT.2) GO TO 40
7      C      .....INITIALIZATION
8      DO 10 IDH = 1,10
9      JM(IDH) = 0
10     DO 10 IDA = 1,20
11     YDM(IDA,IDH) = 0.
12     C      .....READ INSTRUCTIONS
13     READ 101,NDUN,(JM(I),I=1,NDUN)
14     DO 20 IDN=1,NDUN
15     AGBD = JM(IDN)
16     IF (AGBD.EQ.0) GO TO 30
17     DO 20 IDH=1,NDUN
18     YDM(IDH,IDN) = AGBD
19     CONTINUE
20     IF (NSW.GT.2) RETURN
21     C      .....PRINT INSTRUCTIONS
22     PRINT 103
23     DO 60 IDN = 1,20
24     AMX = 0
25     DO 50 IY = 1,10
26     IF (JM(IY).GE.IDN) AMX = IY
27     CONTINUE
28     IF (AMX.EQ.0) GO TO 70
29     PRINT 104,(YDM(IDN,I),I=1,AMX)
30     IF (NSW.NE.1) GO TO 90
31     C      .....PUNCH INSTRUCTIONS
32     PUNCH 101,NDUN,(JM(I),I=1,NDUN)
33     DO 80 IDN = 1,NDUN
34     AGBD = JM(IDN)
35     PUNCH 102,(YDM(I,IDN),I= 1,AGBD)
36     CONTINUE
37     RETURN
38     101 FORMAT (14I5)
39     102 FORMAT (4D18.9)
40     103 FORMAT (' THE DUNHAM COEFFICIENTS *')
41     104 FORMAT (1X,1P8D16.8)
42     END

```

```

1      SUBROUTINE FIPAC(7MU,DE)
2
3      C      ROUTINE RUNNING INVERTED PERTURBATION APP FACH
4      DIMENSION GVSUM(10),FPL(64),MTRMIN(11),PCUT(11),YMAX(11),HJT(11),
5      * MTRIAL(11),GVST(11,10),LTPIAL(11),ER(11),COFF(64),ERROR(64),
6      * FX(11,2403),KA(11,96),KH(11,96)
7      COMMON /EX/XI(921),VI(921),P
8      COMMON /A2/V(2403)
9      COMMON /A3/F(2403)
10     COMMON /A4/ (2403)
11     COMMON /A2/MA,MB
12     COMMON /A4/EPRIAL(100),MTRIAL(100),AJTT,EPRIAL,KV(100)
13     COMMON /YD/YDM(2,10),JM(10)
14     COMMON /YH/YAL(64,64),BL(64)
15     COMMON /PL/YPL(64),AA1,AA2,AA3,PPL
16     COMMON /PD/AINA(100),ADUT(100),EEE(100),BRH(100)
17     INTEGER SCHP
18
19     C      THE ATOMIC UNITS USED INTERNALLY IN THIS PROGRAM ARE DEFINED
20     C      BY THE FOLLOWING CONSTANTS.
21     C      FACHN = RYDBERG CONSTANT * MASS OF THE ELECTRON IN AMU.
22     C      AZERO = BOHR RADIUS
23     C      FACRT= SQRT(H-EAR*AVOGADRO-NUMBER/(4*PI*E)*10**E
24     AZERO= 0.52917706
25     ZIRA = 1.0/AZERO
26     FACHN=60.19972628
27     FACH=FACHN/7MU
28     ZIEN = 1.0/FACH
29     FACR=4.105804544
30     READ 3003, LTEST
31     IF (LTEST.EQ.0) RETURN
32
33     C      .....READ CONTROL VARIABLES FOR SCHROEDINGER ROUTINE
34     READ 3005, N1,NS,IPSI0,MAXIT,EPSC
35     EPS = EPSC*ZIEN
36     READ 3004,RMIN,RMAX,M,NRPTT,IPL,MCH,LSW
37     READ 3021,(MTRMIN(I),MTRIAL(I),HJT(I),I=1,11)
38     IF ((M.EQ.0).OR.(M.GT.2403)) M=2403
39     IF ((NPL.EQ.0).OR.(NPL.GT.31)) NPL=31
40     IF ((NRPTT.EQ.0).OR.(NRPTT.GT.6)) NRPTT = 6
41     DO 80 J= 1,11
42     DO 80 I=1,96
43     KA(J,I) = 0
44     AC    KB(J,I) = 0
45     NTY = 0
46     DO 100 IDA = 1,10
47     IF (BJTT(IDA).LT.1.D-06) GO TO 120
48     NTY = NTY + 1
49     IF (NTY.EQ.0) NTY = 1
50     ABE = YDM(1,2)
51     CBE = ARE*ZIEN
52     RRE = FACRT/SQRT(7MU*ABE)
53     CRE= RRE/AZERO
54     IF (XI(1).GT.RMIN) RMIN = XI(1)
55     IF ((XI(N).LT.RMAX).OR.(RMAX.LT.0.001)) RMAX = XI(N)
56     RM = (RMAX+RMIN)/FLOAT(M-1)
57     DO 140 J = 1,M
58     P(J) = FLOAT(J-1)*RM + RMIN

```

```

56      140 V(J) = FUNC(C,P(J))
57      NT1=NTT +1
58      BJTT(NT1) =C.
59      DO 140 KI = 1,NT1
60      NTRIAL = 99
61      AJTT = BJTT(KI)
62      C .....SEARCH FOR CENTRIFUGAL BATTLE
63      TX = 0.
64      ASX= 1.0+70
65      DO 160 I=1,M
66      SX = V(I) + ABE*(RFE/P(I))*2*AJTT
67      IF (SX.LT.ASX) GO TO 170
68      IF (SX.LE.TX) GO TO 160
69      TX = SX
70      ROUT(KI) = P(I)
71      YMAX(KI)=SX
72      160 ASX=SX
73      CALL BETRL(TX)
74      LTRIAL(KI)=NTRIAL
75      IF (NTRIAL(KI).GT.NTRIAL) NTRIAL(KI) = NTRIAL
76      NTRIAL = NTRIAL(KI)
77      170 ER(KI) = ETRIAL(NTRIAL)
78      C .....SEARCH FOR INNERMOST AND OUTER-MOST TURNING POINTS
79      N3A=M
80      N3B=0
81      DO 240 KI = 1,NTT
82      N3AA = M
83      N3BB = 0
84      ASX = 1.0+70
85      DO 200 I = 1,M
86      SX = V(I) + ABE*(RFE/P(I))*2*BJTT(KI)
87      IF ((SX.LE.ER(KI)).AND. (ASX.GE.ER(KI))) N3AA = I
88      IF ((SX.GE.ER(KI)).AND. (ASX.LE.ER(KI))) N3BB = I
89      IF (N3BB.GT.0) GO TO 220
90      200 ASX = SX
91      220 IF (N3AA.LE.N3A) N3A = N3AA
92      IF (N3BB.GE.N3B) N3B = N3BB
93      240 CONTINUE
94      RMII = P(N3A)
95      RMAA= P(N3B)
96      DO 260 KI = 1,NT1
97      AJTT = BJTT(KI)
98      NTRIAL = LTRIAL(KI)
99      TX =V(N3B) + ABE*(RFE/RMAA)*2*AJTT
100     IF(RMAA.GT.ROUT(KI)) TX = YMAX(KI)
101     SX = V(N3A) + ABE + (RFE/RMII)*2*AJTT
102     IF (SX.LT.TX) TX =SX
103     CALL BETRL(TX)
104     LTRIAL(KI) = NTRIAL
105     IF (NTRIAL.LT.NTRIAL(KI)) LTRIAL(KI) = NTRIAL(KI)
106     260 CONTINUE
107     NREP =1
108     PRINT 3000,MII,RMAX,RH,EPSC,NRPTT,RMII,RMAA,RPE,NPL
109     RMIN = RMIA +ZIFA
110     RMAX = RMAX+7IFA
111     RM = RM+ZIFA
112     AAI = ZIRA*((RMAA+RMII)*RPE-2.0*(RMAA+RMII))/(RMAA-RMII)

```

```

113      AA2= (RMAA+RMI*-2.0+FFE)/(FMAA-RMI)
114      AA3 = Z/PA+KPE
115      DO 270 I = 1,N
116      P(I) = P(I)+7/PA
117      CALL PLEGEN(P(I))
118      DO 270 J = 1,NPL
119      270  FX(J,I) = YPL(J)
120      N3A = M
121      N3B=0
122      280  ISW=LSW
123      IF ((NREP.EQ.1).OR.(NREP.EQ.NRPIT)) ISW=1
124      NT3 = NT1
125      IF (NREP.EQ.NRPIT) GO TO 320
126      C      .....INITIALIZATION
127      DO 300 I = 1,NPL
128      BL(I)= 0.0
129      DO 300 J=1,NPL
130      300  AL(I,J)= 0.0
131      NT3 = NT1
132      320  GVTT2 = 0.
133      AL= 0
134      DO 340 I = 1,N
135      340  V(I) =(V(I)-DE)*ZIEH + CRE*(CRE/P(I))*2*HJT*(1)
136      DO 660 KI = 1,NT3
137      NTRIAL = MTRIAL(KI)
138      NTRMIN = MTRMIN(KI)
139      IF (NREP.LT.NRPIT) GO TO 360
140      NTRIAL = LTRIAL(KI)
141      NTRMIN = 1
142      360  AJTT = BJTT(KI)
143      TX = 1.00+10
144      CALL RETRL(TX)
145      LJT = SORT(AJTT)
146      IF (ISW.EQ.1) PRINT 3007,AJTT,LJT
147      KLIM = 2
148      LLK = 0
149      KLK = 0
150      GVDIF = 0.
151      GVDIF2= 0.
152      C      .....DO SCHRJEDINGER LOOP
153      DO 600 I = NTRMIN,NTRIAL
154      ETRIAL(I) = (ETRIAL(I) - DE)*ZIEH
155      ECALC = ETRIAL(I)
156      MA = KA(KI,I)
157      MB = KB(KI,I)
158      IF (SCHR(NI,MS,MAXIT,EPS,IPSIQ,M,RMIN,RMAX,KV(I),ECALC,FACH)-1)420
159      +,400,350
160      KLK = KLK +1
161      IF (KLK.LT.KLIP) GO TO 420
162      PRINT 3010
163      CALL EXIT
164      400  LLK =LLK +1
165      420  IF (MA.LT.N3A) N3A = MA
166      IF (MB.GT.N3B) N3B = MB
167      KA(KI,I) = MA
168      KB(KI,I) = MB
169      HCALC = (S(1)/P(1))*2 + 4.0*(S(2)/P(2))*2 + (S(4)/P(4))*2

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```

170      KSIMP = M-1
171      DO 440 J=3,KSIMP,2
172      440      BCALC=2.+(S(J)/P(J))**2 + 4.+(S(J+1)/P(J+1))**2 +BCALC
173      BCALC = FACM*BCALC*PH/3.
174      ECALC = DE + ECALC*FACM
175      ETRIAL(I)=ETRIAL(I)*FACM + DE
176      DIFF = ETRIAL(I) - ECALC
177      IF(NREP.EQ.NRPTT) GO TO 540
178      DO 460 K = 1,NPL
179      460      FPL(K) = 0.0
180      DO 490 J = MA,MH
181      AJ = 4 + (J/2)*4 -2*J
182      DO 480 K = 1,NPL
183      480      FPL(K) = FPL(K) + AJ*S(J)**2*FX(K,J)
184      490      CONTINUE
185      DO 500 K = 1,NPL
186      500      FPL(K) = FPL(K)*RH/3.
187      C .....
188      C      STATISTICAL WEIGHT EWG
189      EWG = 1.0
190      C .....
191      DO 520 K = 1,NPL
192      BL(K) = BL(K) + DIFF*FPL(K)*EWG
193      DO 520 J=1,NPL
194      520      AL(K,J) = AL(K,J) + FPL(J)*FPL(K)*EWG
195      540      IF ((I.LT.MTRMIN(KI)).OR.(I.GT.MTRIAL(KI)).OR.(KI.EQ.NT1))GO TO 560
196      *
197      AL= NL + 1
198      GVDIF = GVDIF + DIFF
199      GVDF2 = GVDF2 + DIFF*DIFF
200      GVTT2 = GVTT2 + DIFF*DIFF*EWG
201      560      IF (ISM.EQ.0) GO TO 600
202      DIFR = (BTRIAL(I) -BCALC) *1000.0
203      EEE(I) = ECALC
204      RBB(I) = BCALC
205      IF ((NREP.LT.NRPTT).OR.(KI.EQ.NT1)) GO TO 580
206      IF (I.EQ.MTRMIN(KI)) PRINT 3020
207      C .....PRINT SCHRCDINGER RESULTS
208      580      PRINT 3008,KV(I),ECALC,ETRIAL(I),DIFF,BCALC,DIFR,S(MA),S(MH),MA,MH
209      IF ((NREP.LT.NRPTT).OR.(KI.EQ.NT1)) GO TO 600
210      IF (I.EQ.MTRIAL(KI)) PRINT 3020
211      600      CONTINUE
212      IF ((NREP.LT.NRPTT).OR.(MCH.NE.1)) GO TO 620
213      C      PUNCH 3012,NTRMIN,ETRIAL
214      C      PUNCH 3019,(KV(I),EEE(I),RBB(I),AJTT,I=NTRMIN,NTFIAL)
215      620      IF(ILLK.GE.1) PRINT 3009,LLK
216      APLTST = MTRIAL(KI) - MTRMIN(KI) + 1
217      GVDF2 = SQRT(GVDF2/APLTST)
218      GVST(KI,NREP) = GVDF2
219      GVDA = GVDIF/APLTST
220      IF (ISM.EQ.1) PRINT 3011,GVDIF,GVDA,GVDF2
221      DO 640 I = 1,M
222      640      V(I) = V(I) - CBE*(CRE/P(I))**2*AJT
223      IF (KI.EQ.NT1) GO TO 660
224      AJTT= BJTT(KI)+1
225      DO 650 I = 1,M
226      650      V(I) = V(I) + CHE*(CFE/P(I))**2*AJT

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227      600 CONTINUE
228      GVTT2= GVTT2/FLCAT(PL-NPL)
229      GVSUM(NREP) = SQRT(GVTT2)
230      IF (NREP.EQ.1) GO TO 700
231      NREP=NREP - 1
232      PRINT 3012,NRM1
233      GVT = GVSUM(NREP)
234      DO 680 K= 1,NPL
235      OBAA = COEFF(K)
236      T = SQRT(ERROR(K))*GVT
237      TEMP = ABS(T/OBAA)
238      680 PRINT 3013,K,OBAA,T,TEMP
239      700 DO 710 I = 1,M
240      V(I) = V(I)*FACH + DE
241      IF (NREP.EQ.NRPT) GO TO 800
242      CALL MATINV(DETERM,NPL,1.0)
243      DO 720 K = 1,NPL
244      COEFF(K) = HL(K)
245      720 ERROR(K) = ABS(AL(K,K))
246      C .....CORRECTION OF POTENTIAL AND YDM(1,1)
247      VMIN = 1.00*10
248      DO 760 I = 1,M
249      DO 740 K = 1,NPL
250      740 V(I) = V(I) + HL(K)*FX(K,I)
251      IF (V(I).LT.VMIN) VMIN = V(I)
252      760 CONTINUE
253      YDM(1,1) = YDM(1,1) - VMIN
254      DO 780 I = 1,M
255      780 V(I) = V(I) - VMIN
256      NREP = NREP + 1
257      GO TO 260
258      800 PRINT 3001
259      DO 840 KE = 1,NPL
260      COEFF(KE) = SQRT(ABS(AL(KE,KE)))
261      DO 820 KEE = 1,KE
262      820 FPL(KEE) = (ABS(AL(KE,KEE))/COEFF(KE))/COEFF(KEE)
263      840 PRINT 3002,KE,(FPL(L),L=1,KE)
264      CALL POTTAB(GVT,AZERO,DE,M,NTRIAL)
265      PRINT 3014,NJA,P(NJA),NJB,P(NJB)
266      PRINT 3015
267      DO 860 I = 1,NPT
268      860 PRINT 3016,BJTT(I),(GVST(I,L),L=1,NRPT)
269      CONTINUE
270      PRINT 3020
271      PRINT 3017,(GVSUM(I),I=1,NRPT)
272      RETURN
273      3001 FORMAT('1',* CORRELATION MATRIX OF THE COEFFICIENTS')
274      3002 FORMAT('15,10F10.6,4(75X,10F10.6)')
275      3003 FORMAT(11)
276      3004 FORMAT(2F10.0,6I5)
277      3005 FORMAT(4I4,D10.0)
278      3006 FORMAT(' RMIN = ',F6.3,' , RMAX = ',F6.3,' , PACING = ',F11.7
279      *// CONVERGENCE CRITERION IS ERROR LESS THAN ',D9.2/
280      *// NUMBER OF ITERATIONS = ',I3//* PARAMETERS OF THE FITTING POLY*
281      *// MIAL*//* RMIN = ',F7.3,' RMAX = ',F7.3,' RE = ',F7.3,' NPL = ',I3//)
282      3007 FORMAT(' RESULTS OF SCHRÖDINGER EQUATION FOR J(J+1) = ',F6.1
283      *// AND J = ',I3,'//4X,'V GV CAL GV MEAS GV *-C GV CAL

```

```

284      * HV M-C S(MA) S(MH) MA MH */
285      3008 FORMAT (1X,I4,2F12.5,F11.5,F13.4,F10.5,2(1PD10.1),2I6)
286      3009 FORMAT ('O PROGRAM SUCCESSFUL. (MAXIT REACHED ',I2,' TIME')')
287      3010 FORMAT ('O SCNR NOT SUCCESSFUL')
288      3011 FORMAT('/// SUM OF DIFF.=',1PD12.4,' AVERAGE DIFF. =',D12.4,'
289      * RMS OF GV =',D12.4//)
290      3012 FORMAT ('O COEFFICIENTS OF THE LEGENDRE POLYNOMIALS AFTER ITERATION
291      * N NO. ',I2//)
292      3013 FORMAT('H(',I2,') =',1PD16.9,4X,'RMS ERROR =',D16.6,4X,'RELATIVE
293      * RMS ERROR = ',D14.4)
294      3014 FORMAT(/ 'RECOMMENDED INTEGRATION LIMITS RMIN = R(',I4,') =',F6.1
295      * ,RMAX = R(',I4,') =',F7.3//)
296      3015 FORMAT (1H1,' SUMMARY OF ERRORS OF THE INVERTED PERTURBATION APP
297      * ACH '///3X,'J(J+1)',4X,'1.',-X,'2.',-X,'3.',8X,'4.',-X,'5.',8X,
298      * '6.',8X,'7.',8X,'8.',8X,'9.',7X,'10. ITERATION//)
299      3016 FORMAT (1X,F8.1,10F10.5)
300      3017 FORMAT (/ ' AVERAGE',10F10.5)
301      3018 FORMAT(2I10)
302      3019 FORMAT (I2,3D16.9)
303      3020 FORMAT (1X,57(2H--))
304      3021 FORMAT (6(I2,I3,F7.0)/5(I2,'3,F7.0))
305      END

```

FUNCTION SCHP 74/74 OPT=0,500,DE= A/ 0/ 4/-0,-03 FTM 5.1+55
DO=-LONG/-CT,AFB=-COMMON/-FIXED,CS= USFF/-FIXED,DB= TH/ SR/ CL/ ER/-10/ -ND/-S*,PL
FTN5,08. 10000

```

1      INTEGER FUNCTION SCH (NI,NS,MX,EPS,IPSIQ,NN,PMI,PMAX,KV,E ,FACM)
2      C      SCHROEDINGER EQUATION SOLVING ROUTINE FOR PSI**2*(E-V)*P**1
3      C      NI=1 PRINT ITERATIONS, OTHERWISE NO PRINTOUT
4      C      NS=1: PRINT SOLUTIONS WITH EACH ENERGY LEVEL, OTHER WISE NO PR
5      COMMON/A2/V(2403)
6      COMMON/A4/S(2403)
7      COMMON/A12/MA,PB
8      EPRIN = EG*FACM
9      IF (NI.EQ.1) PRINT 201,KV,EPRIN
10     H = (RMAX -RMIN)/FLCAT(NN-1)
11     H2= H*M
12     HV= H2/12.00
13     E=EG
14     TEST = -1.00
15     DE = 0.00
16     C      .....DETERMINATION OF INNER INTEGRATION LIMIT
17     DO 10 IPP = 1,NN
18     LCRIT = IPP -1
19     IF (V(IPP).LE.E) GO TO 13
20     10 CONTINUE
21     13 KERR =1
22     IF (LCRIT.LT.1) GO TO 83
23     NL1 = LCRIT + 2
24     WCRIT = 0.
25     DO 16 IPP = 1,LCRIT
26     LCT =LCRIT + 1 - IPP
27     WCRIT = WCRIT + SORT(V(LCT) - E)*H
28     IF (WCRIT.GE.20.0) GO TO 20
29     16 CONTINUE
30     20 MA = LCT
31     C      .....DETERMINATION OF OUTER INTEGRATION LIMIT
32     DO 23 IPP= 1,NN
33     LCT = NN + 1 - IPP
34     IF (V(LCT).LE.E) GO TO 26
35     23 CONTINUE
36     26 LCRIT = LCT +1
37     KERR = 2
38     IF (LCRIT.GT.NN) GO TO 83
39     WCRIT = 0.
40     DO 30 IPP = LCRIT,NN
41     LCT = IPP
42     WCRIT=WCRIT +SORT(V(IPP) - E)*H
43     IF (WCRIT.GE.20.0) GO TO 33
44     30 CONTINUE
45     33 MB=LCT
46     DO 35 IPP = NL1,NN
47     IF (V(IPP).GT.E) GO TO 130
48     35 CONTINUE
49     130 NL2 = IPP
50     DO 140 I = 1,MA
51     140 S(I)=0.0
52     DO 150 I = MB,NN
53     150 S(I) = 0.0
54     MAP1 = MA + 1
55     C      .....START ITERATION LOOP

```

```

56      DO 60 IT = 1,MX
57      C      .....START INWARD INTEGRATION
58      S(PB) = 1.0-10
59      GN = V(MB) - E
60      GI = V(MB-1) - E
61      RMOX = RMIA + H*FLOAT(MB-1)
62      S(MB-1) = S(MB)*EXP(-RMOX*SQRT(GN))-(RMOX-H)*SQRT(GI))
63      YA = (1.00 - HV*GN)*S(MB)
64      YB = (1.00 - HV*GI)*S(MB-1)
65      M = MB-2
66      36      YC = YB + ((YB-YA) + H2*GI*S(M+1))
67      GI = V(M) - E
68      S(M) = YC/(1.00-HV*GI)
69      KER = 3
70      IF (S(M).LT.0.000) GO TO 83
71      IF (S(M).LE.S(M+1))GO TO 40
72      YA = YB
73      YH = YC
74      M = M-1
75      GO TO 36
76      40      MSAVE = M
77      PH = S(M)
78      YIN = YB/PH
79      DO 43 J = M,PB
80      43      S(J)=S(J)/PH
81      C      .....START OUTWARD INTEGRATION
82      S(MA) = 1.00-10
83      YA=0.000
84      GI=V(MA) - E
85      YB = (1.00-HV*GI)*S(MA)
86      DO 46 I = MA+1,M
87      YC = YB + ((YB -YA) + H2*GI*S(I-1))
88      GI = V(I) -E
89      S(I) = YC/(1.00-HV*GI)
90      YA=YH
91      46      YH=YC
92      PH=S(M)
93      YOUT= YA/PH
94      YH=YC/PH
95      DO 50 J=MA,M
96      50      S(J)=S(J)/PH
97      C      .....CORRECTION
98      DF = 0.000
99      DO 53 J=MA,MH
100      53      DF= DF - S(J)*S(J)
101      F = (-YOUT -YIN + 2.000*YH)/H2+ (V(M) - E)
102      DOLD = DE
103      DE = -F/DF
104      IF (N1.NE.1) GO TO 56
105      EPRIN =E*FACH
106      DEPRIN = DE*FACH
107      PRINT 203,IT,EPRIN,F,DF,DEPRIN,MSAVE
108      56      EGLO =E
109      E=E +DE
110      TEMP = ABS(DOLD) -AH (DF)
111      IF (TEMP.GT.TEST) TEST =TEMP
112      IF (TEST.LT.0.000) GO TO 60

```

```

113       IF (ABS(E-FOLD).LE.ABS(FPS)) GO TO 63
114       60 CONTINUE
115       SCHR = 1
116       GO TO 66
117       C.....COUNT MODE
118       63 SCHR = 0
119       66 KV = 0
120       DO 70 J = NL1,NL2
121         IF ((S(J-1).LT.0.0).AND.(S(J).GE.0.0).AND.(S(J+1).GT.0.0)) KV=KV+1
122         IF ((S(J-1).GT.0.0).AND.(S(J).LE.0.0).AND.(S(J+1).LT.0.0)) KV=KV+1
123       70 CONTINUE
124       C .....NORMALIZE
125       SA=SQRT(-H*DF)
126       DO 73 J = MA,MB
127       73 S(J) = S(J)/SA
128       C .....PRINT SOLUTION
129       IF (NS.NE.1) GO TO 80
130       PRINT 204,KV,E
131       PRINT 205,(I,S(I),I=1,MR,IPSIQ)
132       80 EQ=E
133       RETURN
134       83 PRINT 202,KEKR
135       SCHR = 2
136       RETURN
137       201 FORMAT('1',* SCHR- SOLUTION OF RADIAL SCHR. EQUATION FOR V= ',I3,*
138       *X,'ETRIAL=',1PE15.7,' (1/CM)**
139       * * ITER=',5X,'E',14X,'F(F)',12X,'DF(E)',11X,'D(E)',4X)
140       202 FORMAT(' KERR = ',I2,' DIFF EQUATION SOLUTION TECHNIQUE FAIL')
141       203 FORMAT('///1',2X,1P4F16.7,5X,' THE CROSSING PT. OCCURS AT ',I4)
142       204 FORMAT('1 SCHR-SOLUTION OF RADIAL SCHR. EQUATION FOR V= ',I3,' E=
143       * ',1PE15.7/'0 1',7X,'S(I) 1',5(20H 1 (I) )
144       205 FORMAT(6(15,1PE15.7))
145       END

```

```

1 SUBROUTINE PLYN
2 COMMON/1/X(2403),Y(2403),NUMX,NPOLY,POLYN,XXX
3 C THE ARRAY X HAS TO BE IN INCREASING ORDER
4 AM = (NPOLY+1)/2
5 AM1 = AM +1
6 NUP = NUMX + AM1 - 1,NPOLY
7 DO 2 J = AM1,NUP
8   IF (XXX.LE.X(J)) GO TO 4
9   2 CONTINUE
10  J=NUP
11  L= J-AM
12  LLL=L + NPOLY -1
13  POLYN = 0.0
14  DO 6 K=L,LLL
15    TERM = 1.0
16    DO 5 M=L,LLL
17      IF (K.NE.M) TERM =TERM*(XXX-X(M))/(X(K)-X(M))
18    CONTINUE
19    5 TERM = Y(K)*TERM
20    6 POLYN=POLYN +TERM
21  RETURN
22  END

```

```

1      SUBROUTINE HETRL(TX)
2      C      THIS SUBROUTINE CALCULATES THE VALUES OF ETRIAL AND HTRIAL. IF
3      C      TRIAL=1 THE VALUES ARE TAKEN WHICH HAVE BEEN READ IN FROM THE
4      C      RK3 DECK.
5      DIMENSION YIA(10)
6      COMMON/YD/YDH(20,10),IM(10)
7      COMMON/AN4/ETRIAL(10),HTRIAL(10),AJTT,ATRIAL,KV(10)
8      IF (NTRIAL.EQ.0) RETURN
9      NC=0
10     NIN=NTRIAL
11     EQ=0.
12     DO 40 I = 1,NIN
13     KV(I) = NC
14     NC = NC + 1
15     ANV = FLGAT(I) - 0.5
16     NAB = 0
17     DO 10 IA = 1,10
18     NGBD = IM(IA)
19     IF (NGBD.EQ.0) GO TO 20
20     NAB = NAB + 1
21     FACV = 1.
22     YIA(IA) = 0.
23     DO 10 IB = 1,NGBD
24     YIA(IA) = YIA(IA) + FACV*YDH(IM,IA)
25     10     FACV = FACV*ANV
26     20     YIA(NAB+1) = 0.
27     ETRIAL(I) = 0.
28     HTRIAL(I) = 0.
29     FACJ = 1.
30     DO 30 IA = 1,NAH
31     ETRIAL(I) = ETRIAL(I) + YIA(IA)*FACJ
32     AIA = IA
33     HTRIAL(I) = HTRIAL(I) + YIA(AIA+1)*FACJ*AIA
34     30     FACJ = FACJ*AJTT
35     IF (ETRIAL(I).LT.EQ) GO TO 50
36     IF (ETRIAL(I).GT.TX) GO TO 50
37     40     EQ = ETRIAL(I)
38     GO TO 60
39     50     NC=NC + 1
40     NTRIAL = NC
41     RETURN
42     END

```

```

1      SUBROUTINE PLEGE(Z)
2      C      THIS SUBROUTINE CALCULATES THE LEGENDRE POLYNOMIALS YPL BY MEANS
3      C      OF A RECURSION RELATION, AND MULTIPLIES THEM BY AN EXPONENTIAL COR-
4      C      RECTION FUNCTION, AS REQUIRED FOR THE CORRECTION FUNCTION WHICH MOD-
5      C      IFIES THE POTENTIAL AFTER EVERY ITERATION.
6      COMMON/PL/YPL(64),AA1,AA2,AA3,NPL
7      ZZ = (Z-AA3)/(AA1-AA2*Z)
8      YPL(1) = 1.
9      YPL(2) = ZZ
10     DO 10 I = 3,NPL
11     AI = I
12     10     YPL(I) = (YPL(I-1)*ZZ*(2.0-AI-1.)-YPL(I-2)*(AI-1.))/AI
13     FAC = ZZ**10*3.
14     IF (FAC.GT.50.) GO TO 20
15     FAC = EXP(-FAC)
16     GO TO 30
17     20     FAC = 0.0
18     30     DO 40 I=1,NPL
19     40     YPL(I) = YPL(I)*FAC
20     RETURN
21     END

```

SUBROUTINE PCTTAB 74/74 OPT=0, EQUAD= A/ 5/ P/-D,-D0 F1 F1+100
DO=-LONG/-GT, AFG=-COMMON/-FIXED, CS= USER/-FIXED, DH= TB/ SB/ CL/ F1/-TD/ MC/-T
FTN5, DH. 0000

```

1      SUBROUTINE PCTTAB(GVT,AZERO,DE,M,NTRIAL)
2      C      ROUTINE FOR INTERPOLATION OF INNER AND OUTER TURNING POINTS
3      DIMENSION ZI(521)
4      COMMON/PO/AINN(100),AOUT(100),EEE(100),HBB(100)
5      COMMON/T1/XR(2403),YR(2403),NUMX,NPOLY,POLY%,XXX
6      COMMON/A2/V(2403)
7      COMMON/A3/P(2403)
8      COMMON/EX/XI(921),YI(921),N
9      COMMON/TM1/AL(64,64),BL(64)
10     COMMON/PL/YPL(64),AA1,AA2,AA3,NPL
11     C      .....SEARCH FOR MINIMUM
12     DO 10 I = 1,M
13     10    P(I) = P(I)+AZERO
14     TX = V(I)
15     DO 15 I = 2,M
16     IF (V(I).GE.TX) GO TO 15
17     TX=V(I)
18     IMIN = I
19     15    CONTINUE
20     C      .....INTERPOLATION OF THE POTENTIAL
21     NPOLY = 4
22     DO 30 NR = 1,2
23     NA =1
24     NB = IMIN
25     IF (NR.EQ.1) GO TO 20
26     NA=YPIN
27     NB=M
28     20    DO 25 I = NA,NB
29     NUMX= I + 1 -NA
30     K=I
31     IF (NR.EQ.1) K = IMIN + 1 - I
32     XR(NUMX)= V(K)
33     25    YR(NUMX)=P(K)
34     DO 30 I = 1,NTRIAL
35     XXX=EEE(I)
36     CALL PLLYN
37     IF (NR.EQ.1) AINN(I) = POLYN
38     IF (NR.EQ.2) AOUT(I) = POLYN
39     30    CONTINUE
40     C      .....PRINTOUT OF THE TURNING POINTS
41     PRINT 101
42     C      PUNCH 101
43     DO 35 I = 1,NTRIAL
44     IA=I-1
45     BBB(I)=BHB(I)+100.0
46     IF (IA.EQ.40) PRINT 101
47     C      PUNCH 102,IA,EEE(I),AINN(I),AOUT(I),HBB(I)
48     35    PRINT 102,IA,EEE(I),AINN(I),AOUT(I),HBB(I)
49     DO 40 I = 1,M
50     XR(I) = P(I)
51     40    YR(I)=V(I)
52     NUMX = M
53     IA = 0
54     IB = N +1
55     DO 55 I=1,N

```

SUBROUTINE POTRAD

74/74

OPT=0,ROUND= A/ 0/ M/-0,-00

FT= 9.1+004

```

56      XXX = XI(I)
57      IF (XXX.GE.P(1)) GO TO 45
58      IA = I
59      GO TO 55
60      45  IF (XXX.LE.P(M)) GO TO 50
61      IB = I
62      GO TO 60
63      50  CALL PLYNN
64      ZI(I) = YI(I) - POLYX
65      YI(I) = POLYX
66      55  CONTINUE
67      60  IF (IA.EQ.0) GO TO 70
68      DO 65 I = 1, A
69      ZI(I) = ZI(IA+1)
70      65  YI(I) = YI(IA+1) - ZI(I)
71      70  IF (IB.EQ.(N+1)) GO TO 80
72      DO 75 I = IB, N
73      ZI(I) = ZI(IB-1)
74      75  YI(I) = YI(IA+1) - ZI(I)
75      C    .....PRINTOUT OF THE FINAL POTENTIAL AND OF THE STANDARD ERROR
76      80  PRIN 103
77      DO 99 I = 1, A
78      ST = XI(I)/AZERO
79      CALL PLEGEN(ST)
80      ST=0.0
81      C    DO 85 K = 1,NPL
82      C 85  ST = ST + BL(K,1)*YPL(K)
83      C    IF (ABS(ST).GT.1.0D-6) GO TO 90
84      C    ST=0.0
85      C    GO TO 99
86      C 90  ST=0.0
87      DO 95 J=1,NFL
88      DO 95 K=1,NPL
89      95  ST = ST + YPL(K)*AL(K,J)*YPL(J)
90      ST = SQRT(ABS(ST))*CVT
91      95  FPRINT 104,XI(I),YI(I),ZI(I),ST
92      101  FORMAT(1H1,' FINAL SET OF TURNING POINTS',//5X,1HV,5X,'L(H)',1V
93      +,'R(PIN)',11X,'R(PAX)',10X,'R(V+100%')
94      102  FORMAT(1X,15,F15.3,F14.6,F15.6,F15.7)
95      103  FORMAT(1H1,' FINAL POTENTIAL',//12X,'P',15X,'L(P)',15X,'K--IPA',1
96      +2X,'ERROR'//)
97      104  FORMAT (1X,1PD20.9,3D20.9)
98      RETURN
99      END

```

POTENTIAL OF THE PHC MOLECULE (TCTAL FI)
GROUND STATE FOR LEAD OXIDE

THE CODE NUMBER FOR THIS STATE IS

THE MASSES OF THE TWO ATOMS,
BASED ON C=12 ARE 1.599940000D+01 AND 2.071900000D+02

DE = .3157000D+05

TE = 0.

LIM1 = 1.0000 LIM2 = 7.5000 WFA = 74.0' VMIC = .25
 IOPFG = 0 IPNRK = 0 IPNIPA = 0

POTENTIAL GENERATED BY AKR IS AS FOLLOWS

V	POTENTIAL ENERGY	INERTIAL ENERGY	EMIC	SWAN	
-0.25	179.5606	.30682513-0+00	1.633560991	1.060082 20	.177 001000-1
0.00	359.5572	.3063006500+00	1.660376556	1.060082 21	.177 001000-1
.25	538.7080	.30553428-0+00	1.670323006	1.060082 22	.177 001000-1
.50	717.8136	.3050760500+00	1.676367774	2.000084 23	.177 001000-1
.75	895.6741	.3050359300+00	1.680475743	2.000084 24	.177 001000-1
1.00	1073.4498	.3045639500+00	1.683224564	2.027014 25	.177 001000-1
1.25	1250.2612	.3041300500+00	1.685666144	2.027014 26	.177 001000-1
1.50	1427.7844	.3036743500+00	1.687624122	2.045222 27	.177 001000-1
1.75	1604.2717	.3032167300+00	1.689151555	2.045222 28	.177 001000-1
2.00	1780.3114	.3027572500+00	1.690776230	2.054202 29	.177 001000-1
2.25	1955.5077	.3022958500+00	1.692496155	2.054202 30	.177 001000-1
2.50	2131.0609	.3018326500+00	1.694316654	2.077484 31	.177 001000-1
2.75	2305.7712	.3013675300+00	1.696237403	2.077484 32	.177 001000-1
3.00	2480.6388	.3009005500+00	1.698257154	2.091770 33	.177 001000-1
3.25	2653.4634	.3004316400+00	1.699423240	2.091770 34	.177 001000-1
3.50	2827.2465	.2999609500+00	1.702661444	2.105362 35	.177 001000-1
3.75	3000.0171	.2994823300+00	1.705503513	2.111932 36	.177 001000-1
4.00	3172.6657	.2990138500+00	1.707532553	2.116374 37	.177 001000-1
4.25	3344.7425	.2985374800+00	1.709188365	2.124704 38	.177 001000-1
4.50	3516.3575	.2980592500+00	1.710555574	2.130522 39	.177 001000-1
4.75	3687.5310	.2975791300+00	1.711653743	2.137060 40	.177 001000-1
5.00	3858.2630	.2970971500+00	1.712220106	2.143097 41	.177 001000-1
5.25	4028.5536	.2966132800+00	1.712959502	2.149055 42	.177 001000-1
5.50	4198.4030	.2961275500+00	1.713666076	2.154936 43	.177 001000-1
5.75	4367.8112	.2956399300+00	1.714341512	2.160744 44	.177 001000-1
6.00	4536.7782	.2951504500+00	1.714986435	2.166490 45	.177 001000-1
6.25	4705.3042	.2946590400+00	1.715594921	2.172174 46	.177 001000-1
6.50	4873.3491	.2941658500+00	1.716165953	2.177805 47	.177 001000-1
6.75	5041.0330	.2936707300+00	1.716700773	2.183377 48	.177 001000-1
7.00	5208.2359	.2931737500+00	1.717206334	2.188886 49	.177 001000-1
7.25	5374.9979	.2926748400+00	1.717682576	2.194334 50	.177 001000-1
7.50	5541.3184	.2921741500+00	1.718129420	2.199725 51	.177 001000-1
7.75	5707.1987	.2916715300+00	1.718544922	2.205057 52	.177 001000-1
8.00	5872.6376	.2911670500+00	1.718926004	2.210329 53	.177 001000-1
8.25	6037.6353	.2906606600+00	1.719272236	2.215546 54	.177 001000-1
8.50	6202.1720	.2901524500+00	1.719584607	2.220707 55	.177 001000-1
8.75	6366.3574	.2896423300+00	1.719863164	2.225792 56	.177 001000-1
9.00	6529.4915	.2891303500+00	1.720112121	2.230802 57	.177 001000-1

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12.75	9555.7471	27909633.0+00	1.66726214	2.331671110	2.331671110
14.00	9710.5597	27895625.0+00	1.667933771	2.332545250	2.332545250
14.25	9864.5265	27794540.0+00	1.667406022	2.333545250	2.333545250
14.50	10318.1472	2773.225.0+00	1.665003020	2.334151750	2.334151750
14.75	10172.3214	2768.1713.0+00	1.663623261	2.334151750	2.334151750
15.00	10325.3487	2762.015.0+00	1.662266643	2.334151750	2.334151750
15.25	10477.9286	2757.120.0+00	1.660927046	2.335522.71	2.335522.71
15.50	10630.6413	2751.635.0+00	1.659511341	2.336522.71	2.336522.71
15.75	10781.7458	2745.9793.0+00	1.6579315773	2.337522.71	2.337522.71
16.00	10932.5417	2740.330.0+00	1.65774.35	2.337522.71	2.337522.71
16.25	11083.768	2734.670.0+00	1.657574695	2.337522.71	2.337522.71
16.50	11234.1065	2728.9245.0+00	1.657454542	2.338004362	2.338004362
16.75	11383.9945	2723.267.0+00	1.6573331054	2.338004362	2.338004362
17.00	11533.5322	2717.5675.0+00	1.6572132350	2.338004362	2.338004362
17.25	11682.4192	2711.828.0+00	1.6570951930	2.338004362	2.338004362
17.50	11830.9549	2706.0715.0+00	1.6569767453	2.338004362	2.338004362
17.75	11979.0349	2700.2555.0+00	1.6568464542	2.338004362	2.338004362
18.00	12126.6706	2694.5005.0+00	1.656717014	2.338004362	2.338004362
18.25	12273.2496	2688.7545.0+00	1.6565864550	2.338004362	2.338004362
18.50	12420.5753	2682.545.0+00	1.6564564550	2.338004362	2.338004362
18.75	12566.8470	2676.033.0+00	1.656326406	2.338004362	2.338004362
19.00	12712.6644	2669.5244.0+00	1.656196406	2.338004362	2.338004362
19.25	12858.6267	2663.0112.0+00	1.656066406	2.338004362	2.338004362
19.50	13002.5335	2656.5005.0+00	1.655936406	2.338004362	2.338004362
19.75	13147.340	2650.0112.0+00	1.655806406	2.338004362	2.338004362
20.00	13291.3774	2643.5005.0+00	1.655676406	2.338004362	2.338004362
20.25	13434.9141	2637.0112.0+00	1.655546406	2.338004362	2.338004362
20.50	13577.9523	2630.5005.0+00	1.655416406	2.338004362	2.338004362
20.75	13720.6118	2624.0112.0+00	1.655286406	2.338004362	2.338004362
21.00	13862.7720	2617.5005.0+00	1.655156406	2.338004362	2.338004362
21.25	14004.9721	2611.0112.0+00	1.655026406	2.338004362	2.338004362
21.50	14145.7114	2604.5005.0+00	1.654896406	2.338004362	2.338004362
21.75	14286.9693	2598.0112.0+00	1.654766406	2.338004362	2.338004362
22.00	14426.8051	2591.5005.0+00	1.654636406	2.338004362	2.338004362
22.25	14566.6575	2585.0112.0+00	1.654506406	2.338004362	2.338004362
22.50	14704.8472	2578.5005.0+00	1.654376406	2.338004362	2.338004362

22.75	14099.5722	25804353.0+00	1.6495011160	2.501649570	425.621810+30	103.02170+00
23.00	14083.5320	2574665500+00	1.644147280	2.505522045	425.621810+30	103.02170+00
23.25	15121.3260	25664768.0+00	1.647376006	2.510404041	434.3629150+30	104.70020+00
23.50	15258.1533	2562269500+00	1.646567144	2.512992955	437.00420+30	104.70020+00
23.75	15356.0131	25560432.0+00	1.645770547	2.520187131	442.00450+30	104.70020+00
24.00	15532.6047	2549758500+00	1.644946064	2.525091377	447.00450+30	104.70020+00
24.25	15668.7273	2543533400+00	1.644213500	2.53000264	447.00450+30	104.70020+00
24.50	15804.3799	2537252500+00	1.643452131	2.534922124	447.00450+30	104.70020+00
24.75	15939.5618	2530951300+00	1.642703791	2.539850437	447.00450+30	104.70020+00
25.00	16074.2721	25246631500+00	1.641966294	2.544767125	447.00450+30	104.70020+00
25.25	16208.5099	2518292200+00	1.641240143	2.5496840134	447.00450+30	104.70020+00
25.50	16342.2743	2511935500+00	1.640525337	2.55460134	447.00450+30	104.70020+00
25.75	16475.5646	2505559300+00	1.639821632	2.559516501	447.00450+30	104.70020+00
26.00	16608.3797	2499164500+00	1.639124521	2.56443160	447.00450+30	104.70020+00
26.25	16740.7187	2492750500+00	1.638447037	2.569346745	447.00450+30	104.70020+00
26.50	16872.5608	2486318500+00	1.637776030	2.574261840	447.00450+30	104.70020+00
26.75	17003.9649	2479867500+00	1.637115626	2.579176920	447.00450+30	104.70020+00
27.00	17134.4702	2473357500+00	1.636465704	2.584092000	447.00450+30	104.70020+00
27.25	17265.2956	2466908500+00	1.635826179	2.589007080	447.00450+30	104.70020+00
27.50	17395.2402	2460461500+00	1.635187002	2.593922160	447.00450+30	104.70020+00
27.75	17524.7030	2454014500+00	1.634547743	2.598837240	447.00450+30	104.70020+00
28.00	17653.6631	2447567500+00	1.633908952	2.603752320	447.00450+30	104.70020+00
28.25	17782.1793	2441120500+00	1.633270094	2.608667400	447.00450+30	104.70020+00
28.50	17910.1507	2434673500+00	1.632631236	2.613582480	447.00450+30	104.70020+00
28.75	18037.7162	2428226500+00	1.631992378	2.618497560	447.00450+30	104.70020+00
29.00	18164.7548	2421779500+00	1.631353520	2.623412640	447.00450+30	104.70020+00
29.25	18291.3054	2415332500+00	1.630714662	2.628327720	447.00450+30	104.70020+00
29.50	18417.3670	2408885500+00	1.630075804	2.633242800	447.00450+30	104.70020+00
29.75	18542.5344	2402438500+00	1.629436946	2.638157880	447.00450+30	104.70020+00
30.00	18752.6065	2395991500+00	1.628798088	2.643072960	447.00450+30	104.70020+00
30.25	18916.7009	2389544500+00	1.628159230	2.647988040	447.00450+30	104.70020+00
30.50	19080.8004	2383097500+00	1.627520372	2.652903120	447.00450+30	104.70020+00
30.75	19244.9000	2376650500+00	1.626881514	2.657818200	447.00450+30	104.70020+00
31.00	19409.0000	2370203500+00	1.626242656	2.662733280	447.00450+30	104.70020+00
31.25	19573.1000	2363756500+00	1.625603798	2.667648360	447.00450+30	104.70020+00
31.50	19737.2000	2357309500+00	1.624964940	2.672563440	447.00450+30	104.70020+00
31.75	19901.3000	2350862500+00	1.624326082	2.677478520	447.00450+30	104.70020+00
32.00	20065.4000	2344415500+00	1.623687224	2.682393600	447.00450+30	104.70020+00
32.25	20229.5000	2337968500+00	1.623048366	2.687308680	447.00450+30	104.70020+00
32.50	20393.6000	2331521500+00	1.622409508	2.692223760	447.00450+30	104.70020+00
32.75	20557.7000	2325074500+00	1.621770650	2.697138840	447.00450+30	104.70020+00
33.00	20721.8000	2318627500+00	1.621131792	2.702053920	447.00450+30	104.70020+00
33.25	20885.9000	2312180500+00	1.620492934	2.706969000	447.00450+30	104.70020+00
33.50	21050.0000	2305733500+00	1.619854076	2.711884080	447.00450+30	104.70020+00
33.75	21214.1000	2299286500+00	1.619215218	2.716799160	447.00450+30	104.70020+00
34.00	21378.2000	2292839500+00	1.618576360	2.721714240	447.00450+30	104.70020+00
34.25	21542.3000	2286392500+00	1.617937502	2.726629320	447.00450+30	104.70020+00
34.50	21706.4000	2279945500+00	1.617298644	2.731544400	447.00450+30	104.70020+00
34.75	21870.5000	2273498500+00	1.616659786	2.736459480	447.00450+30	104.70020+00
35.00	22034.6000	2267051500+00	1.616020928	2.741374560	447.00450+30	104.70020+00

20.75	20549.6424	22635313	0.000	1.612799007	2.74744772	1.61227737000	1.61227737000
21.00	21064.6696	22636110	0.000	1.6126626102	2.752550474	1.61177130000	1.61177130000
21.25	21179.1593	22637270	0.000	1.61226722	2.75894936	1.61136130000	1.61136130000
21.50	21292.1507	22638650	0.000	1.61152060	2.76494962	1.61022300000	1.61022300000
21.75	21406.5522	22639320	0.000	1.61157445	2.76713141	1.61016000000	1.61016000000
22.00	21519.5126	22639540	0.000	1.611245403	2.77220000	1.61007000000	1.61007000000
22.25	21631.5205	22639300	0.000	1.61116166	2.77520000	1.61000000000	1.61000000000
22.50	21742.4093	22639400	0.000	1.61155174	2.78665655	1.61044740000	1.61044740000
22.75	21855.1628	22639470	0.000	1.61129642	2.79223552	1.61030000000	1.61030000000
23.00	21965.5594	21592275	0.000	1.6117541617	2.79911067	1.61025120000	1.61025120000
23.25	22076.2578	21592800	0.000	1.61164340	2.8028266	1.61019000000	1.61019000000
23.50	22186.0714	21592715	0.000	1.611732166	2.80563612	1.61012100000	1.61012100000
23.75	22295.3137	21592530	0.000	1.611707014	2.80743645	1.61006440000	1.61006440000
24.00	22404.0234	21592160	0.000	1.611683027	2.809212667	1.61000000000	1.61000000000
24.25	22512.1505	21592000	0.000	1.61165510	2.81115471	1.61000000000	1.61000000000
24.50	22619.4297	21591450	0.000	1.611554923	2.812255421	1.61000000000	1.61000000000
24.75	22726.4432	21591620	0.000	1.611603795	2.813450422	1.61000000000	1.61000000000
25.00	22833.5032	21591750	0.000	1.611571702	2.814482706	1.61000000000	1.61000000000
25.25	22939.5267	21591400	0.000	1.6115542594	2.815080125	1.61000000000	1.61000000000
25.50	23045.0104	21591570	0.000	1.611530572	2.815772745	1.61000000000	1.61000000000
25.75	23149.9487	21591610	0.000	1.611507247	2.816241452	1.61000000000	1.61000000000
26.00	23254.3420	21591650	0.000	1.6114847492	2.816493150	1.61000000000	1.61000000000
26.25	23358.1046	21591620	0.000	1.611462205	2.816745712	1.61000000000	1.61000000000
26.50	23461.4471	20561400	0.000	1.611441235	2.816900022	1.61000000000	1.61000000000
26.75	23564.2522	20561750	0.000	1.611420252	2.81703743	1.61000000000	1.61000000000
27.00	23667.4221	20561550	0.000	1.6114007262	2.81717056	1.61000000000	1.61000000000
27.25	23766.0773	20561200	0.000	1.611362204	2.81729779	1.61000000000	1.61000000000
27.50	23865.1667	20560650	0.000	1.611323010	2.81741055	1.61000000000	1.61000000000
27.75	23965.6597	20560420	0.000	1.611283602	2.81751076	1.61000000000	1.61000000000
28.00	24069.6747	20560550	0.000	1.611261915	2.81760000	1.61000000000	1.61000000000
28.25	24169.0095	20560760	0.000	1.6112406406	2.81768019	1.61000000000	1.61000000000
28.50	24267.9437	20560450	0.000	1.6112192407	2.81775024	1.61000000000	1.61000000000
28.75	24366.2342	20560550	0.000	1.6111975407	2.81781024	1.61000000000	1.61000000000
29.00	24463.5595	20560250	0.000	1.6111762430	2.81786024	1.61000000000	1.61000000000
29.25	24561.1389	20560250	0.000	1.6111546720	2.81791024	1.61000000000	1.61000000000
29.50	24657.7056	15532020	0.000	1.6111331115	2.81796024	1.61000000000	1.61000000000
29.75	24753.7203	15532020	0.000	1.6111117216	2.81801024	1.61000000000	1.61000000000
30.00	24849.1727	15532020	0.000	1.6110904017	2.81806024	1.61000000000	1.61000000000
30.25	24944.0535	15532020	0.000	1.6110692466	2.81811024	1.61000000000	1.61000000000
30.50	25038.3255	15532020	0.000	1.6110481584	2.81816024	1.61000000000	1.61000000000
30.75	25132.0765	15532020	0.000	1.6110270477	2.81821024	1.61000000000	1.61000000000
31.00	25225.2177	15532020	0.000	1.6110059427	2.81826024	1.61000000000	1.61000000000
31.25	25317.7798	15532020	0.000	1.6109848277	2.81831024	1.61000000000	1.61000000000
31.50	25409.7565	15532020	0.000	1.6109637342	2.81836024	1.61000000000	1.61000000000
31.75	25501.1522	15532020	0.000	1.6109426432	2.81841024	1.61000000000	1.61000000000
32.00	25591.9612	15532020	0.000	1.6109215540	2.81846024	1.61000000000	1.61000000000
32.25	25682.1467	15532020	0.000	1.6109004540	2.81851024	1.61000000000	1.61000000000

EC 2) = .62549517D-01 RMS ERROR = .370575347D-02 RELATIVE RMS ERROR = .0000000000000000

LOOP OF ENTRIES : 4 STANDARD ERROR = 2.02171D-05

FIT OF OLTFPOST TRAINING POINTS FOR INTERPOLATING L(H) WITH H GREATER THAN 4.0552 CAC+10 USING

FUNCTION OF THE FORM $B(1)+E(2)+...+(-1)^{N+1}H(N)+...+H(N)$ WITH N=10

F	L(H)	FCALC	DIFF
4.86528040D+00	3.13174376D+04	2.1517437645D+04	1.72124376D+02
4.80252405D+00	3.15070661D+04	2.1507066140D+04	-2.22632405D-02
4.74541276D+00	3.16558221D+04	2.145582253D+04	-2.60041576D-04
4.69202616D+00	3.18237087D+04	2.148370724D+04	1.60258224D-02
4.64222554D+00	3.19707254D+04	2.147072759D+04	1.41575085D-02
4.59582532D+00	3.19568703D+04	2.145687772D+04	-6.41568006D-04
4.55156034D+00	3.14421850D+04	2.144218713D+04	-2.12672760D-02
4.51001963D+00	3.14266264D+04	2.142662515D+04	1.20525705D-02

CONSTANTS OF FIT

EC 1) = .315483461D+05	RMS ERROR = .847261745D+04	RELATIVE RMS ERROR = .261550754D-04
EC 2) = .251650254D+07	RMS ERROR = .890964232D+05	RELATIVE RMS ERROR = .30541571D-03
EC 3) = -.700695122D+04	RMS ERROR = .202055255D+07	RELATIVE RMS ERROR = .41305227D-02
EC 4) = -.204783164D+09	RMS ERROR = .2549581404D+09	RELATIVE RMS ERROR = .124512002D+00

LOOP OF ENTRIES : 4 STANDARD ERROR = 2.02171D-05

BEGINNING OF INVERTED FERTURBATION APPROACH

FPIA = 1.400, RAPAX = 7.500, SPACING = .001000
CONVERGENCE CRITERION IS ERROR LESS THAN .10D-02

ALPHER OF ITERATIONS = 4

PARAMETERS OF THE FITTING POLYNOMIAL

FPIA = 1.558RAPAX = 4.115 RE = 1.522,APLE = 10

RESULTS OF SCHROEDINGER EQUATION FOR J(J+1) = 2, AND J = 1

N	GN CAL	EV MEAS	GV P-C	EV CAL	EV P-C	S(PA)	C(PA)	MA	AD
0	360.13800	360.16592	-.01607	30627690	.00454	6.20-10	7.40-11	12	155
1	1074.14582	1074.09502	-.04670	30457566	.00517	-5.20-10	7.10-11	21	160
2	1710.55104	1710.51652	-.07412	30275232	.00551	7.50-10	6.60-11	20	164
3	2440.73220	2440.64056	-.05584	30085457	.00646	-4.10-10	6.40-11	28	16
4	3173.35292	3173.24374	-.10515	2990762	.00711	5.40-10	6.20-11	27	172
5	3854.97005	3854.85119	-.11278	29709025	.00774	-7.60-10	7.20-11	26	176
6	4531.47352	4531.36553	-.10455	29514255	.00834	7.10-10	1.00-10	25	17
7	5206.90649	5206.82230	-.08415	29316571	.00892	-7.20-10	6.30-11	24	17
8	5882.26522	5882.16941	-.04521	29115444	.00945	6.50-10	1.10-11	23	17
9	6557.55919	6557.45712	.00052	28912126	.00997	-6.50-10	6.50-11	22	17
10	7190.77098	7190.63691	.06558	28705406	.01047	5.60-10	1.10-11	21	17
11	7823.85626	7824.04277	.14735	28495547	.01076	-6.20-10	6.30-11	20	17
12	8455.92430	8456.16520	.24404	28282565	.01145	4.50-10	1.10-11	19	200
13	9088.84108	9089.19521	.25814	28067230	.01204	-5.20-10	1.40-11	18	200
14	9710.62595	9711.11666	.48671	27848500	.01233	7.10-10	1.00-11	17	200
15	10325.27164	10325.650125	.62565	27626741	.01362	-6.40-10	1.20-11	16	200
16	10932.74420	10932.52975	.78555	27401551	.01492	5.20-10	1.00-11	15	214
17	11532.00202	11532.87571	.55265	27174116	.01497	-6.70-10	1.20-11	14	217
18	12126.00101	12127.2053	1.12452	26943216	.01477	7.10-10	1.00-11	13	221
19	12711.60461	12713.19862	1.31052	26709225	.02174	-6.20-10	1.40-11	14	224
20	13290.41261	13291.90128	1.45141	26472125	.02527	5.10-10	1.10-11	13	227
21	13861.62241	13862.29624	1.67427	2623176	.03517	-5.10-10	1.50-11	12	231
22	14431.40533	14432.09402	2.00000	2598174	.06314	4.20-10	1.00-11	10	234
23	15000.90407	15001.61471	2.1474	25736514	.07404	-7.00-10	1.40-11	10	234
24	15570.50851	15571.1655	2.26715	25490485	.08494	7.40-10	1.20-11	9	234
25	16140.52072	16141.6750	2.35718	25242370	.09584	-5.20-10	1.20-11	8	234
26	16710.54551	16711.36464	2.41133	24994255	.10674	5.20-10	1.00-11	7	234
27	17280.57030	17281.7252	2.44528	24746140	.11764	-7.20-10	1.20-11	6	234
28	17850.59509	17851.9957	2.45141	24498025	.12854	7.20-10	1.00-11	5	234
29	18420.61988	18421.9957	2.43050	24249910	.13944	-5.20-10	1.40-11	4	234
30	18990.64467	18991.9957	2.38644	24001795	.15034	7.20-10	1.00-11	3	234
31	19560.66946	19561.9957	2.36064	23753680	.16124	-7.20-10	1.20-11	2	234
32	20130.69425	20131.9957	2.33717	23505565	.17214	7.20-10	1.00-11	1	234
33	20700.71904	20701.9957	2.31370	23257450	.18304	-5.20-10	1.20-11	1	234
34	21270.74383	21271.9957	2.29023	23009335	.19394	7.20-10	1.00-11	1	234
35	21840.76862	21841.9957	2.26676	22761220	.20484	-7.20-10	1.20-11	1	234
36	22410.79341	22411.9957	2.24329	22513105	.21574	7.20-10	1.00-11	1	234
37	22980.81820	22981.9957	2.21982	22264990	.22664	-5.20-10	1.20-11	1	234
38	23550.84299	23551.9957	2.19635	22016875	.23754	7.20-10	1.00-11	1	234
39	24120.86778	24121.9957	2.17288	21768760	.24844	-7.20-10	1.20-11	1	234
40	24690.89257	24691.9957	2.14941	21520645	.25934	7.20-10	1.00-11	1	234
41	25260.91736	25261.9957	2.12594	21272530	.27024	-5.20-10	1.20-11	1	234
42	25830.94215	25831.9957	2.10247	21024415	.28114	7.20-10	1.00-11	1	234

P(1) =	-1.03281E+06	RMS ERROR =	1.32925E+03	RELATIVE	RMS ERROR =	1.2 31E+1
P(2) =	2.3262E+05	RMS ERROR =	2.05467E+03	RELATIVE	RMS ERROR =	1.1 31E+1
P(3) =	-1.33041E+06	RMS ERROR =	2.34141E+03	RELATIVE	RMS ERROR =	1.1 31E+1
P(4) =	-3.1790E+07	RMS ERROR =	4.51142E+02	RELATIVE	RMS ERROR =	2.1 31E+1
P(5) =	-9.3252E+05	RMS ERROR =	1.15255E+03	RELATIVE	RMS ERROR =	2.0 31E+1
P(6) =	1.97530E+05	RMS ERROR =	1.54276E+03	RELATIVE	RMS ERROR =	1.2 31E+1
P(7) =	-1.1032E+06	RMS ERROR =	2.12412E+02	RELATIVE	RMS ERROR =	1.1 31E+1
P(8) =	1.15747E+05	RMS ERROR =	2.28011E+02	RELATIVE	RMS ERROR =	1.1 31E+1
P(9) =	-2.84657E+05	RMS ERROR =	2.23356E+02	RELATIVE	RMS ERROR =	1.1 31E+1
P(10) =	2.80451E+05	RMS ERROR =	1.26278E+02	RELATIVE	RMS ERROR =	1.1 31E+1

RESULTS OF SCHROEDINGER EQUATION FOR J(J+1) = 2. A'D J= 1

N	GV CAL	GV MEAS	GV P-C	BA CAL	LV P-C	SCPA	CPFF	MA	NI
0	359.71150	359.75210	.04100	.25427567	2.10536	7.10-10	7.10-11	24	154
1	1073.70610	1073.69227	-.02311	.20263144	1.04439	7.10-10	7.10-11	22	164
2	17-0.52566	1700.50017	-.03565	.20055102	1.04005	7.10-10	7.10-11	20	164
3	2400.24558	2400.22391	-.02178	.25522063	1.64040	7.10-10	7.10-11	25	164
4	3172.66762	3172.66655	-.00083	.25744630	1.56843	7.10-10	7.10-11	28	174
5	3854.42249	3854.44444	.01655	.25562534	1.46465	7.10-10	7.10-11	27	174
6	4536.52570	4536.55174	.02808	.25277114	1.34019	7.10-10	7.10-11	26	174
7	5208.37549	5208.40554	.02605	.25187241	1.30112	7.10-10	7.10-11	25	174
8	5872.78440	5872.80316	.01276	.24992540	1.23244	7.10-10	7.10-11	24	174
9	6530.12553	6530.14297	.00744	.24756016	1.17107	7.10-10	7.10-11	23	174
10	7180.42461	7180.42120	-.00446	.24594763	1.11630	7.10-10	7.10-11	22	174
11	7823.64100	7823.62102	-.01318	.24340461	1.06522	7.10-10	7.10-11	21	174
12	8453.77162	8453.75245	-.01917	.24181367	1.02746	7.10-10	7.10-11	20	174
13	9088.80174	9088.78246	-.01528	.23969332	.99111	7.10-10	7.10-11	19	174
14	9710.71463	9710.69591	-.01412	.23753801	.95972	7.10-10	7.10-11	18	174
15	10325.45139	10325.48454	-.00614	.23534225	.93274	7.10-10	7.10-11	17	174
16	10933.11661	10933.11204	.00243	.23312455	.90974	7.10-10	7.10-11	16	174
17	11533.54792	11532.55496	.01134	.23086752	.89010	7.10-10	7.10-11	15	174
18	12126.77559	12126.79278	.01720	.22857790	.87303	7.10-10	7.10-11	14	174
19	12712.76220	12712.78188	.01588	.22625647	.85776	7.10-10	7.10-11	13	174
20	13291.47248	13291.49053	.01816	.22390411	.84342	7.10-10	7.10-11	12	174
21	13863.86719	13862.87593	.01274	.22152172	.82910	7.10-10	7.10-11	11	174
22	14426.90329	14426.90415	.00416	.21911026	.81387	7.10-10	7.10-11	10	174
23	14983.52418	14982.53019	-.00295	.21667058	.79845	7.10-10	7.10-11	9	174
24	15532.76591	15532.69146	-.01282	.21420350	.77723	7.10-10	7.10-11	8	174
25	16074.37788	16074.36024	-.01764	.21170975	.75924	7.10-10	7.10-11	7	174
26	16608.48246	16608.46275	-.01971	.20918497	.72736	7.10-10	7.10-11	6	174
27	17134.96580	17134.94409	-.01771	.20664474	.69545	7.10-10	7.10-11	5	174
28	17653.76768	17653.75577	-.01191	.20407458	.65335	7.10-10	7.10-11	4	174
29	18164.82542	18164.82222	.00452	.20144002	.61721	7.10-10	7.10-11	3	174
30	18668.07392	18664.00075	.00652	.20046164	.56844	7.10-10	7.10-11	2	174
31	19163.44479	19162.96158	.01675	.20222006	.51377	7.10-10	7.10-11	1	174
32	19650.86715	19650.89185	.02470	.20355597	.45116	7.10-10	7.10-11	0	174
33	20130.26631	20130.24559	.02528	.20487016	.38027	7.10-10	7.10-11	0	174
34	20601.56412	20601.59373	.02581	.22162346	.30027	7.10-10	7.10-11	0	174
35	21064.67870	21064.70412	.02541	.22542672	.21031	7.10-10	7.10-11	0	174
36	21515.52438	21515.54150	.01711	.22269077	.10556	7.10-10	7.10-11	0	174
37	21966.01181	21966.01751	.00570	.22552632	-.00263	7.10-10	7.10-11	0	174
38	22404.04802	22404.04072	-.00732	.22714396	-.12701	7.10-10	7.10-11	0	174
39	22833.53679	22833.51657	-.02023	.22434410	-.26347	7.10-10	7.10-11	0	174
40	23254.27670	23254.34142	-.03127	.22152646	-.41333	7.10-10	7.10-11	0	174
41	23666.47144	23666.43256	-.03444	.20865210	-.57527	7.10-10	7.10-11	0	174
42	24069.70996	24065.66414	-.04112	.20583535	-.74922	7.10-10	7.10-11	0	174
43	24463.98668	24462.94123	-.03446	.20296781	-.93439	7.10-10	7.10-11	0	174
44	24849.15157	24845.15581	-.03176	.20067631	-1.12352	7.10-10	7.10-11	0	174
45	25225.21216	25225.18275	-.01940	.19716731	-1.33327	7.10-10	7.10-11	0	174
46	25591.93342	25591.55246	-.00357	.19422617	-1.54354	7.10-10	7.10-11	0	174
47	25945.23781	25945.25141	.01400	.19126471	-1.75400	7.10-10	7.10-11	0	174
48	26297.00501	26297.03619	.03114	.18827412	-1.97419	7.10-10	7.10-11	0	174

50 26562.01137 26562.01136
 51 27241.01403 27201.04246
 52 27590.11622 27590.24155
 53 27804.35010 27804.35369
 54 28176.14332 28176.20176
 55 28453.54292 28453.54272
 56 28720.21602 28720.2442
 57 28976.22555 28976.17556
 58 29221.20593 29221.17079
 59 29455.16296 29455.07162
 60 29677.02001 29677.73653
 61 29889.04070 29889.04444
 62 30088.61398 30088.65680
 63 30276.56002 30276.58256
 64 30452.51303 30452.59219
 65 30616.32207 30616.51064
 66 30768.00985 30768.15177
 67 30907.24262 30907.35336
 68 31032.92075 31032.91208
 69 31147.91491 31147.64551

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SUP OF DIFF. = 1.9422D-02 AVERAGE DIFF. = 2.7747C-04 RMS (F (V = 5.259, D-02)

RESULTS OF SCHROEDINGER EQUATION FOR J(J+1) = 0. AND J = 0

N	GV CAL	EV MEAS	GV P-C	BV CAL	BV M-C	S(MA)	S(PF)	MA	ME
0	359.10303	359.14042	.03729	.20427655	2.10412	5.20-10	7.10-11	11	34
1	1072.10090	1072.07210	-.027-1	.30263733	1.94662	7.10-10	1.10-10	10	32
2	1779.93396	1779.89466	-.03521	.20055107	1.40524	4.50-10	7.20-11	11	30
3	2479.64714	2479.62200	-.02514	.29522153	1.67402	-6.50-10	4.00-11	11	28
4	3172.21272	3172.26496	-.00377	.25744721	1.56664	4.20-10	7.10-11	11	26
5	3857.83322	3857.84624	-.01401	.25563024	1.46446	-1.40-10	1.10-10	10	24
6	4536.33816	4536.36144	-.02332	.25277206	1.37430	1.00-05	6.50-11	11	22
7	5207.79575	5207.81-20	-.02345	.25147373	1.30002	-1.00-05	1.70-10	10	20
8	5872.20553	5872.22483	-.01620	.24935641	1.23064	1.00-05	5.40-11	11	18
9	6525.55761	6525.56471	-.00510	.24796104	1.16427	-5.50-10	1.20-11	11	16
10	7179.85277	7179.84604	-.00670	.24594556	1.11509	4.70-10	5.20-11	11	14
11	7822.07120	7822.05702	-.01612	.24389954	1.06741	-7.70-10	1.20-11	11	12
12	8459.20199	8459.18177	-.02122	.24161455	1.02566	6.70-10	8.20-11	11	10
13	9084.24235	9084.22109	-.02126	.23924423	.98-32	-5.80-10	1.10-10	10	8
14	9710.15555	9710.14291	-.01664	.23753493	.95742	4.00-10	1.40-10	10	6
15	10324.94069	10324.93198	-.00771	.23534416	.93355	-1.50-10	1.10-10	10	4
16	10932.56126	10932.56497	-.00441	.23325446	.90744	7.20-10	1.40-10	10	2
17	11533.00218	11533.01545	-.00526	.23086443	.84432	-6.40-10	1.40-10	10	21
18	12126.23443	12126.25288	-.01545	.22857440	.77125	5.20-10	1.40-10	10	22
19	12712.22569	12712.24765	-.01757	.22625737	.65594	-5.40-10	1.10-10	10	23
20	13290.94467	13290.96104	-.01637	.22370500	.44165	7.60-10	1.40-10	10	24
21	13862.34414	13661.35522	-.01107	.22152262	.22733	-6.20-10	1.20-10	10	25
22	14426.34501	14426.38430	-.00323	.21911114	.41211	5.00-10	1.60-10	10	26
23	14982.02684	14983.01526	-.00558	.21667146	.79509	-5.60-10	1.40-10	10	27
24	15532.20157	15532.18400	-.01351	.21420437	.77544	7.20-10	1.20-10	10	28
25	16073.87446	16073.85532	-.01514	.21171062	.75253	-5.70-10	1.40-10	10	29
26	16607.94407	16607.96242	-.02116	.20919283	.72542	4.70-10	1.60-10	10	30
27	17134.47251	17134.45341	-.01510	.20664559	.69416	-7.50-10	1.60-10	10	31
28	17652.23553	17653.26631	-.01123	.20407543	.65762	6.60-10	1.60-10	10	32
29	18164.34247	18164.33403	-.00444	.20144027	.61544	-5.50-10	1.50-10	10	33
30	18667.59610	18667.60149	-.00575	.23862249	.56716	4.70-10	1.70-10	10	34
31	19162.97235	19162.94411	-.01576	.23622640	.51205	-7.00-10	1.60-10	10	35
32	19650.40004	19650.42244	-.02340	.23355441	.44544	6.50-10	1.60-10	10	36
33	20129.80457	20129.83309	-.02451	.23047100	.37555	-7.00-10	2.00-10	10	37
34	20601.10760	20601.13440	-.02501	.22416430	.28455	5.20-10	1.60-10	10	38
35	21064.22182	21064.25243	-.02495	.22543757	.20454	-4.50-10	1.60-10	10	39
36				.22543757	.20454	4.10-10	2.60-10	10	40

FINAL SET OF TURNING POINTS

V	U(P)	RPIA	FPAK	HV-100
0	359.103	1.875111	1.927533	30.4278540
1	1073.101	1.838699	2.024213	30.2637322
2	1779.534	1.614881	2.064430	30.0951170
3	2475.647	1.796367	2.077640	29.221527
4	3172.273	1.780990	2.124004	29.7447207
5	3897.832	1.767616	2.145505	29.5630010
6	4536.338	1.755847	2.171701	29.377205
7	5207.796	1.745249	2.193925	29.1873720
8	5872.205	1.735712	2.215411	28.9936413
9	6529.560	1.726953	2.236325	28.7961075
10	7179.853	1.718891	2.256789	28.5944556
11	7823.073	1.711432	2.276899	28.3895336
12	8459.208	1.704505	2.296730	28.1814591
13	9088.242	1.698050	2.316345	27.9694234
14	9710.160	1.692021	2.335793	27.7536430
15	10324.941	1.686379	2.355120	27.5349157
16	10932.564	1.681090	2.374361	27.3125457
17	11533.006	1.676126	2.393550	27.0864434
18	12126.238	1.671464	2.412716	26.8578002
19	12712.230	1.667062	2.431886	26.6257368
20	13290.945	1.662960	2.451093	26.3904995
21	13862.344	1.659081	2.470325	26.1522617
22	14426.385	1.655425	2.489546	25.9111142
23	14983.021	1.651989	2.508652	25.6671456
24	15532.202	1.648748	2.527657	25.4204370
25	16073.874	1.645694	2.546620	25.1710620
26	16607.984	1.642814	2.565592	24.919033
27	17134.473	1.640098	2.584539	24.6645595
28	17652.280	1.637537	2.603463	24.4075431
29	18164.342	1.635121	2.622364	24.149073
30	18667.596	1.632845	2.641251	23.886247
31	19162.972	1.630701	2.660142	23.6220101
32	19650.400	1.628682	2.679056	23.355610
33	20129.805	1.626788	2.711978	23.0870592
34	20601.108	1.625012	2.733548	22.8164303
35	21064.228	1.623344	2.755425	22.5437561
36	21519.079	1.621801	2.777631	22.2691622
37	21965.572	1.620365	2.800149	21.9927177
38	22403.614	1.619046	2.823121	21.714435
39	22833.109	1.617843	2.846454	21.434483

FINAL SET OF TURNING POINTS

V	U(R)	RPIN	RPAK	HV=100
40	23253.556	1.616741	2.670214	21.1527765
41	23666.054	1.615732	2.674431	20.6633027
42	24069.298	1.614612	2.678135	20.5840280
43	24463.581	1.613573	2.681261	20.2961750
44	24848.791	1.613735	2.690146	20.2077516
45	25224.818	1.614496	2.696532	19.7164351
46	25571.545	1.615416	3.003561	19.422753
47	25948.855	1.616416	3.051285	19.126542
48	26296.628	1.617435	3.079756	18.6275286
49	26634.741	1.618407	3.109041	18.525322
50	26963.667	1.619287	3.135202	18.2196127
51	27281.476	1.620034	3.170317	17.9100057
52	27589.834	1.620616	3.202471	17.5960659
53	27888.005	1.621010	3.235762	17.2773040
54	28175.845	1.621198	3.270295	16.9532047
55	28453.210	1.621171	3.306207	16.6231714
56	28719.950	1.620924	3.343628	16.2865724
57	28975.911	1.620460	3.382727	15.9427130
58	29220.534	1.619786	3.423693	15.590332
59	29454.859	1.618914	3.466746	15.2301060
60	29677.523	1.617862	3.512145	14.8596280
61	29888.755	1.616645	3.560152	14.474040
62	30088.402	1.615295	3.611250	14.0453424
63	30276.286	1.613837	3.665752	13.6752227
64	30452.248	1.612293	3.724225	13.2586732
65	30616.126	1.610695	3.787324	12.822070
66	30767.763	1.609074	3.855863	12.367593
67	30907.005	1.607461	3.930893	11.992705
68	31033.701	1.617871	4.013796	11.3945230
69	31147.698	1.619633	4.106466	10.666272

FINAL PCTENTIAL

R	U(R)	RKE-IPA	PERCENT
1.4000000000+00	3.1885015200+04	4.1675115630-01	0.
1.4072131820+00	3.1647577600+04	4.1675115600-01	0.
1.4144261660+00	3.1630140370+04	4.1675115760-01	0.
1.4216395480+00	3.1612723820+04	4.1675115600-01	0.
1.4288527310+00	3.1755311100+04	4.1675115510-01	0.
1.4360659140+00	3.1777907920+04	4.1675115670-01	0.
1.4432790970+00	3.1760514260+04	4.1675115670-01	0.
1.4504922790+00	3.1743130130+04	4.1675115550-01	0.
1.4577054620+00	3.1725755500+04	4.1675115710-01	0.
1.4649186450+00	3.1708350290+04	4.1675115700-01	0.
1.4721318280+00	3.1691034780+04	4.1675115800-01	0.
1.4793450100+00	3.1673688680+04	4.1675115770-01	0.
1.4865581920+00	3.1656352060+04	4.1675115800-01	0.
1.4937713760+00	3.1639024940+04	4.1675115740-01	0.
1.5009845590+00	3.1621707200+04	4.1675115760-01	0.
1.5081977410+00	3.1604395140+04	4.1675115940-01	0.
1.5154105240+00	3.1587100450+04	4.1675115950-01	0.
1.5226241070+00	3.1569811230+04	4.1675115850-01	0.
1.5298372960+00	3.1552531470+04	4.1675115760-01	0.
1.5370504720+00	3.1535267230+04	4.1069432800-01	0.
1.5442636550+00	3.1517848180+04	-4.1055354800-01	1.20044807400-10
1.5494639520+00	3.1506311000+04	7.5437033540-01	2.8534455500-11
1.5541233620+00	3.1495444870+04	3.7729445240-01	2.5904757620-09
1.5583231920+00	3.1482296710+04	4.1213559940-01	3.5505555600-08
1.5621275940+00	3.1470314040+04	4.1536626520-01	1.4163425100-04
1.5655859600+00	3.1456424010+04	4.5506049940-01	2.0322681450-07
1.5687515480+00	3.1441748060+04	4.3694515840-01	1.5354674460-02
1.5716495230+00	3.1426553470+04	7.2922959750-02	7.3114120550-02
1.5743122710+00	3.1411114060+04	-9.6564974010-01	2.4004425470-03
1.5767656540+00	3.1397243610+04	-4.2914193470+00	6.5785614450-01
1.5790311420+00	3.1384770240+04	-9.9273506510+00	1.4262806070+00
1.5811271640+00	3.1375034910+04	-1.9145283610+01	2.1005282020+00
1.5830699060+00	3.1368503680+04	-3.2405162310+01	4.5555555550+00
1.5848733680+00	3.1366465930+04	-5.1002200590+01	7.0005526130+00
1.5865498780+00	3.1366834960+04	-7.2837783640+01	1.0000495450+01
1.5881103020+00	3.1365033660+04	-5.7334552370+01	1.3555164060+01
1.5895643040+00	3.1373655670+04	-1.2508312430+02	1.7452716200+01
1.5909203720+00	3.1380963230+04	-1.5634270120+02	2.1730204920+01
1.5921662940+00	3.1387734320+04	-1.8789219780+02	2.6162451570+01
1.5933688600+00	3.1393309580+04	-2.1905723970+02	3.0652751240+01
1.5944743280+00	3.1397270660+04	-2.4942845990+02	3.5241053740+01
1.5955082450+00	3.1401612040+04	-2.8099331690+02	3.9736072060+01
1.5964759010+00	3.1408356250+04	-3.1550535620+02	4.4125262540+01
1.5973815770+00	3.1411636850+04	-3.4789316020+02	4.8366524760+01
1.5982257580+00	3.1410916050+04	-3.7681794290+02	5.2438373060+01
1.5990242650+00	3.1406063620+04	-4.0243274740+02	5.6315225750+01
1.5997685990+00	3.1377203500+04	-4.2479794680+02	5.9905513550+01
1.6004660290+00	3.1364441200+04	-4.4411672150+02	6.3453678800+01
1.6011195580+00	3.1368218640+04	-4.6068786750+02	6.6710615420+01
1.6017319720+00	3.1407444070+04	-5.3353673000+02	6.9762071940+01
1.6023058000+00	3.1460102540+04	-6.2060546200+02	7.2616211100+01
1.6028434180+00	3.1459113510+04	-6.9481062320+02	7.5275525560+01
1.6033470020+00	3.1523270220+04	-7.5442597100+02	7.7750870420+01
1.6038146640+00	3.1532298500+04	-8.0072433490+02	8.0081532400+01
1.6042602460+00	3.1526547060+04	-8.3254170960+02	8.2211850940+01
1.6046735680+00	3.1506990140+04	-8.5124612700+02	8.4222222220+01
1.6050602670+00	3.1474670210+04	-8.5799720970+02	8.6045761070+01
1.6054215060+00	3.1430976430+04	-8.5414326400+02	8.7761502000+01
1.6057595240+00	3.1377356260+04	-8.4112322690+02	8.9344301650+01

1.60363705560+00	3.1246216420+04	-7.73463.640+02	4.217667.1.1+01
1.6066454470+00	3.1171547360+04	-7.6167675000+02	7.341415760+01
1.6069021060+00	3.1052602420+04	-7.2636232710+02	9.4556655560+01
1.6071410150+00	3.1010599070+04	-6.4473565450+02	9.557022.1520+01
1.6073633870+00	3.0926645210+04	-6.4551819430+02	9.6650255040+01
1.6075701620+00	3.0772830560+04	-5.417251240+02	9.7575255230+01
1.6077622720+00	3.0610464410+04	-4.2622152130+02	9.8422551670+01
1.6079405340+00	3.0455165170+04	-3.1425683900+02	9.9271067560+01
1.6081057660+00	3.0307456850+04	-2.1865981300+02	9.9917723720+01
1.6082547480+00	3.0167701560+04	-1.2773026650+02	1.005771.050+01
1.6084001520+00	2.0035971470+04	-0.5556523850+01	1.0116336560+01
1.6085207800+00	2.9912341260+04	2.778191540+01	1.0172555170+01
1.6086511970+00	2.9756711140+04	9.2406673620+01	1.0225065350+01
1.6087620360+00	2.9689963120+04	1.484187940+02	1.0271845620+01
1.6088635000+00	2.9588874300+04	1.9604635200+02	1.031464.430+01
1.6089573720+00	2.9496162090+04	2.2557026450+02	1.0357763470+01
1.6090429660+00	2.9410611410+04	2.6725051370+02	1.039544.50+01
1.6091212200+00	2.9331824720+04	2.4143442200+02	1.0421952440+01
1.6091926010+00	2.9255514720+04	3.0843066900+02	1.0451508700+01
1.6092575260+00	2.9193325040+04	3.1859454700+02	1.0478337230+01
1.6093166260+00	2.9132916310+04	3.2227958490+02	1.0502644550+01
1.6093701710+00	2.9077903490+04	3.1986552800+02	1.0524625030+01
1.6094185970+00	2.9027964940+04	3.1167033710+02	1.054447.250+01
1.6094623260+00	2.8982730820+04	2.9867566240+02	1.0562255560+01
1.6095016950+00	2.8941894720+04	2.7938765800+02	1.057842.760+01
1.6095371170+00	2.8905063400+04	2.5600177920+02	1.0592862440+01
1.6095688950+00	2.8871947240+04	2.2821020550+02	1.0605793150+01
1.6095973980+00	2.8842196860+04	1.9636476130+02	1.0617372300+01
1.6096229150+00	2.8815516170+04	1.6076396400+02	1.06277270.0+01
1.6096457820+00	2.87915708.0+04	1.2174454710+02	1.0636595750+01
1.6096662690+00	2.8770091950+04	7.957792.600+01	1.0645252940+01
1.6096846790+00	2.8750763350+04	3.4576637450+01	1.0652741340+01
1.6097012720+00	2.8733334660+04	-1.2556620517+01	1.065944.70+01
1.6097163240+00	2.8717506520+04	-6.2824486720+01	1.0665520480+01
1.6097300820+00	2.8703027110+04	-1.1469851450+02	1.0671085660+01
1.6097427910+00	2.8689643420+04	-1.64229608.0+02	1.0676212240+01
1.6097546870+00	2.8677106660+04	-2.2347320350+02	1.068100.250+01
1.6097660120+00	2.8665164310+04	-2.7577545370+02	1.0685573450+01
1.6097769670+00	2.8653605310+04	-3.3732299300+02	1.0695566260+01
1.6097877730+00	2.8642196810+04	-3.9558066340+02	1.0699433630+01
1.6097986520+00	2.8630705070+04	-4.5441241530+02	1.0705714690+01
1.6098057760+00	2.8618947560+04	-5.1363345010+02	1.070218.60+01
1.6098123490+00	2.8606707770+04	-5.7362494450+02	1.0707841420+01
1.6098335590+00	2.8593787370+04	-6.3238643610+02	1.0712747020+01
1.6098465950+00	2.8579984440+04	-6.9151363310+02	1.0717981310+01
1.6098606090+00	2.8565134750+04	-7.5024010910+02	1.0722605250+01
1.6098757920+00	2.8549036220+04	-4.0836157530+02	1.0725653650+01
1.6098923000+00	2.8531518160+04	-8.6570515140+02	1.0736304440+01
1.6099103020+00	2.8512396780+04	-9.2208677950+02	1.0742517270+01
1.6099259320+00	2.8491532410+04	-5.7735667640+02	1.0751370240+01
1.6099513620+00	2.8468731570+04	-1.0313311590+03	1.0755924460+01
1.6099747220+00	2.8443841870+04	-1.0636476850+03	1.0765265050+01
1.6100001790+00	2.8416711600+04	-1.1347545960+03	1.0775412220+01
1.6100278480+00	2.8387176640+04	-1.1838500290+03	1.0780432650+01
1.6100573700+00	2.8355091450+04	-1.2310915210+03	1.0782237320+01
1.6100503760+00	2.8320307450+04	-1.2762243660+03	1.0785263530+01
1.6101254920+00	2.8282675370+04	-1.3151350430+03	1.0788207.60+01
1.6101633420+00	2.8242066320+04	-1.355680.250+03	1.0794125640+01
1.6102040620+00	2.8198304890+04	-1.3977015540+03	1.0796027750+01
1.6102477530+00	2.8151244070+04	-1.4330748200+03	1.07977504140+01
1.6102945400+00	2.8100868050+04	-1.465660.120+03	1.07995411560+01
1.6103445340+00	2.8046905420+04	-1.4953167430+03	1.08015534720+01
1.6103974420+00	2.7992771500+04	-1.5215171080+03	1.08034400660+01
1.6104545400+00	2.7927851650+04	-1.54532.4750+03	1.08058560510+01
1.6105144400+00	2.7862516160+04	-1.5654357540+03	1.08082025570+01

1.610646360+00	2.7719411540+00	-1.610224630+03	1.104255210+00
1.6107172390+00	2.7641-13620+04	-1.61046775370+03	1.1200550240+00
1.6107932290+00	2.755966040+00	-1.6103712940+03	1.110551110+00
1.6108726540+00	2.747203270+00	-1.612155580+03	1.111990400+00
1.6109561470+00	2.738135720+00	-1.610047410+03	1.115173700+00
1.6110433400+00	2.728603050+00	-1.6035498460+03	1.119503150+00
1.6111355900+00	2.7185452210+00	-1.593530560+03	1.121575570+00
1.611234320+00	2.704016750+00	-1.570154000+03	1.125604150+00
1.6113333420+00	2.6970020350+00	-1.5602614450+03	1.125377100+00
1.6114368270+00	2.685450340+00	-1.537203650+03	1.131299550+00
1.611548470+00	2.673505090+00	-1.5046402350+03	1.1373716750+00
1.6116637980+00	2.6610223160+00	-1.475102230+03	1.141525550+00
1.611783460+00	2.644042070+00	-1.4421241750+03	1.145625760+00
1.6119040190+00	2.6345877070+00	-1.4018235430+03	1.1504425800+00
1.6120375400+00	2.620645260+00	-1.3572805970+03	1.155149140+00
1.6121721160+00	2.6062254500+00	-1.305644050+03	1.155562670+00
1.6123116150+00	2.5913495260+00	-1.2557997910+03	1.1645213150+00
1.6124567200+00	2.5760201510+00	-1.195082960+03	1.170237040+00
1.6126069060+00	2.5602572970+00	-1.136130570+03	1.175267460+00
1.6127624390+00	2.5440828560+00	-1.074543240+03	1.1806512710+00
1.6129234050+00	2.527519200+00	-1.0072555320+03	1.1841719620+00
1.6130898740+00	2.5105591680+00	-9.3650176160+02	1.1918266250+00
1.6132619150+00	2.4932530050+00	-8.6386134170+02	1.1976125000+00
1.6134396020+00	2.4758227930+00	-7.865219130+02	1.202526050+00
1.6136230100+00	2.4622618200+00	-7.534515050+02	1.2055639140+00
1.6138122060+00	2.4507535770+00	-7.354551710+02	1.2157019070+00
1.6140072620+00	2.4392485860+00	-7.2605277370+02	1.2215556260+00
1.6142042520+00	2.427752220+00	-7.134163870+02	1.228380550+00
1.6144152390+00	2.4163220370+00	-7.0173322160+02	1.234872400+00
1.6146282950+00	2.4045367210+00	-6.9117856240+02	1.2414661150+00
1.6148474920+00	2.3936261300+00	-6.8191934450+02	1.248155550+00
1.6150728970+00	2.382406060+00	-6.7411738190+02	1.2549357500+00
1.6153045720+00	2.3712936880+00	-6.6782648260+02	1.2618003250+00
1.6155425940+00	2.360301040+00	-6.634821370+02	1.268742460+00
1.6157870320+00	2.349413310+00	-6.6050815260+02	1.275758660+00
1.6160375520+00	2.3387255380+00	-6.6031405820+02	1.282839460+00
1.6162954220+00	2.328162210+00	-6.6179047230+02	1.2899796350+00
1.6165595100+00	2.3177606640+00	-6.6540770050+02	1.2971717650+00
1.6168302870+00	2.3075232010+00	-6.7120857950+02	1.3044071660+00
1.6171078140+00	2.297452560+00	-6.792159360+02	1.3116803150+00
1.617392160+00	2.287548600+00	-6.8941744130+02	1.3189821660+00
1.6176834080+00	2.2778070460+00	-7.0177270150+02	1.3263000130+00
1.6179816170+00	2.2682196080+00	-7.1620168300+02	1.3336472420+00
1.6182864420+00	2.2587757520+00	-7.3254472420+02	1.3409925360+00
1.6185951740+00	2.2494591290+00	-7.5074695450+02	1.3483364630+00
1.6189186690+00	2.2402498410+00	-7.7057792650+02	1.3556707670+00
1.6192454030+00	2.2311224420+00	-7.9171177610+02	1.3629876310+00
1.6195754450+00	2.2220462630+00	-8.138803370+02	1.3702790000+00
1.6199204600+00	2.2106706750+00	-8.357606650+02	1.377536050+00
1.6202637220+00	2.1951095890+00	-8.51194055430+02	1.3847532630+00
1.6206261090+00	2.1875167250+00	-8.7049767560+02	1.391920640+00
1.6209900740+00	2.1758947070+00	-8.9228424650+02	1.3990331020+00
1.6213617160+00	2.1642464120+00	-9.16832383980+02	1.4060771130+00
1.6217410440+00	2.1525744160+00	-9.43764072200+02	1.4130512170+00
1.6221242650+00	2.1408798520+00	-9.724495590+02	1.4199465010+00
1.6225233310+00	2.1291635670+00	-10.014371230+02	1.4267555240+00
1.6229263500+00	2.1174255460+00	-10.3073350440+02	1.4334725630+00
1.6233374080+00	2.1056644730+00	-10.6070550840+02	1.4400902410+00
1.6237565760+00	2.0938763420+00	-10.9253356140+02	1.4466027160+00
1.6241835240+00	2.082064510+00	-11.2694622800+02	1.4530041550+00
1.6246155360+00	2.0702173370+00	-11.63061907630+02	1.4592550410+00
1.6250635010+00	2.058332510+00	-12.01187209750+02	1.4654525440+00
1.6255154430+00	2.0464015880+00	-12.4131752460+02	1.4714857320+00
1.625976760+00	2.034200210+00	-12.822705030+02	1.477250360+00
1.6264462430+00	2.0217910390+00	-13.24978917050+02	1.482766540+00

1.6274112790+00	1.572771-300+00	-7.0401343500+02	1.442760-1+00
1.6275070070+00	1.5642049650+00	-7.011744-2100+02	1.4464475200+00
1.6284116550+00	1.5715613400+00	-7.0281244460+02	1.5045512430+00
1.6289253340+00	1.5574613500+00	-7.0600706400+02	1.504551-6510+00
1.6294460950+00	1.9461052650+00	-7.0304004900+02	1.5146175130+00
1.6299803590+00	1.5332503210+00	-7.000017-3+0+02	1.5155772030+00
1.6305213030+00	1.9204254570+00	-7.0658755720+02	1.5241472650+00
1.6310713170+00	1.9074584060+00	-7.0364265830+02	1.520647-210+00
1.6316320130+00	1.8945120340+00	-7.0036556000+02	1.5325593570+00
1.6322016700+00	1.881295-130+00	-7.07624195360+00	1.5371227600+02
1.6327809950+00	1.8661877170+00	-7.07164651370+00	1.5411352440+00
1.6333700960+00	1.8549177560+00	-7.0650870640+02	1.5450103300+00
1.6339650520+00	1.8415277550+00	-7.0218449130+02	1.5477374500+00
1.6345779830+00	1.8281594760+00	-7.05728173290+00	1.5523245270+00
1.6351070020+00	1.8147512350+00	-7.0227212610+02	1.5557722250+00
1.6358261950+00	1.8012467550+00	-7.0717236010+02	1.55500-3+510+00
1.6364657040+00	1.7876453170+00	-7.04106300720+02	1.5622623610+00
1.6371156060+00	1.7740674340+00	-7.03670-45920+02	1.5653107070+00
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1.6384470970+00	1.7466309780+00	-7.02559107340+02	1.5710255130+00
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1.6398216320+00	1.7189254000+00	-7.0136842420+02	1.5762675260+00
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6.408853502000	3.156363449000	4.248335639001	2.902871358000
6.435466832000	3.156347574000	4.241242306001	2.646624354000
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6.488693490000	3.156314541000	4.228742170001	2.205651026000
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7.287093366000	3.155811089000	4.171609961001	1.495185688000
7.313706695000	3.155795794000	4.171265275001	1.374081656000
7.340320025000	3.155780905000	4.170950222001	1.255654656000
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7.420160012000	3.155737304000	4.170158079001	9.715238320000
7.446773342000	3.155723125000	4.169937840001	8.513655752000
7.473386671000	3.155709125000	4.169736375001	8.174331260000
7.500000000000	3.155695320000	4.169573637500	7.507210673000

ECOMMENCED INTEGRATION LIMITS RPIA = (1) = 1.400RMAX =R(651)= 5.265

SUMMARY OF ERRORS OF THE INVERTED PERTURBATION APPROACH

J(J+1)	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	PERCENTAGE
2.0	15.03964	3.85281	.79174	.05260							

AVERAGE 16.24466 4.16151 .65529 .05661
THE DUNHAM COEFFICIENTS

-4.987263730-01 3.072677500-01 2.200000000E-07
7.210628490-02 -1.746700000E-03
-3.571019040-00 -1.500000000E-05
2.650763740-03
-1.290000000-04

Appendix C

Supplementary References

The following are references which contain information about the reduction of spectroscopic data and the construction of potential energy curves. They were not cited elsewhere in this report.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This thesis presents the tools necessary to transform spectral data from diatomic molecules into potential energy curves which are most consistent with the experimental data and the quantum mechanical model (i.e., the Schrodinger wave equation (SWE)) for a diatomic molecule. The first of these tools, a computer program called DUNCON, generates spectroscopic constants by performing least-squares fits to spectroscopic data. The program performs fits to		

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separate groups of data and then merges the results in a manner based upon the relative errors and correlations of the separate data sets. The second tool is a computer program provided by C. R. Vidal which contains two major routines. The first routine generates potential energy curves using the Rydberg-Klein-Rees (RKR) method. The second routine through an inverted perturbation analysis (IPA) adjusts the RKR curve so it is consistent with the SWE model. Finally, techniques are presented for extending potential energy curves to the dissociation energy, D_e , when the spectroscopic data alone is inadequate for the purpose.

Use of the programs is demonstrated for the diatomic molecule lead-oxide. Constants are produced for the A, B, D, a, b, and X states from previously published experimental data. A new set of assignments is made for the b state experimental data producing constants with significantly improved accuracy over those reported in literature. The b state constants are:

$$T_e = 16325.1 \pm 11.2 \text{ cm}^{-1}$$

$$W_e = 430.99 \pm 2.47 \text{ cm}^{-1}$$

$$W_e X_e = -0.757 \pm 0.441 \text{ cm}^{-1}$$

These are one standard error limits. Potential energy curves are generated for the a, A, and X states of lead-oxide. The X state potential energy curve is extended to its dissociation energy.

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