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Authors
Cashion, J.K.
Herschbach, D.R.

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Ernest O. Lawrence Radiation Laboratory

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J.K. Cashion and D.R. Herschbach

December, 1963

EMPIRICAL EVALUATION OF THE LONDON POTENTIAL ENERGY SURFACE FOR THE $H + H_2$ REACTION*

J.K. Cashion[†] and D.R. Herschbach[†]
Department of Chemistry and Lawrence Radiation
Laboratory, University of California, Berkeley, California

Abstract

An empirical potential surface for the hydrogen exchange reaction is derived from the simplest form of the London approximation (neglecting overlap), by evaluating the Coulomb and exchange integrals from the potential curves for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2. This procedure gives an activation energy of 8.9 ± 1.2 kcal/mole, in good agreement with the experimental value of 8.0 ± 0.5 kcal/mole. The potential surface has a single saddle point, and the H_3 complex is linear and symmetrical, with a bond length of 0.96 A. Simple, explicit formulas for the activation energy and the vibrational force constants are also obtained. The results emphasize the important contribution from the triplet repulsion between the end atoms with parallel spins in the complex.

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[†] Present address: Department of Chemistry, Harvard University,
Cambridge, Massachusetts

The long history of theoretical attempts to estimate potential surfaces for simple bimolecular exchange reactions indicates that even for the $H + H_2$ case it will be necessary for some time to come to rely on more or less empirical methods which synthesize the three-body interactions from two-body potentials. Several such methods have been offered.[1-5] The procedure to be considered here, like most others, is based on the London formula originally employed by Eyring and Polanyi, but avoids further empirical adjustments.

In the simplest form of the Heitler-London approximation, the binding energy of a diatomic molecule is given by

$$E = Q \mp \alpha, \tag{1}$$

where Q and α are the Coulomb and exchange integrals. London's formula for a triatomic system is

$$E = Q_a + Q_b + Q_c \pm 2^{-\frac{1}{2}}[(\alpha_a - \alpha_b)^2 + (\alpha_b - \alpha_c)^2 + (\alpha_c - \alpha_a)^2]^{\frac{1}{2}}, \tag{2}$$

and involves only these same diatomic integrals, evaluated at the three internuclear distances a, b, c. In these formulas, the zero of energy refers to separated atoms, and the lower sign in each case refers to the spin configuration of lower energy.

For the H_2 molecule accurate potential energy curves are now available for both the ground electronic state, ${}^1\Sigma_g^+$, and the first repulsive state, ${}^3\Sigma_u^+$. Thus if Eq. (1) is adopted the integrals may be evaluated from the sum and difference of the empirical curves,

$$Q = \tfrac{1}{2}({}^1\Sigma + {}^3\Sigma) \tag{3a}$$

and

$$\alpha = \tfrac{1}{2}({}^1\Sigma - {}^3\Sigma). \tag{3b}$$

This permits the London potential energy surface for the $H + H_2 \rightarrow H_2 + H$ reaction to be constructed over a wide range of interatomic distances, without introducing parametric adjustments. The surface derived in this way gives an activation energy of 8.9 kcal/mole, in good agreement with the experimental value of 8 kcal/mole, and gives vibrational force constants close to those estimated from other approximate surfaces. The use of Eqs. (3) also leads to explicit formulas for the activation energy and for the bending force constant of the complex. These bring out the important contribution from the triplet repulsion between the end atoms with parallel spins in the complex.

DIATOMIC POTENTIAL CURVES

In order that the potential surface defined by (2) and (3) be accurate to within one kcal/mole over the range $0.5\text{Å} < r_{12}$, $r_{23} < 2.5\text{Å}$, it is necessary to know the diatomic potential curves to within about 0.2 kcal/mole over the range $r = 0.5$ to 5Å. Such accuracy is presently available for the singlet state of H_2 but not for the triplet.

The classical turning points for all the vibrational levels of the $^1\Sigma_g^+$ state of H_2 have been derived from the recent spectroscopic data of Herzberg and Howe[6] by means of the Rydberg-Klein-Rees (RKR) method.[7] These points span the region r = 0.411 to 3.284Å. The perturbation calculation of Dalgarno and Lynn,[8] which extends from r = 2.1Å to beyond 6Å, agrees very closely with the RKR points in the region of their overlap (0.15 kcal/mole disparity at worst). The variational calculation of Kolos and Roothaan,[9] which covers r = 0.425 to 2.2Å, is found to agree with the RKR results within 0.2 kcal in the range of 0.5 to 1.3Å but is high by 2.4 kcal/mole at r = 2.2Å. The potential curve employed in our calculations was obtained by seventh order Lagrangian interpolation using the RKR turning points up to r = 3.2Å and the points given by Dalgarno and Lynn outside this.[10]

It might be noted that very recently Vanderslice, et al have derived even more accurate values for the turning points by use of an improved version of the RKR method which employs numerical integration of the Klein equations.[11] The improvement in accuracy provided by a similar procedure has been demonstrated by Kasper[12] and by Zare,[13] who have compared the eigenvalues derived from various versions of the RKR method with the input vibrational term values. They find that with the new method the disparities are in the range of only tenths or even hundredths of a wavenumber, about 10-100 times smaller than those obtained with the method of Tobias and

Vanderslice.[13] Although this improvement is quite significant for some applications,[13] it is negligible here since at present the triplet potential curve introduces a much larger uncertainty in the potential surface.

For information about the potential energy curve of the ${}^3\Sigma_u^+$ state of H_2 we must rely on theoretical calculations. It is disappointing to find that relatively large uncertainties still remain for a significant range of internuclear distances, as indicated in Fig. 1. The variational calculation of Kolos and Roothaan[9] provides an upper bound to the true curve over the range $r = 0.59$ to 1.85Å, and is probably quite accurate near the equilibrium internulcear separation for the ground state, $r = 0.74$Å. Another variational calculation has been carried out by Hirschfelder and Linnett,[14] who used a trial wave function which should be superior to that of Kolos and Roothan at larger distances. The perturbation calculation by Dalgarno and Lynn[8] is recommended by them as the best yet obtained for $r > 4$ atomic units or 2.1Å, and this is supported by the excellent agreement which their procedure gave for the ${}^1\Sigma_g^+$ state in the region of overlap with the RKR results. In the original paper, their results are tabulated only at integral values of r, beginning at $r = 4$ a.u. which corresponds in Fig. 1 to the lone triangle at $r = 2.12$Å. However, in a later paper Dalgarno[15] gives the following empirical equation for the calculated energy separation of the triplet and singlet states (in Rydbergs),

$$ {}^3\Sigma - {}^1\Sigma = 6.87R^2 \exp(-1.974R), \qquad (4a) $$

where R is in atomic units, or

$$^3\Sigma - {}^1\Sigma = 7696.8r^2 \exp(-3.730r), \qquad (4b)$$

where the energy is in kcal/mole and r is in Angstroms. The solid curve in Fig. 1 was plotted by adding Eq. (4b) to the energy of the $^1\Sigma_g^+$ state.

In Fig. 1 it is evident that the results of Kolos and Roothaan must be preferred below $r = 1.3$Å but that they are inferior to the calculations of Hirschfelder and Linnett beyond about 1.4Å. Since the curve of Dalgarno and Lynn comes from a perturbation calculation it provides neither an upper nor a lower bound to the true energy. If we accept it as being quite accurate for $r \gtrsim 2.1$Å, we have to interpolate smoothly to join the Kolos and Roothaan results at $r \leqslant 1.3$Å, with only the condition that the interpolation must not exceed the upper bound given by the variational calculations. We have chosen arbitrarily to follow the perturbation result of Eq. (4b) down to $r = 1.4$Å and then join smoothly to the Kolos and Roothaan curve for $r \lesssim 1.3$Å. On the basis of the comparison shown in Fig. 1 and the results obtained for the singlet state, ± 2 kcal/mole appears to be a generous estimate of the uncertainty in the interpolated portion of the potential curve for the $^3\Sigma_u^+$ state.

POTENTIAL SURFACE FOR THE H + H_2 REACTION

Fig. 2 shows a contour map of the potential surface obtained from Eqs. (2) and (3) for a linear complex of three hydrogen atoms.[16] The height of the surface at any point, $E(r_{12}, r_{23}, r_{13})$, is in general a function of six different diatomic energies, namely the singlet and triplet potentials at each of r_{12}, r_{23}, and r_{13} ($= r_{12} + r_{23}$ for the linear case). However, along the diagonal the general formula (2) reduces to

$$E(\mathrm{diag}) = \frac{3}{2}\,{}^1\Sigma(r) + \frac{1}{2}\,{}^3\Sigma(r) + {}^3\Sigma(2r), \qquad (5)$$

where $r = r_{12} = r_{23} = \frac{1}{2}r_{13}$. The surface is symmetrical about the diagonal and has a single saddle point at $r_s = 0.963$Å. At the saddle point Eq. (5) gives the energy as

$$E(\mathrm{S.P.}) = -144.5 + 39.8 + 4.9 = -99.8 \pm 1 \text{ kcal/mole.} \qquad (6)$$

The uncertainty in the first two terms of (5) is negligible in comparison with that in the third. As seen in Fig. 1, the value we have used for the ${}^3\Sigma(2r)$ term at $2r_s = 1.93$Å lies about 2 kcal/mole below the upper bound for it. However, if the Dalgarno and Lynn result is accurate to a few percent at 2.1Å, it is unlikely to be in error by 2 kcal/mole, or 50%, at 1.93Å, and thus we have assigned to (6) an uncertainty of ± 1 kcal/mole.

To obtain the activation energy we must subtract from (6) the (negative) dissociation energy of H_2 and take account of the contributions from zero-point vibration. A small vibrations treatment of the linear H_3 complex (see Table I) gives 5.42 ± 0.2 kcal/mole for the sum of the zero-point energy of the symmetrical stretching and the doubly degenerate bending modes. Thus the energy of the complex relative to its lowest vibrational level is

$$-(99.8 \pm 1) + (5.4 \pm 0.2) = -94.4 \pm 1.2 \text{ kcal/mole.} \qquad (7)$$

The corresponding terms for the H_2 molecule are[17]

$$-109.49 + 6.23 = -103.26 \text{ kcal/mole,} \tag{8}$$

and hence the activation energy is 8.9 ± 1.2 kcal/mole.

The force constants and vibrational frequencies of the complex were evaluated in the usual way,[18] and in Table I the results are compared with those obtained by other methods. A quadratic expansion of Eq. (2) about the saddle point gives

$$\Delta E = \tfrac{1}{2}f_r(\Delta r_{12}^2 + \Delta r_{23}^2) + f_{rr}\Delta f_{12}\Delta r_{23} + \tfrac{1}{2}f_\theta(\Delta\theta)^2, \tag{9}$$

with

$$f_r + f_{rr} = \tfrac{3}{4}\,{}^1\Sigma''(r) + \tfrac{1}{4}\,{}^3\Sigma''(r) + 2\,{}^3\Sigma''(2r) \tag{10a}$$

$$f_{rr} = {}^3\Sigma''(2r) + \tfrac{3}{4}[\alpha'(r)]^2/[\alpha(2r) - \alpha(r)] \tag{10b}$$

$$f_\theta/r_s{}^2 = -{}^3\Sigma'(2r)/(2r), \tag{10c}$$

where the primes indicate derivatives of the diatomic curves, evaluated for $r = r_s$, the saddle point distance, and θ is the angle between the 1-2 and 2-3 bonds ($\theta = 180°$ for the linear configuration). The sum and difference of the stretching force constants, $f_r \pm f_{rr}$, determine respectively the frequency of the symmetric stretching mode, ω_1, and the antisymmetric stretching mode, ω_3 (the imaginary frequency). From Eqs. (10a) and (10b) it is seen that these depend mostly on the curvature of the diatomic potential functions at $r = r_s$, as the terms involving $2r_s$ make somewhat smaller contributions. The numerical values are

$$f_r + f_{rr} = 0.90 + 1.11 + 0.72 = 2.73 \text{ md/Å} \tag{11a}$$

Table I. Properties of linear H_3 activated complex.

	Eyring[a] $\rho = 0.20$	Sato[b] $k = 0.1475$	Boys and Shavitt[c]	Present work
r_s, Å	1.354, 0.753	0.929	0.942	0.963
$\omega_1(\Sigma_g^+)$, cm^{-1}	3626	2108	1945	2144
$\omega_3(\Sigma_u^+)$, cm^{-1}	630i	1918i	1361i	2464i
$\omega_2(\pi_u)$, cm^{-1}	665	877	952	823
f_r, md/Å	4.34, - 0.10	0.96	0.94	0.76
f_{rr}, md/Å	0.436	1.68	1.31	1.97
f_θ/r_s^2, md/Å	0.0394	0.0761	0.090	0.0670
E(Z.P.)[d], kcal/mole	7.09	5.52	5.51	5.42
E_{act}[e], kcal/mole	8.50	8.03	14.8	8.9

[a] From reference 24; ρ denotes the Coulombic fraction, $Q/^1\Sigma$, assumed to be constant and adjusted to fit E_{act}.

[b] From reference 19; k denotes the square of the overlap integral, S^2, assumed to be constant and adjusted to fit E_{act}.

[c] From reference 20.

[d] Zero-point energy of the activated complex.

[e] Activation energy, including zero-point energy but not thermal excitation of the complex or the reactant molecule. The experimental value according to the analysis given in reference 19 is 8.0 ± 0.5 kcal/mole.

and

$$f_{rr} = 0.36 + 1.61 = 1.96 \text{ md/Å}. \qquad (11b)$$

In contrast, the bending frequency, ω_2, and the force constant f_θ given by Eq. (10c) depend only on the slope of the triplet curve at $2r_s$.

The evaluation of the terms in Eqs. (10) was carried out by numerical differentiation of the appropriate diatomic potential curves in the vicinity of r_s and $2r_s$. An interval of 0.0005 Å was used in the lower region, and one of 0.001 Å in the higher region. Under these conditions second differences were nearly constant over a span of several intervals, indicating that the quadratic approximation could be applied validly. To ensure that the results were not extremely sensitive to the potential values employed in the integration scheme, the calculations were repeated using a different set of eight points to define the interpolating polynomial. The results of the two procedures agreed to within 1%.

DISCUSSION

The results of the other methods included in Table I have been discussed recently by Weston[19] and by Shavitt,[20] who also give a critical summary of the existing experimental data. They evaluated the kinetic parameters from transition state theory for the H_3 complexes defined in columns (b) and (c) and obtained reasonably good agreement with the pre-exponential factors and isotope effects. Unfortunately, the disparities and probable inaccuracies in the experimental data are too large to permit a satisfactory test of the calculations.[20] The saddle point distance, the real frequencies ω_1 and ω_2, and the zero-point energy obtained from our potential surface are practically the same as for (b) and (c), and the only possibly significant difference is our large value of the imaginary frequency, ω_3. Weston noted that the predicted tunnel effect correction, evaluated as usual from a one-dimensional parabolic barrier approximation, appeared to be larger than is compatible with the data, and thus suggested that the value of ω_3 was too large.[19] However, other approximate methods of evaluating this correction indicate that even for $\omega_3 \simeq 2500$ cm^{-1} this would probably not occur in a more rigorous treatment of the tunneling.[20,21]

The work of Boys and Shavitt is the most extensive non-empirical calculation that has been attempted for the H_3 system, and included some 66 configurations. Although the activation energy is about 7 kcal/mole too high, the other properties obtained from the saddle point region of their surface are expected to be much more reliable.[20] The comparison with their result thus is probably a significant indication that our value of ω_3 is too large.

The original "semi-empirical" method of Eyring and Polanyi[1,2] employs

$$Q = \rho\,{}^1\Sigma \text{ and } \alpha = (1-\rho)\,{}^1\Sigma \qquad (12)$$

instead of Eqs. (3). The diatomic potential ${}^1\Sigma(r)$ is usually approximated by a Morse function and ρ, the Coulombic fraction of the binding energy, is taken as an adjustable constant. The method has often been used to estimate activation energies for

A + BC reactions by setting $\rho = 0.14$ for each diatomic pair, with surprisingly good results in some cases even though the London formula applies only to s-electrons and ρ may become much larger for bonds involving higher orbitals.[22] For H_2, $\rho = 0.14$ conforms approximately to the ratio calculated from the Heitler-London-Sugiura integrals[23] (see Fig. 3), but this gives $E_{act} \simeq 14$ kcal/mole, and $\rho = 0.20$ is required to approach the experimental activation energy.[24] However, for any $\rho \gtrsim 0.10$, the surface exhibits a "washbowl" transition state[1,24] and thus the activated complex is unsymmetrical. This feature now definitely appears to be spurious, since none of the nonempirical calculations have given any evidence for it.[20]

In the modification suggested by Sato ρ is allowed to vary and an adjustable constant k is introduced, which in the diatomic limit represents the square of the overlap integral.[3] For a given k, the Coulomb and exchange energies are obtained from

$$Q + \alpha = (1 + k)\,{}^1\Sigma \tag{13a}$$

$$Q - \alpha = (1 - k)\,{}^3\Sigma \tag{13b}$$

where ${}^1\Sigma$ is taken as a Morse function and ${}^3\Sigma$ as an "Anti-Morse function", defined by

$${}^3\Sigma\,(r) = \tfrac{1}{2}D_e\left\{\exp[-\,2\beta(r-r_e)] + 2\exp[-\,\beta(r-r_e)]\right\}, \tag{14}$$

with the usual Morse parameters D_e, β, and r_e. Sato makes only a very rough allowance for overlap in the London formula, by dividing the right hand side of Eq. (2) by $(1 + k)$. As shown by Weston,[19] this procedure, with $k = 0.1475$, yields a reasonable potential surface for the H + H_2 reaction, without a "washbowl". He points out, however, that the squared overlap integral actually varies quite rapidly with internuclear distance and becomes much larger than 0.1475 for $r < 1.6$ Å

Fig. 3 gives the variation of the Coulombic ratio, $\rho = Q/{}^1\Sigma$, with internuclear distance. The solid curve is obtained from Eqs. (3) and the dashed curve from Sato's method (with k = 0.1475). It is interesting to note that near $r_s = 0.96$ Å and $2r_s = 1.93$ Å these curves are fairly close together and that $\rho(r_s)$ and $\rho(2r_s)$ differ by more than a factor of two. This sort of variation appears to be required (unless ρ were $\lesssim 10\%$) if the "washbowl" is to be eliminated from the London potential surface. Neither Sato's $\rho(r)$ nor that calculated from the Heitler-London-Sugiura integrals,[23] shown as the dot-dashed curve in Fig. 3, approach the proper limit at large distances, where $\rho(r)$ should become unity.[8,14] This "dispersion force" region, in which the ${}^1\Sigma(r)$ and ${}^3\Sigma(r)$ potentials are practically identical, would play an important role in scattering of hydrogen atoms at thermal energies.

Fig. 4 compares Sato's approximations with the ${}^1\Sigma(r)$ and ${}^3\Sigma(r)$ potentials we have employed. The triplet curve given by Eq. (14) is too high at r_s by 14.6 kcal/mole (a factor of 1.18) and at $2r_s$ by 6.6 kcal/mole (a factor of 2.35). The slope at $2r_s$ is approximately correct, however, and thus Sato's bending force constant is close to ours (see Table I).

The empirical Coulomb and exchange integrals evaluated from Eqs. (3) represent effective values which incorporate part of the contributions from overlap in the Heitler-London treatment. Thus, if Eq. (1) is replaced by

$$E = (Q \mp \alpha)/(1 \mp S^2), \qquad (15)$$

where S is the overlap integral, an expansion including terms in S^6 gives

$$E \simeq (Q^* \mp \alpha^*)(1 + S^4) + \ldots, \qquad (16)$$

where

$$Q^* = Q - \alpha S^2 \text{ and } \alpha^* = \alpha - QS^2. \qquad (17)$$

Eq. (15) gives

$$\tfrac{1}{2}({}^1\Sigma + {}^3\Sigma) = Q^*/(1 - S^4) \qquad (18a)$$

and

$$\tfrac{1}{2}({}^1\Sigma - {}^3\Sigma) = \alpha^*/(1 - S^4) \qquad (18b)$$

in place of Eqs.(3); thus, up to terms in S^6, the Coulombic ratio plotted in Fig. 3 is

$$\rho = [Q^*/(Q^* + \alpha^*)](1 + S^8) + \ldots \qquad (19)$$

The proper allowance for overlap in the London formula, Eq. (2), is much more complicated, and three-center integrals would have to be included at the same level of approximation.[25,26]

Perhaps we hardly need to emphasize the purely empirical status of the close agreement with the experimental activation energy which is obtained from our naive application of Eqs. (2) and (3). The idealizations involved in the London formula and the concepts of Coulomb and exchange energy have been carefully examined by Coolidge and James,[25] who conclude, "It is indeed surprising that ... a reasonable degree of accuracy has been obtained through what is, from a theoretical point of view, the happy cancellation of serious and apparently unrelated approximations." As with any empirical method, the procedure considered here can only be judged by its simplicity, accuracy, and scope.

It is of interest that, contrary to the general experience with primitive chemical valence theory, the surprisingly accurate prediction of the H + H_2 activation energy persists in the next approximation. This has recently been demonstrated by Karplus and Porter,[26] who have calculated the various overlap and three-center integrals and have evaluated the diatomic Coulomb and exchange integrals by an empirical method similar to ours.

In order to apply the empirical interpolation used here to other reactions, it will be necessary to establish some means of accurately estimating the repulsive potential curves for other diatomic molecules, at least in the neighborhood of r_s and $2r_s$. As part of a correlation scheme for activation energies of hydrogen atom transfer reactions, which appeared to be uniformly successful for a wide range of bonds, Johnston and Paar[5] have employed Sato's repulsive function, Eq. (14), with the factor of $\frac{1}{2}$ replaced by $\frac{1}{4}$ on the basis of an approximate "calibration" to the H_2 triplet potential. It is disappointing that thirty years after the calculations of James and Coolidge on H_2, this is still the only molecule for which even portions of the repulsive potential curve are known to a useful accuracy.

Footnotes[**]

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$$E(\text{diag}) = \frac{1}{2}\,{}^{1}\Sigma(r) + \frac{3}{2}\,{}^{3}\Sigma(r) + {}^{1}\Sigma(2r)$$

and, for example, at $r_s = 0.962$ Å the energy is $-48 + 119 - 17 = 54$ kcal/mole. Instead of Eq. (10c), the bending force constant is given by $-{}^{1}\Sigma(2r)/(2r)$, which gives -0.141 md/Å at $r = r_s$ and is negative anywhere on the diagonal. Thus, any linear symmetric configuration of this complex would be unstable with respect to bending.

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FIGURE CAPTIONS

Fig. 1	Comparison of calculated potential curves for the $^3\Sigma_u^+$ state of the H_2 molecule.
Fig. 2	Potential surface for the reaction $H + H_2 \longrightarrow H_2 + H$. Energies are in kcal/mole, relative to a zero of energy at infinite separation of the three atoms.
Fig. 3	Coulombic fraction of the binding energy of H_2 as a function of internuclear distance. The solid curve is the empirical result obtained in this work; the dashed curve is implicit in the method of Sato; and the dot-dashed curve is derived from the Heilter-London-Sugiura approximation. The traditional "14% Coulombic" rule for plotting potential surfaces corresponds to using the dashed line.
Fig. 4	Comparison of the "best" potential curves for H_2 which were used in this work with the Morse and "Anti-Morse" functions employed by Sato. Arrows indicate the regions which contribute to the activation energy and vibrational force constants of the linear H_3 complex according to Eqs. (5) and (10) of the text.
Fig. 5	Potential curves for the H_2 molecule, estimated from "best" available data. Arrows indicate the regions which contribute to the activation energy and vibrational force constants of the linear H_3 complex, according to Eqs. (5) and (10) of the text.

APPENDIX

Potential Curves for the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ States of the H_2 Molecule

Table II and Fig. 5 give the potential energy curves for the lowest singlet and triplet states of H_2, determined as described in the text. Also given in Table II are the Coulomb and exchange integrals defined by Eqs. (4) of the text. The zero of energy refers to separated hydrogen atoms. Conversion factors were based on the value $N_{chem} = 6.02326 \times 10^{23}$ for Avogadro's number and the physical constants given by J.W.M. Dumond and E.R. Cohen in Chapter 4 of *Fundamental Formulas of Physics*, D.H. Menzel, Ed. (Dover Publications, Inc., New York, 1960). In particular:

1 Bohr radius = 0.529172 Å

1 electron volt = 23.063 kcal/mole.

1 Rydberg = 0.073502 ev

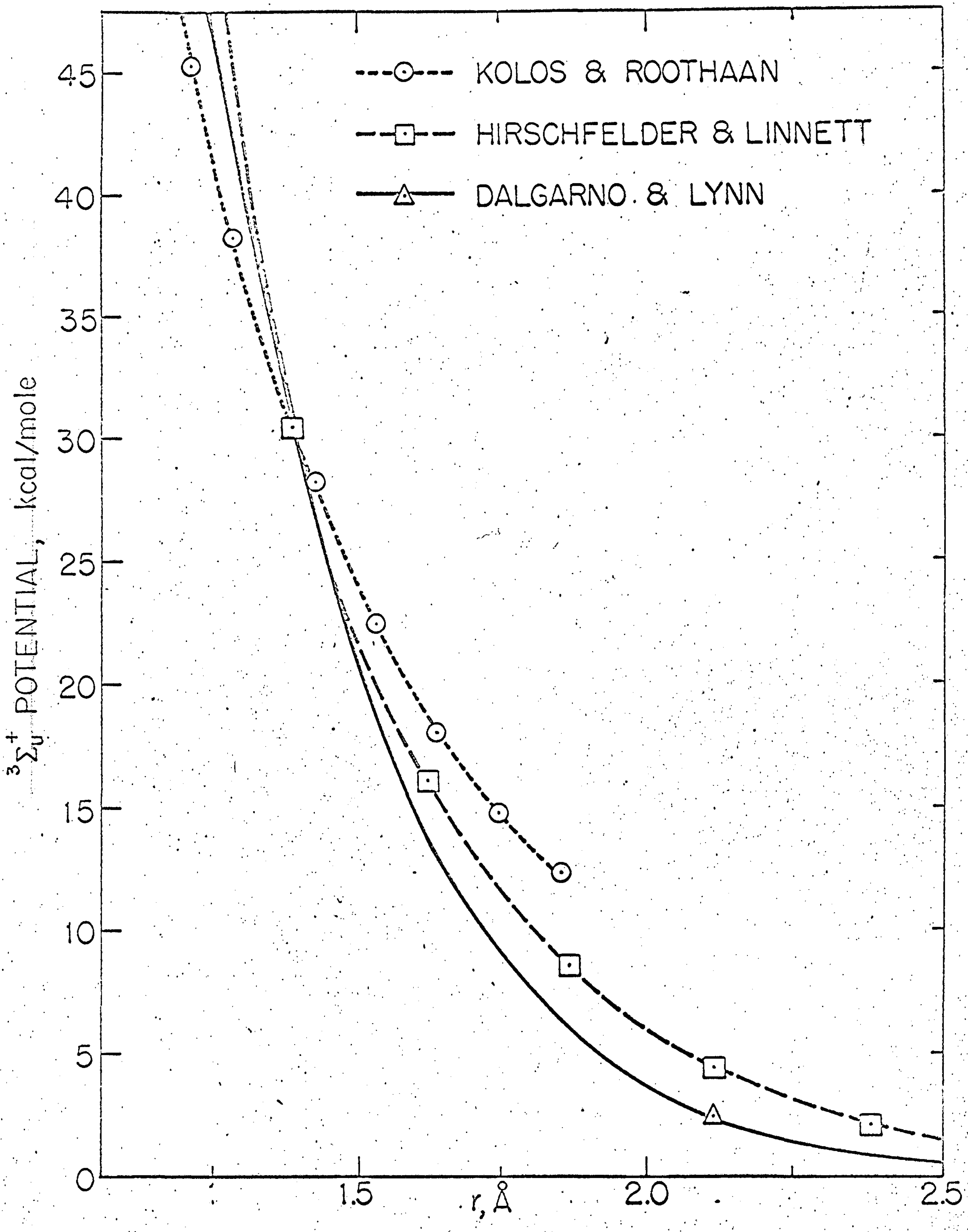
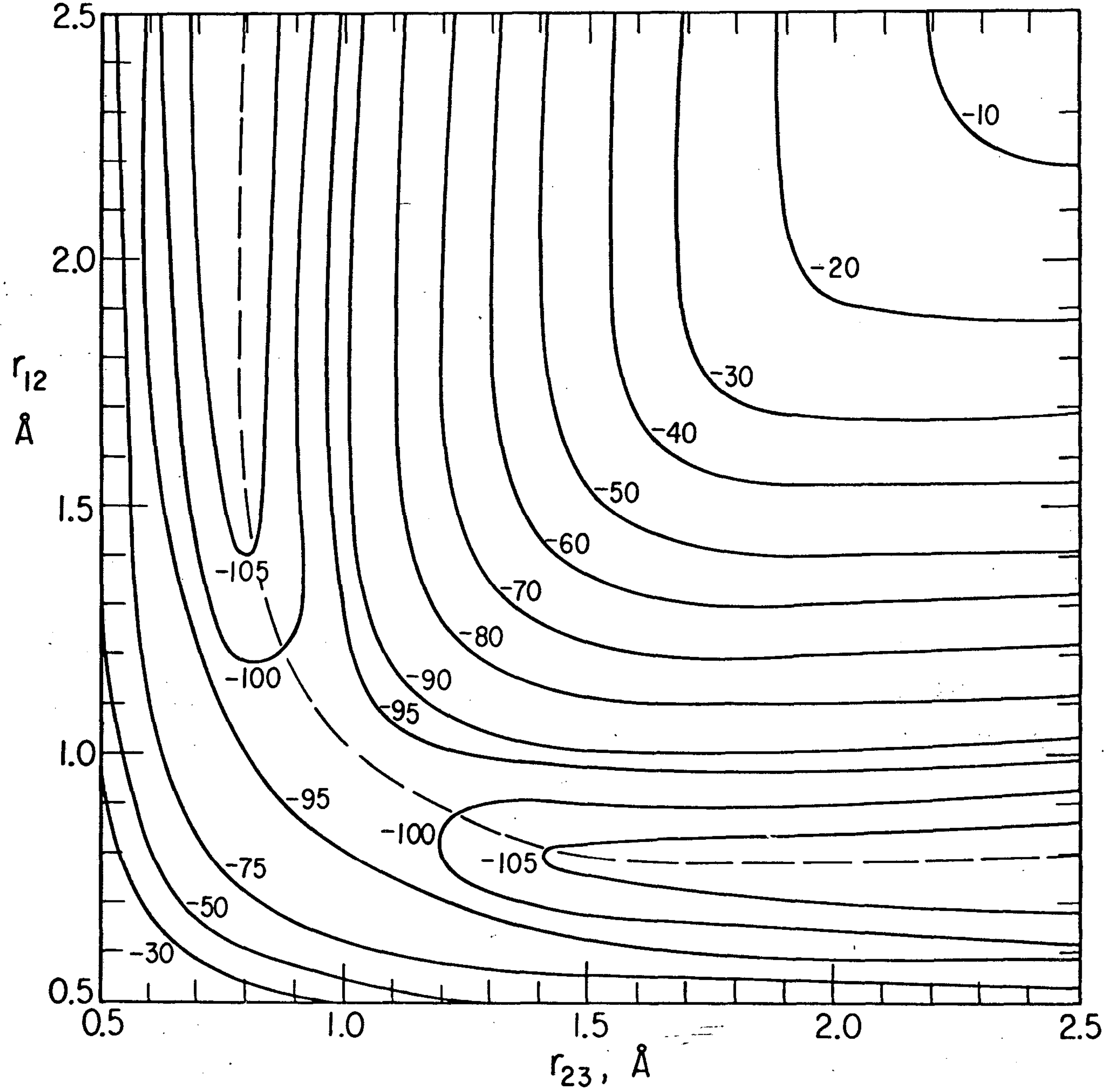

KOLOS & ROOTHAAN
HIRSCHFELDER & LINNETT
DALGARNO & LYNN
$^3\Sigma_u^+$ POTENTIAL, kcal/mole
45
40
35
30
25
20
15
10
5
0
1.5
2.0
2.5
r, Å

FIG . 1

Fig-1


2.5
2.0
1.5
1.0
0.5
r12
Å
0.5
1.0
1.5
2.0
2.5
r23, Å
-10
-20
-30
-40
-50
-60
-70
-80
-90
-95
-100
-105
-95
-100
-105
-75
-50
-30

MU-29332

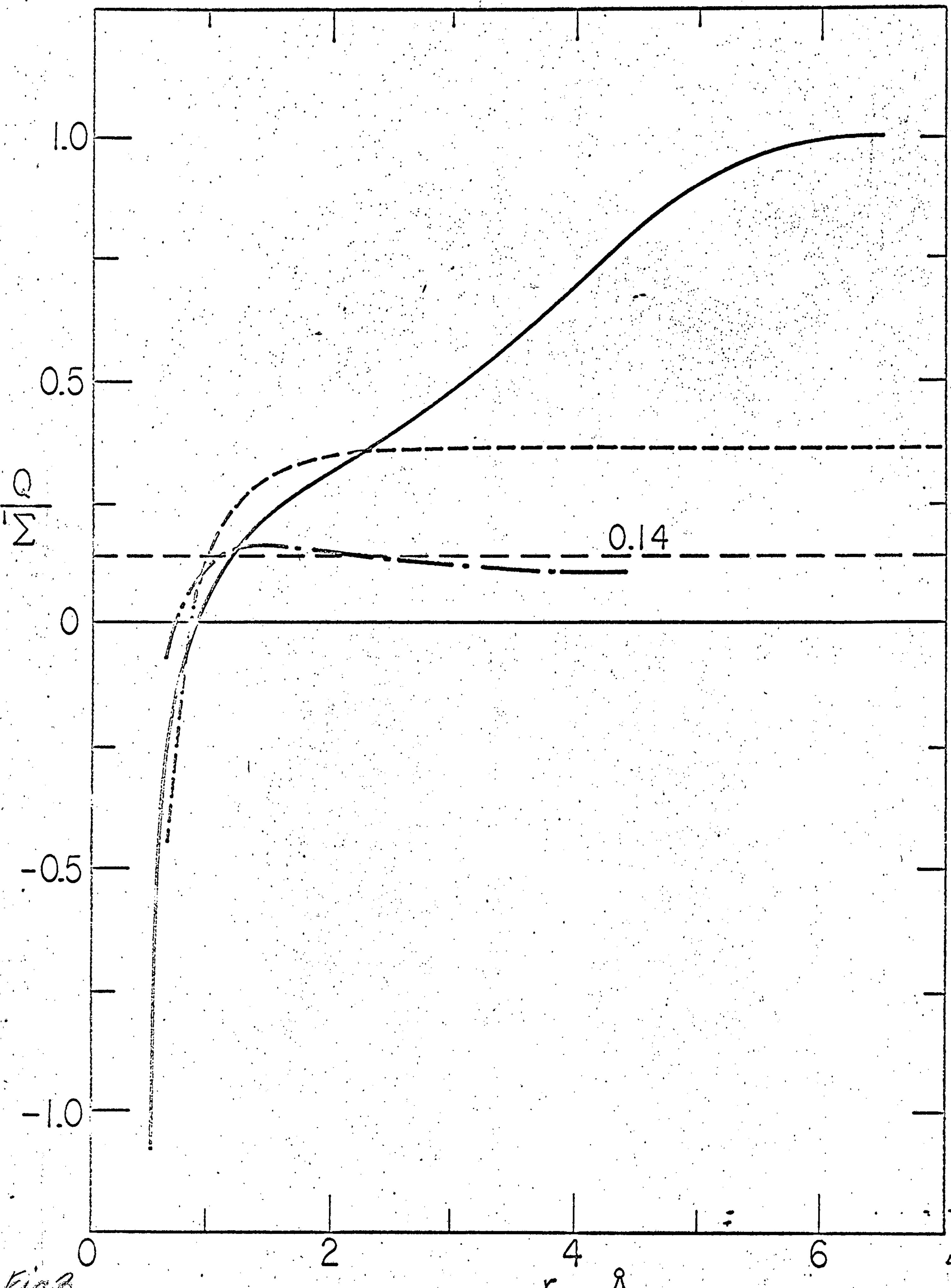


Fig 8

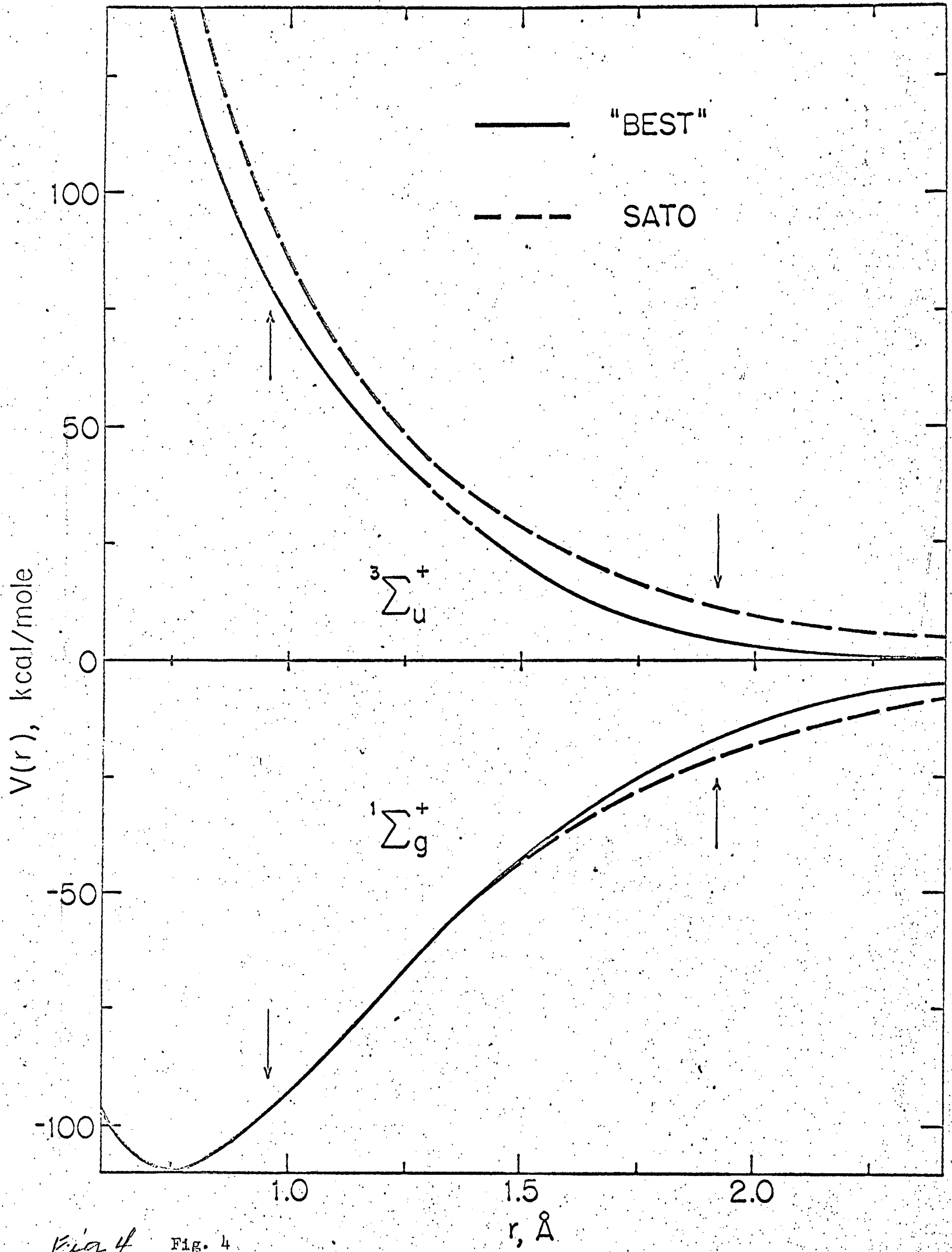
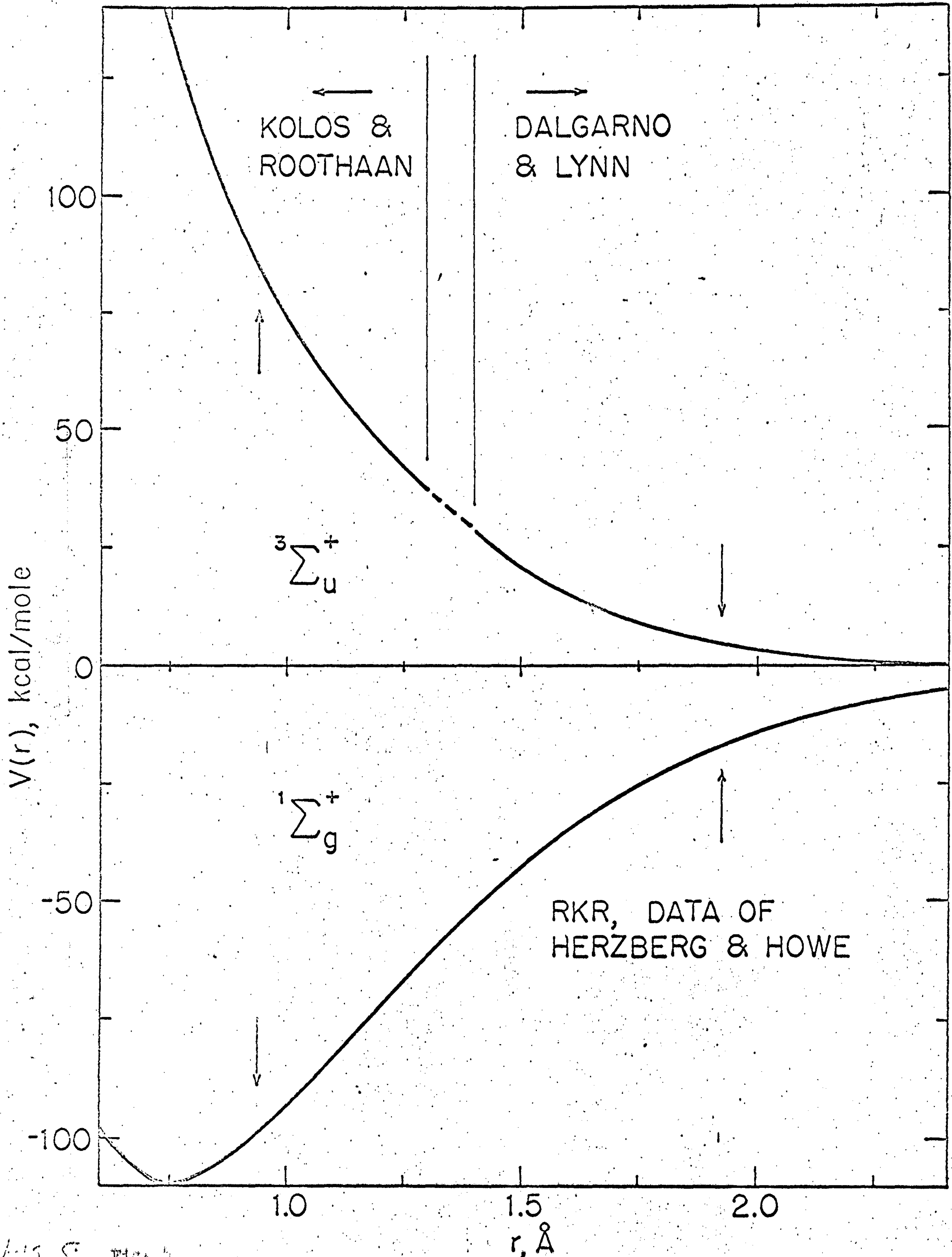

"BEST"
SATO
100
50
0
-50
-100
V(r), kcal/mole
$^3\Sigma_u^+$
$^1\Sigma_g^+$
1.0
1.5
2.0
r, Å

Fig. 4 Fig. 4


KOLOS &
ROOTHAAN
DALGARNO
& LYNN
$^3\Sigma_u^+$
$^1\Sigma_g^+$
RKR, DATA OF
HERZBERG & HOWE
V(r), kcal/mole
100
50
0
-50
-100
1.0
1.5
2.0
r, Å

```
R, ANG.   SING., KCAL   TRIP., KCAL    COULOMBIC      EXCHANGE

  0.50     -65.30840     301.31189     118.00175    -183.31014
  0.52     -74.33488     271.22574      98.44543    -172.78031
  0.54     -81.91063     247.53840      82.81388    -164.72452
  0.56     -88.29860     228.48207      70.09174    -158.39033
  0.58     -93.62569     212.74210      59.55820    -153.18389
  0.60     -97.94858     199.36558      50.70850    -148.65708
  0.62    -101.35975     187.68228      43.16127    -144.52101
  0.64    -103.98773     177.23713      36.62470    -140.61243
  0.66    -106.02139     167.73338      30.85599    -136.87738
  0.68    -107.51422     158.98577      25.73577    -133.25000
  0.70    -108.54557     150.88285      21.16864    -129.71421
  0.72    -109.17759     143.35728      17.08984    -126.26744
  0.74    -109.45658     136.36383      13.45363    -122.91020
  0.76    -109.34886     129.86381      10.25747    -119.60633
  0.78    -108.93736     123.81518       7.43891    -116.37627
  0.80    -108.26020     118.16780       4.95380    -113.21400
  0.82    -107.34873     112.86246       2.75687    -110.10559
  0.84    -106.23190     107.83338       0.80074    -107.03264
  0.86    -104.93653     103.01294      -0.96180    -103.97474
  0.88    -103.48739      98.33813      -2.57463    -100.91276
  0.90    -101.92129      93.75476      -4.08326     -97.83802
  0.92    -100.24397      89.10198      -5.57100     -94.67297
  0.94     -98.46824      84.54933      -6.95946     -91.50879
  0.96     -96.60794      80.16460      -8.22167     -88.38627
  0.98     -94.67567      76.02680      -9.32444     -85.35123
  1.00     -92.68305      72.36011     -10.16147     -82.52158
  1.02     -90.63879      69.18477     -10.72701     -79.91178
  1.04     -88.55241      66.35312     -11.09964     -77.45277
  1.06     -86.43890      63.79769     -11.32061     -75.11829
  1.08     -84.30810      61.43611     -11.43599     -72.87211
  1.10     -82.16869      59.18200     -11.49335     -70.67535
  1.12     -80.02842      56.95597     -11.53622     -68.49220
  1.14     -77.89892      54.69625     -11.60134     -66.29758
  1.16     -75.77619      52.36761     -11.70429     -64.07190
  1.18     -73.66210      49.96799     -11.84706     -61.81505
  1.20     -71.55810      47.53154     -12.01328     -59.54482
  1.22     -69.46532      45.12737     -12.16897     -57.29635
  1.24     -67.38108      42.85302     -12.26403     -55.11705
  1.26     -65.31415      40.82159     -12.24628     -53.06787
  1.28     -63.26864      39.14176     -12.06344     -51.20520
  1.30     -61.24871      37.88953     -11.67959     -49.56912
  1.32     -59.25904      37.07106     -11.09399     -48.16505
  1.34     -57.30495      36.57526     -10.36485     -46.94010
  1.36     -55.38548      36.11552      -9.63498     -45.75050
  1.38     -53.50185      35.15950      -9.17117     -44.33067
  1.40     -51.65484      32.84600      -9.40442     -42.25042
  1.42     -49.84419      27.88834     -10.97793     -38.86626
  1.44     -48.06944      26.12182     -10.97381     -37.09563
  1.46     -46.33344      24.45055     -10.94144     -35.39200
  1.48     -44.63715      22.87072     -10.88321     -33.75394
```

R, ANG.	SING., KCAL	TRIP., KCAL	COULOMBIC	EXCHANGE
1.50	-42.98126	21.37861	-10.80133	-32.17993
1.52	-41.36706	19.96978	-10.69864	-30.66842
1.54	-39.79612	18.63946	-10.57833	-29.21779
1.56	-38.26409	17.38867	-10.43771	-27.82638
1.58	-36.76904	16.21601	-10.27652	-26.49252
1.60	-35.30896	15.12009	-10.09443	-25.21452
1.62	-33.88201	14.09934	-9.89134	-23.99067
1.64	-32.48196	13.15658	-9.66269	-22.81927
1.66	-31.11371	12.28350	-9.41510	-21.69861
1.68	-29.77889	11.47510	-9.15190	-20.62699
1.70	-28.47938	10.72610	-8.87664	-19.60274
1.72	-27.21746	10.03093	-8.59327	-18.62419
1.74	-25.99730	9.38212	-8.30759	-17.68971
1.76	-24.82155	8.77381	-8.02387	-16.79768
1.78	-23.68941	8.20360	-7.74291	-15.94650
1.80	-22.60176	7.66753	-7.46712	-15.13464
1.82	-21.55902	7.16211	-7.19846	-14.36057
1.84	-20.56122	6.68436	-6.93843	-13.62279
1.86	-19.60838	6.23135	-6.68852	-12.91986
1.88	-18.69988	5.80087	-6.44950	-12.25037
1.90	-17.83349	5.39240	-6.22055	-11.61295
1.92	-17.00728	5.00522	-6.00103	-11.00625
1.94	-16.21894	4.63903	-5.78996	-10.42898
1.96	-15.46595	4.29384	-5.58606	-9.87989
1.98	-14.74562	3.96992	-5.38785	-9.35777
2.00	-14.05380	3.66905	-5.19238	-8.86142
2.02	-13.38339	3.39607	-4.99366	-8.38973
2.04	-12.73771	3.14546	-4.79613	-7.94158
2.06	-12.11536	2.91650	-4.59943	-7.51593
2.08	-11.51524	2.70826	-4.40349	-7.11175
2.10	-10.93655	2.51958	-4.20849	-6.72807
2.12	-10.37877	2.34908	-4.01485	-6.36392
2.14	-9.84166	2.19518	-3.82324	-6.01842
2.16	-9.32519	2.05617	-3.63451	-5.69068
2.18	-8.83722	1.92251	-3.45735	-5.37986
2.20	-8.37304	1.79730	-3.28787	-5.08517
2.22	-7.93047	1.68117	-3.12465	-4.80582
2.24	-7.50909	1.57307	-2.96801	-4.54108
2.26	-7.10845	1.47203	-2.81821	-4.29024
2.28	-6.72802	1.37722	-2.67540	-4.05262
2.30	-6.36726	1.28789	-2.53968	-3.82757
2.32	-6.02555	1.20341	-2.41107	-3.61448
2.34	-5.70222	1.12325	-2.28949	-3.41274
2.36	-5.39658	1.04700	-2.17479	-3.22179
2.38	-5.10643	0.97574	-2.06534	-3.04108
2.40	-4.82763	0.91259	-1.95752	-2.87011
2.42	-4.56342	0.85332	-1.85505	-2.70837
2.44	-4.31318	0.79762	-1.75778	-2.55540
2.46	-4.07630	0.74519	-1.66555	-2.41074
2.48	-3.85217	0.69578	-1.57820	-2.27398

R, ANG.	SING., KCAL	TRIP., KCAL	COULOMBIC	EXCHANGE
2.50	-3.64022	0.64916	-1.49553	-2.14469
2.52	-3.43988	0.60511	-1.41738	-2.02249
2.54	-3.25057	0.56346	-1.34356	-1.90702
2.56	-3.07178	0.52405	-1.27386	-1.79791
2.58	-2.90296	0.48673	-1.20812	-1.69485
2.60	-2.74362	0.45137	-1.14612	-1.59749
2.62	-2.59325	0.41786	-1.08769	-1.50556
2.64	-2.45137	0.38611	-1.03263	-1.41874
2.66	-2.31754	0.35603	-0.98076	-1.33678
2.68	-2.19130	0.32753	-0.93188	-1.25941
2.70	-2.07213	0.30066	-0.88574	-1.18639
2.72	-1.95970	0.27526	-0.84222	-1.11748
2.74	-1.85362	0.25130	-0.80116	-1.05246
2.76	-1.75352	0.22870	-0.76241	-0.99111
2.78	-1.65905	0.20744	-0.72580	-0.93325
2.80	-1.56987	0.18747	-0.69120	-0.87867
2.82	-1.48565	0.16875	-0.65845	-0.82720
2.84	-1.40608	0.15124	-0.62742	-0.77866
2.86	-1.33089	0.13491	-0.59799	-0.73290
2.88	-1.25980	0.11973	-0.57003	-0.68976
2.90	-1.19254	0.10566	-0.54344	-0.64910
2.92	-1.12889	0.09267	-0.51811	-0.61078
2.94	-1.06861	0.08072	-0.49395	-0.57467
2.96	-1.01150	0.06977	-0.47086	-0.54064
2.98	-0.95736	0.05980	-0.44878	-0.50858
3.00	-0.90600	0.05075	-0.42762	-0.47837
3.02	-0.85725	0.04260	-0.40733	-0.44993
3.04	-0.81097	0.03530	-0.38784	-0.42313
3.06	-0.76700	0.02880	-0.36910	-0.39790
3.08	-0.72521	0.02307	-0.35107	-0.37414
3.10	-0.68549	0.01805	-0.33372	-0.35177
3.12	-0.64771	0.01370	-0.31700	-0.33071
3.14	-0.61179	0.00998	-0.30091	-0.31088
3.16	-0.57762	0.00682	-0.28540	-0.29222
3.18	-0.54513	0.00419	-0.27047	-0.27466
3.20	-0.51424	0.00202	-0.25611	-0.25813
3.22	-0.48488	0.00028	-0.24230	-0.24258
3.24	-0.45700	-0.00111	-0.22905	-0.22795
3.26	-0.43054	-0.00218	-0.21636	-0.21418
3.28	-0.40545	-0.00298	-0.20421	-0.20123
3.30	-0.38362	-0.00552	-0.19457	-0.18905
3.32	-0.36349	-0.00831	-0.18590	-0.17759
3.34	-0.34451	-0.01088	-0.17769	-0.16682
3.36	-0.32661	-0.01324	-0.16992	-0.15669
3.38	-0.30972	-0.01540	-0.16256	-0.14716
3.40	-0.29379	-0.01739	-0.15559	-0.13820
3.42	-0.27876	-0.01920	-0.14898	-0.12978
3.44	-0.26458	-0.02085	-0.14272	-0.12186
3.46	-0.25120	-0.02235	-0.13677	-0.11442
3.48	-0.23857	-0.02371	-0.13114	-0.10743

R, ANG.	SING., KCAL	TRIP., KCAL	COULOMBIC	EXCHANGE
3.50	-0.22665	-0.02494	-0.12579	-0.10086
3.52	-0.21539	-0.02604	-0.12072	-0.09468
3.54	-0.20477	-0.02702	-0.11589	-0.08887
3.56	-0.19473	-0.02789	-0.11131	-0.08342
3.58	-0.18525	-0.02866	-0.10695	-0.07830
3.60	-0.17629	-0.02933	-0.10281	-0.07348
3.62	-0.16782	-0.02990	-0.09886	-0.06896
3.64	-0.15981	-0.03039	-0.09510	-0.06471
3.66	-0.15223	-0.03079	-0.09151	-0.06072
3.68	-0.14506	-0.03112	-0.08809	-0.05697
3.70	-0.13828	-0.03137	-0.08482	-0.05345
3.72	-0.13184	-0.03154	-0.08169	-0.05015
3.74	-0.12575	-0.03165	-0.07870	-0.04705
3.76	-0.11996	-0.03170	-0.07583	-0.04413
3.78	-0.11447	-0.03168	-0.07307	-0.04140
3.80	-0.10926	-0.03160	-0.07043	-0.03883
3.82	-0.10430	-0.03146	-0.06788	-0.03642
3.84	-0.09958	-0.03127	-0.06543	-0.03416
3.86	-0.09509	-0.03103	-0.06306	-0.03203
3.88	-0.09081	-0.03073	-0.06077	-0.03004
3.90	-0.08672	-0.03039	-0.05855	-0.02817
3.92	-0.08282	-0.03000	-0.05641	-0.02641
3.94	-0.07908	-0.02956	-0.05432	-0.02476
3.96	-0.07551	-0.02908	-0.05230	-0.02322
3.98	-0.07209	-0.02856	-0.05033	-0.02177
4.00	-0.06881	-0.02800	-0.04840	-0.02040
4.02	-0.06566	-0.02740	-0.04653	-0.01913
4.04	-0.06263	-0.02677	-0.04470	-0.01793
4.06	-0.05972	-0.02611	-0.04292	-0.01681
4.08	-0.05692	-0.02542	-0.04117	-0.01575
4.10	-0.05422	-0.02469	-0.03946	-0.01476
4.12	-0.05162	-0.02395	-0.03779	-0.01384
4.14	-0.04912	-0.02318	-0.03615	-0.01297
4.16	-0.04670	-0.02240	-0.03455	-0.01215
4.18	-0.04437	-0.02160	-0.03298	-0.01139
4.20	-0.04213	-0.02079	-0.03146	-0.01067
4.22	-0.03996	-0.01997	-0.02997	-0.01000
4.24	-0.03788	-0.01915	-0.02852	-0.00937
4.26	-0.03588	-0.01833	-0.02711	-0.00877
4.28	-0.03396	-0.01752	-0.02574	-0.00822
4.30	-0.03212	-0.01671	-0.02442	-0.00770
4.32	-0.03036	-0.01593	-0.02314	-0.00721
4.34	-0.02868	-0.01516	-0.02192	-0.00676
4.36	-0.02709	-0.01442	-0.02075	-0.00633
4.38	-0.02558	-0.01372	-0.01965	-0.00593
4.40	-0.02416	-0.01305	-0.01861	-0.00555
4.42	-0.02283	-0.01243	-0.01763	-0.00520
4.44	-0.02160	-0.01186	-0.01673	-0.00487
4.46	-0.02046	-0.01134	-0.01590	-0.00456
4.48	-0.01943	-0.01089	-0.01516	-0.00427

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R, ANG.   SING., KCAL   TRIP., KCAL   COULOMBIC     EXCHANGE

  4.50     -0.01850      -0.01050      -0.01450      -0.00400
  4.52     -0.01768      -0.01019      -0.01394      -0.00375
  4.54     -0.01698      -0.00996      -0.01347      -0.00351
  4.56     -0.01638      -0.00982      -0.01310      -0.00328
  4.58     -0.01591      -0.00976      -0.01284      -0.00307
  4.60     -0.01556      -0.00981      -0.01268      -0.00288
  4.62     -0.01534      -0.00995      -0.01264      -0.00269
  4.64     -0.01524      -0.01020      -0.01272      -0.00252
  4.66     -0.01527      -0.01055      -0.01291      -0.00236
  4.68     -0.01543      -0.01101      -0.01322      -0.00221
  4.70     -0.01573      -0.01159      -0.01366      -0.00207
  4.72     -0.01615      -0.01227      -0.01421      -0.00194
  4.74     -0.01670      -0.01307      -0.01488      -0.00181
  4.76     -0.01737      -0.01397      -0.01567      -0.00170
  4.78     -0.01816      -0.01498      -0.01657      -0.00159
  4.80     -0.01906      -0.01609      -0.01758      -0.00149
  4.82     -0.02008      -0.01729      -0.01869      -0.00139
  4.84     -0.02118      -0.01858      -0.01988      -0.00130
  4.86     -0.02237      -0.01994      -0.02115      -0.00122
  4.88     -0.02363      -0.02135      -0.02249      -0.00114
  4.90     -0.02495      -0.02281      -0.02388      -0.00107
  4.92     -0.02629      -0.02429      -0.02529      -0.00100
  4.94     -0.02765      -0.02578      -0.02671      -0.00093
  4.96     -0.02899      -0.02724      -0.02811      -0.00087
  4.98     -0.03028      -0.02865      -0.02947      -0.00082
  5.00     -0.03150      -0.02997      -0.03074      -0.00076
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