they, in fact, have their moments in opposite directions. This indicates that, for at least one of the two, $\mu(R)$ has undergone a sign change between $R=0$ and $R=R_e$, and that the limiting behavior for small R has ceased to have validity near the equilibrium point.

Normally, a power series about R_e is employed for the dipole moment function. It is found[10] that it is necessary to go past the quadratic term in the series to fit all the experimental data, which means the use of a function with more than 3 parameters.

ACKNOWLEDGMENT

I wish to thank Professor William Klemperer and Dr. David Buckingham for helpful discussions.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 38, NUMBER 11 1 JUNE 1963

Semiclassical Analysis of the Extrema in the Velocity Dependence of Total Elastic-Scattering Cross Sections: Relation to the Bound States*

RICHARD B. BERNSTEIN

Chemistry Department, University of Michigan, Ann Arbor

(Received 25 January 1963)

The phenomenon of extrema in the velocity dependence of the total elastic cross section $Q(v)$ for atom–atom scattering in the thermal-energy region is shown to be a quite general one, whenever the interaction potential consists of both attractive and repulsive parts and the resulting well has a "capacity" for one or more discrete levels. The phase shift vs angular-momentum dependence exhibits a maximum; since this maximum is a function of the de Broglie wavelength, the cross section exhibits an undulatory velocity dependence. A semiclassical analysis of the extrema velocities (and undulation amplitudes) is presented. Suitable plots are suggested from which one may deduce certain information on the interatomic potential and the diatom bound states. The following rule is proposed: the observation of m maxima in the elastic atom–atom impact spectrum implies the existence of at least m discrete vibrational levels of zero angular momentum for the diatom.

INTRODUCTION

IN a previous communication[1] a procedure was outlined for the analysis of the undulatory velocity dependence of the total elastic-scattering cross section $Q(v)$. It was shown that such an analysis can yield significant information bearing on the interaction potential and the existence of bound states for the composite system or "collision complex." The present paper amplifies and extends this work.

The phenomenon of extrema in the energy dependence of the cross section should be a general one. For any colliding system described by an interaction potential with a minimum, where the potential well has a "capacity" for one or more discrete levels, the dependence of the phase shift upon the angular-momentum quantum number is characterized by an energy-dependent maximum, in the neighborhood of which there are a significant number of nonrandom phases. The velocity dependence of the maximum phase leads to an undulatory velocity dependence of the cross section.

Making use of the semiclassical approximation,[2] general methods are developed to establish the relation between the extrema velocities (and undulation amplitudes) and the parameters of the potential. For the case of atomic scattering the connection between the extrema and the diatom bound states is explored. Consideration is given to the extension of these concepts to the molecular-scattering problem.

EXTREMA-VELOCITIES AND UNDULATION AMPLITUDE

We assume the existence of a single,[3] static, central potential of a "realistic" type, i.e., with a long-range

* Financial support of this work by the U.S. Atomic Energy Commission, Division of Research, is gratefully acknowledged.

[1] R. B. Bernstein, J. Chem. Phys. **37**, 1880 (1962).

[2] See, for example, (a) R. B. Bernstein, J. Chem. Phys. **36**, 1403 (1962); also the basic paper: (b) K. W. Ford and J. A. Wheeler, Ann. Phys. (N. Y.) **7**, 259, 287 (1959).

[3] In the present paper attention is restricted to collisions between unlike atoms, in which one is in the $^1S_0$ state (i.e., an atom belonging to Group II or VIII) while the other may be either $^1S_0$ (Group II) or $^2S_{\frac{1}{2}}$ (Group I), yielding the single molecular state $^1\Sigma^+$ or $^2\Sigma^+$, respectively. Extension is straightforward to the case of two $^2S_{\frac{1}{2}}$ atoms, yielding both $^1\Sigma^+$ and $^3\Sigma^+$ molecular states (the singlet state with a relatively deep "binding" well, the triplet with only a shallow "van der Waals" well). However, the analysis becomes cumbersome in the general case for scattering of state-unselected beams. See the Appendix for an enumeration of the possible molecular electronic states. Where the colliding atoms are identical, the following modifications are required:

(a) for spinless atoms, only doubly weighted even- or odd-order phases are to be used in the summation for Q according as the atoms are bosons or fermions, respectively. This has the effect of halving the necessary number of phases (at any given collision energy) but at the same time making for poorer "statistics" in the semiclassical treatment.

(b) for atoms with spin, proper weighting (according to the multiplicity of the molecular state) of the above-mentioned even- or odd-type cross-section sums is required. Normally, different potentials are used for each molecular state, so that Pauli exclusion is automatically taken into account [see reference 17(a)].

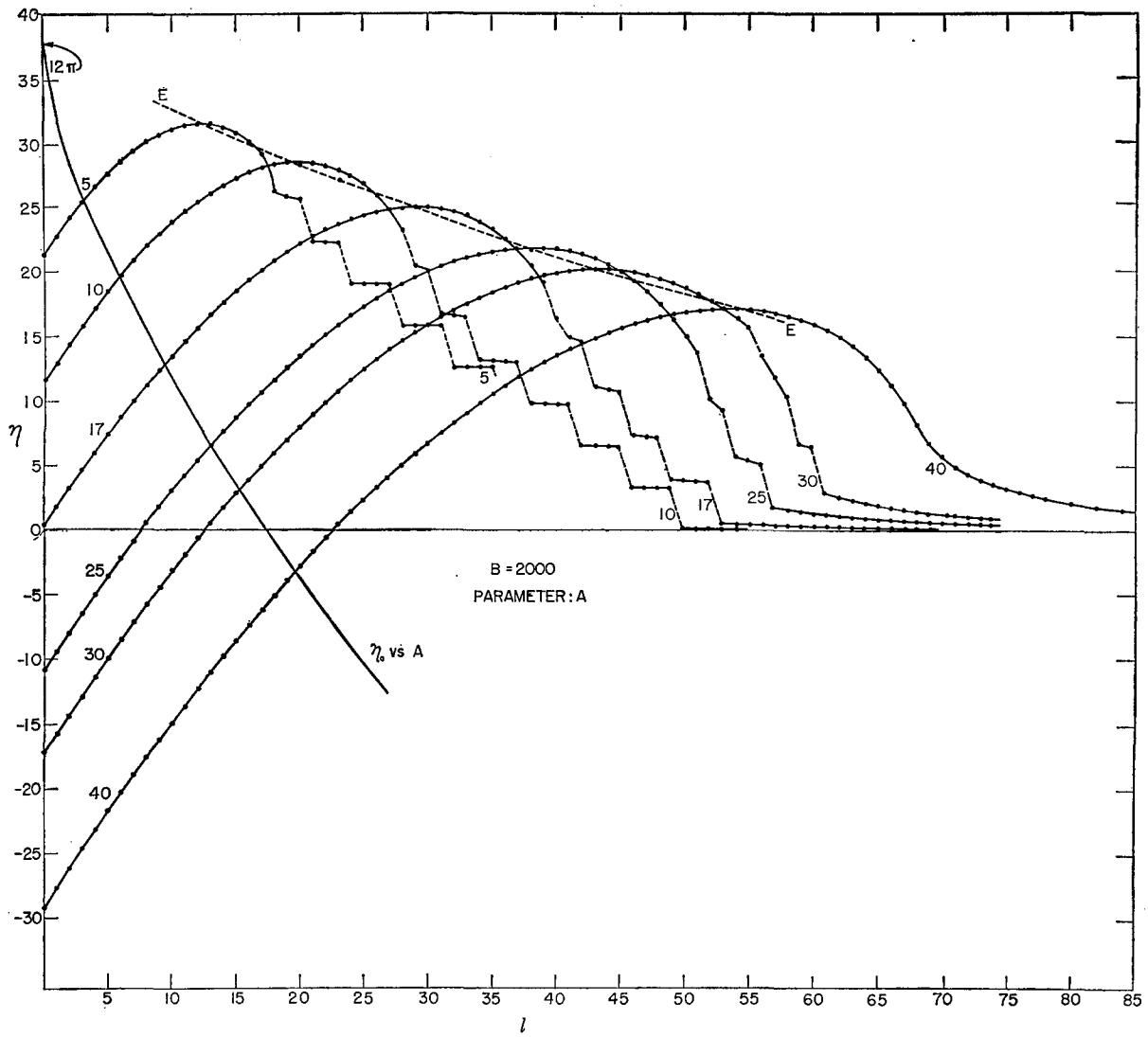

FIG. 1. Dependence of phase shift upon l and A for $B=2000$; [LJ (12, 6) potential]. The dashed curve (E) is the envelope of the maxima. The solid curve $\eta_0(A)$ is a plot with abscissa A, (*not l*!) of the s-wave phases.

attraction and a short-range repulsion. The principles of the analysis to be presented are general; however, it is convenient to illustrate the procedures with specific examples. For simplicity, the LJ(12, 6) potential has been chosen for this purpose: $V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. The notation is in accordance with previous papers of this series.[1,2,4]

For most atomic and molecular collisions in the "thermal"-energy region many scattering phase shifts are required to evaluate the total cross section

$$Q(k)=(4\pi/k^2)\sum_l(2l+1)\sin^2\eta_l(k). \qquad (1)$$

Here, as usual, $\eta_l(k)$ is the phase shift for the lth-order partial wave, and $k=\mu v/\hbar$. Massey and Mohr[5] (MM) introduced the random-phase approximation: i.e., the large, low-order phases are essentially random after removing multiples of π; their contribution to Q, say $Q_<$, is obtained by replacing $\sin^2\eta(k)$ by its average value of $\frac{1}{2}$, and removing it from the summation. Thus $Q_<\cong 2\pi(L+\frac{1}{2})^2/k^2$, where L is the largest value of l for which the phases may be assumed to be random; according to MM, L is defined by the relation $\eta_L(k)=\frac{1}{2}$. For a long-range attractive potential $V=-C/r^s$, they employ the Jeffreys–Born (JB) approximation, to obtain the contribution, $Q_>$, from the higher-order phases, yielding

$$L\cong[(2\mu/\hbar^2)Ck^{s-2}f(s)]^{1/(s-1)}, \qquad (2)$$

$$Q_>=[1/(2s-4)]Q_<, \qquad (3)$$

[4] R. B. Bernstein, (a) J. Chem. Phys. **33**, 795 (1960); (b) **34**, 361 (1961); (c) **38**, 515 (1963); *re* Appendix I, an important related paper by E. M. Baroody, Phys. Fluids **5**, 925 (1962), had been overlooked.

[5] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).

and thus

$$Q_{MM}=\frac{\pi L^2}{k^2}\left(\frac{2s-3}{s-2}\right)=\pi[2f(s)]^{2/(s-1)}\left(\frac{2s-3}{s-2}\right)\left(\frac{C}{\hbar v}\right)^{2/(s-1)}, \quad (4)$$

where

$$f(s)=\tfrac{1}{2}(\pi^{\frac{1}{2}})\Gamma(\tfrac{1}{2}s-\tfrac{1}{2})/\Gamma(\tfrac{1}{2}s).$$

Thus, for a monotonic potential, a monotonic velocity dependence of Q is predicted. For the usual case of atomic and molecular scattering, $s=6$ and

$$Q_{MM}=7.55(C/\hbar v)^{\frac{2}{5}}. \quad (5)$$

It was shown earlier[1,4b] that the influence of the short-range repulsion manifests itself in the following way. The low-order phases (primarily repulsive) are always negative with respect to the higher-order (attractive) phases; thus there is always a maximum in η_l, located in the intermediate l region. This maximum provides a significant number of nonrandom phases which contribute either positive or negative deviations to the $Q_<$ summation depending on whether the maximum phase is near $\pi/2$ or π, etc.

In the analysis which follows, it is convenient to express the results in terms of the fractional deviation of the cross section from the MM-approximated value, i.e., $\Delta Q/Q_{MM}\equiv Q/Q_{MM}-1$, assuming[6] that Q_{MM} serves as an accurate "reference" cross section. We consider *only* the influence upon the cross section of the nonrandom phases associated with the maximum in the intermediate l region.

As an illustration of the general phase behavior, Fig. 1 summarizes calculations of the dependence of η_l upon the velocity parameter $A(\equiv k\sigma)$ for a given value of the potential-well parameter $B(\equiv 2\mu\epsilon\sigma^2/\hbar^2)=2000$. Here σ and ϵ are the usual LJ(12,6) potential constants. The dashed line (E) designates the envelope of the maxima in the phase-shift curves. The maximum phase, designated η_{max} (or η_m) is seen to increase with decreasing velocity, passing successively through integral multiples of $\pi/2$. At the same time the corresponding value of l (designated l_m) decreases monotonically as the velocity decreases. Other features of Fig. 1 are discussed later.

An alternative representation is a plot of η vs β [the reduced angular-momentum function[4a]: $\beta\equiv(l+\frac{1}{2})/A$]; such a plot is shown in Fig. 2. Based on the $Q-i-K$ curves[4a] of reduced phases $\eta^*(\beta, K)$, it is possible to construct graphs of $\eta(\beta)$ at various reduced collision energies K, for the given value of B (in this particular example $B=125$). Here $\eta^*\equiv\eta/A$ and $K=\frac{1}{2}\mu v^2/\epsilon$, as usual. The maximum occurs at $\beta=\beta_m$. Referring to Fig. 2, it is seen that as K is decreased, η_m passes upward successively through the shaded zones, corresponding to regions where $\sin^2\eta>\frac{1}{2}$, and the unshaded ones, where $\sin^2\eta<\frac{1}{2}$, which gives rise, successively, to positive and negative deviations from the random-phase approximation. Inspection of Fig. 2 suggests that the largest positive deviation should occur when the maximum phase shift is $(N-\frac{1}{4})\pi$ (where N is an integer); when the maximum phase rises slightly above this value a large number of phases (near the maximum) enter the unshaded zone and contribute to a decline in Q. Similar arguments apply to the case of negative deviations. Thus the *approximate* condition for extrema in $\Delta Q/Q_{MM}$ is[1]

$$\eta_m\cong(N-\tfrac{1}{4})\pi. \quad (6)$$

[See Eq. (24) below.]

Positive or negative extrema (maxima or minima in $\Delta Q/Q_{MM}$) occur when N (always ≥ 1) is an even or odd multiple, respectively, of $\frac{1}{2}$. A more quantitative analysis of the condition for an extremum is presented below, leading to a slightly different, more accurate, result (i.e., $\frac{1}{4}$ is replaced by $\frac{3}{8}$); see Eq. (24), which *supplants* Eq. (6).

Next we evaluate the dependence of the maximum

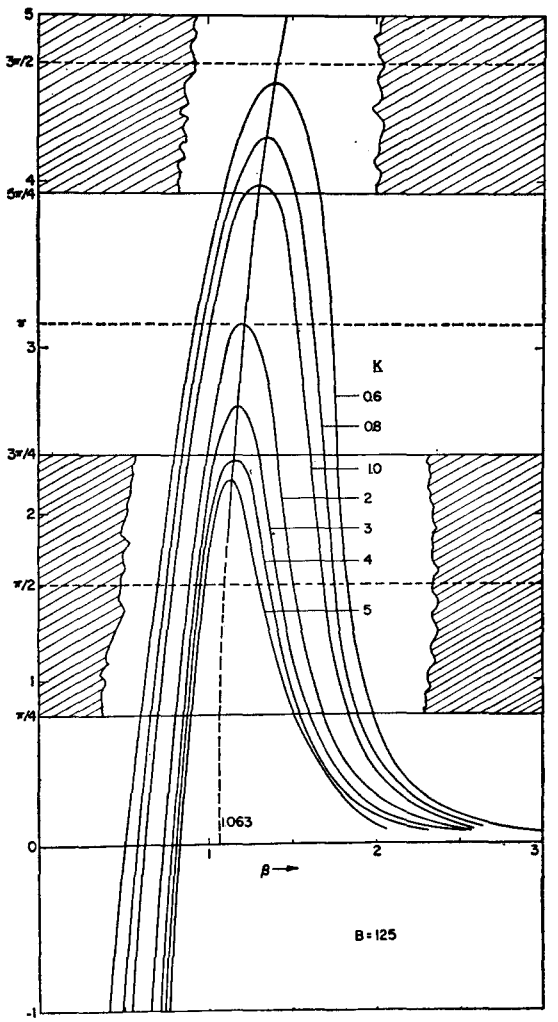

FIG. 2. Dependence of η upon $\beta(\equiv(l+\frac{1}{2})/A)$ and $K(\equiv\frac{1}{2}\mu v^2/\epsilon)$ for $B=125$; [LJ (12,6) potential]. Shaded zones correspond to regions in which $\sin^2\eta>\frac{1}{2}$.

[6] The question of the absolute accuracy of the over-all MM approximation treatment is discussed in another paper: R. B. Bernstein and K. H. Kramer, J. Chem. Phys. **38**, 2507 (1963).

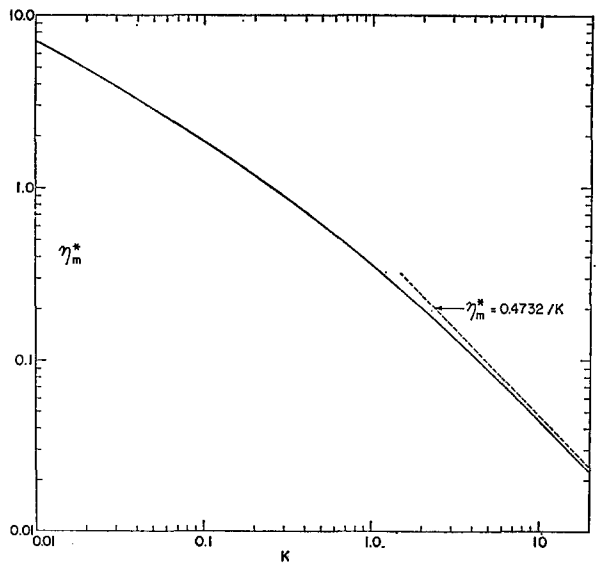

FIG. 3. Dependence of η_{max}^* upon K; [LJ (12,6) potential].

phase upon the collision energy and the parameters of the potential. From the semiclassical relationship the maximum in the reduced phase η_m^* is a function only of K. We consider the classical deflection function $\theta(b^*, K)$, where $b^*=b/\sigma$. Designating by $b_0^*(K)$ the first zero of the deflection function [i.e., $\theta(b_0^*)=0$, with $0<b_0^*<\infty$], and recalling the semiclassical equivalence relationship[2]

$$\eta^*(b^*, K)=-\tfrac{1}{2}\int_{b^*}^{\infty}\theta(b^*, K)db^*, \tag{7}$$

it follows that η^* attains its maximum value at $b^*=b_0^*$, so that $b_0^*=\beta_m=(l_m+\frac{1}{2})/A$ and $\eta^*(b_0^*)=\eta_m^*$.

Figure 3 shows a graph of η_m^* vs K; the points from which the curve was drawn were taken from (a) the maxima of the $Q-i-K$ reduced phase curves, and (b) confirmatory calculations via Eq. (7), i.e., graphical integration of the deflection functions, available in tabular form.[7] Figure 4 illustrates the dependence of β_m upon K; the curve is based on points taken from (a) the $Q-i-K$ curves and (b) the zeros of the deflection functions.[7] In both cases (Figs. 3 and 4), Sources (a) and (b) yielded identical results (i.e., unique curves), establishing confidence in the semiclassical procedures.

The high-energy limit of β_m and the corresponding asymptotic behavior of η_m^* are readily obtained from the JB approximation for the reduced phases[4b,c] [for the LJ(12,6) potential]:

$$\eta_{JB}^*\sim[3\pi/(8K\beta^5)](1-\tfrac{21}{32}\beta^{-6}), \tag{8}$$

so that

$$\beta_m\sim(\tfrac{21}{32}\cdot\tfrac{11}{5})^{\frac{1}{6}}=1.0631, \tag{9a}$$

and

$$\eta_m^*\sim K^{-1}(\tfrac{120}{847}\pi)(\tfrac{231}{160})^{\frac{1}{6}}=0.4732/K. \tag{9b}$$

These asymptotic results are designated on the graphs.

It is convenient to express the deviation of $\eta_m^*(K)$ from the high-velocity limit as an expansion in powers of $K^{-\frac{1}{2}}$ (proportional to v^{-1})

$$\eta_m^*(K)=(0.4732/K)g(K), \tag{10a}$$

where

$$g(K)=1-c_1K^{-\frac{1}{2}}\pm c_2K^{-1}+\cdots. \tag{10b}$$

For $K\geq 0.25$, only the term in $K^{-\frac{1}{2}}$ is required; a good fit is achieved with $c_1=0.25$. Thus we may write

$$\eta_m\cong 0.4732D\cdot(1-0.25D/B^{\frac{1}{2}}) \tag{11}$$

(valid for $D\leq 2B^{\frac{1}{2}}$), where $D\equiv B/A=2\epsilon\sigma/\hbar v$.

Combining Eq. (24) with Eq. (11) we obtain the condition for an extremum in $\Delta Q/Q_{MM}$

$$N-\tfrac{3}{8}=0.1506D_N\cdot(1-0.25D_N\cdot B^{-\frac{1}{2}})$$

$$=0.3012\frac{\epsilon\sigma}{\hbar v_N}\cdot\left[1-\frac{0.354}{v_N}\left(\frac{\epsilon}{\mu}\right)^{\frac{1}{2}}\right], \qquad (D\leq 2B^{\frac{1}{2}}), \tag{12}$$

where v_N is the velocity corresponding to the Nth extremum (similarly for D_N).

Equation (12) is shown in graphical form in Fig. 5. Horizontal lines corresponding to different extrema intersect the curves at the appropriate D_N values.

Figure 5 and Eq. (12) suggest the method of analysis[1] of experimental extrema-velocity data. A plot of $N-\frac{3}{8}$ vs $1/v_N$ is made; since it must pass through the origin, we can ascertain immediately the correctness of the assignment of the indices N to the various extrema. The initial slope of the line yields the $\epsilon\sigma$ product; the

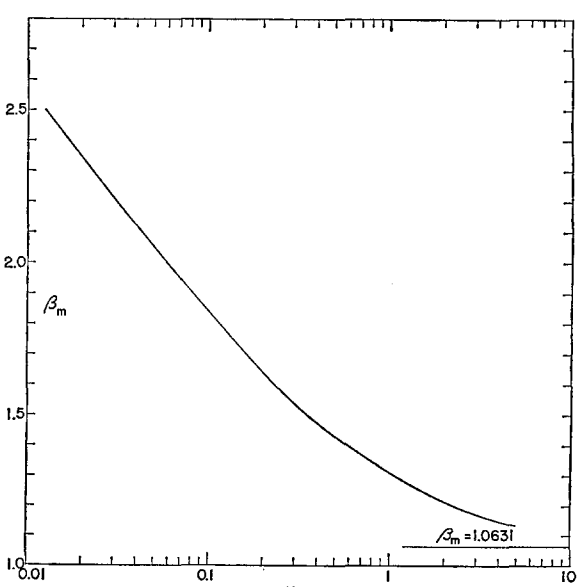

FIG. 4. Dependence of β_{max} upon K; [LJ (12,6) potential].

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

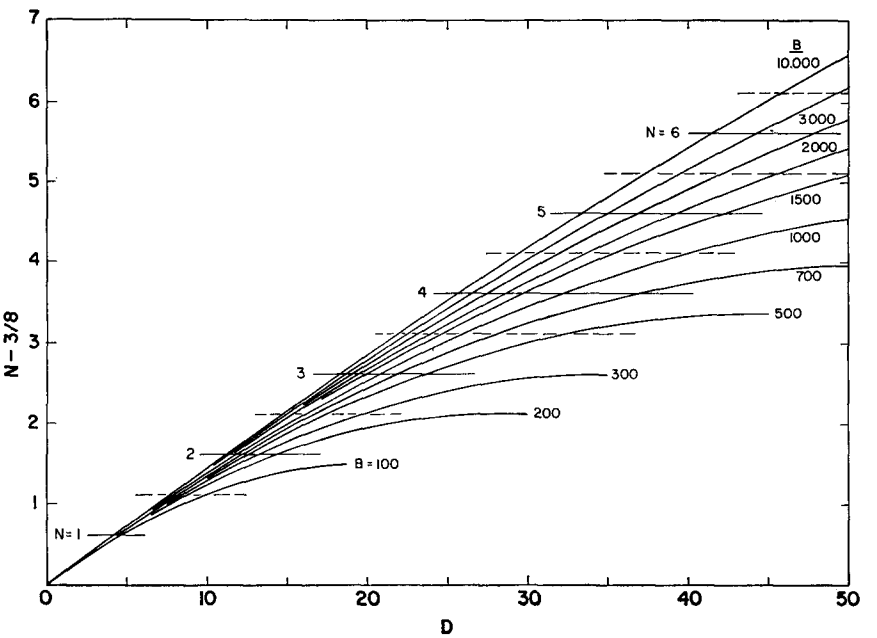

FIG. 5. Extrema plot: $N-\frac{3}{8}$ vs D $(\equiv B/A)$ for various values of B; [LJ (12,6) potential]. The horizontal lines corresponding to different extrema intersect the curves at the appropriate D_N values.

curvature depends on ϵ/μ. As an alternative one may plot $(N-\frac{3}{8})v_N$ vs $1/v_N$; the intercept gives $\epsilon\sigma$, and the ratio of slope to intercept yields separately ϵ (but, unfortunately, with low sensitivity). Equation (12) also suggests that the velocities of the low-order extrema would be invariant under isotopic substitution.

Next, we proceed to evaluate the amplitude of the undulations in $\Delta Q/Q_{\mathrm{MM}}$. Using the "reduced" notation[1,2,4] the MM formula may be expressed as

$$Q_{\mathrm{MM}}{}^{*}\equiv Q_{\mathrm{MM}}/\pi\sigma^2=2\beta_L{}^2+Q_{>}{}^{*}=\tfrac{9}{4}\beta_L{}^2, \qquad (13)$$

where $\beta_L=(L+\frac{1}{2})/A$, with L given by Eq. (2). The deviation due to the nonrandom phases (defined as those corresponding to β values lying within a range β_1 to β_2, to be evaluated) is expressed in terms of the difference between $\langle\sin^2\eta(\beta)\rangle_{\mathrm{av}}$ and $\frac{1}{2}$:

$$\Delta Q^{*}\equiv Q^{*}-Q_{\mathrm{MM}}{}^{*}=4\cdot(\beta_2{}^2-\beta_1{}^2)(X-\tfrac{1}{2}), \qquad (14)$$

where

$$X\equiv(\beta_2{}^2-\beta_1{}^2)^{-1}\int_{\beta_1}^{\beta_2}\sin^2\eta(\beta)\,d\beta^2. \qquad (15)$$

The limits on β are taken to be symmetrical around β_m, so that $\beta_1=\beta_m-\alpha_0$, $\beta_2=\beta_m+\alpha_0$, and $\beta_2{}^2-\beta_1{}^2=4\alpha_0\beta_m$, where α_0 is as yet unspecified. [We note that the upper and lower bounds on ΔQ^{*} are $\pm2(\beta_2{}^2-\beta_1{}^2)=\pm8\alpha_0\beta_m$, corresponding to $X=1$ or 0, respectively, in accord with expectation.]

We define a difference angle $\phi(>0)$ as

$$\phi\equiv\eta_m-\eta_1, \qquad (16)$$

where $\eta_1=\eta(\beta_1)=\eta(\beta_2)$, which represents the range of the nonrandom phases (expected to be of the order of $\pi/4$ to $\pi/2$ rad), whose magnitude is yet to be determined.

We express $\eta(\beta)$, over the nonrandom region, in parabolic form,

$$\eta=\zeta-c\alpha^2, \qquad (17a)$$

where ζ stands for η_m, $\alpha=\beta-\beta_m$, and

$$c=\phi/\alpha_0{}^2. \qquad (17b)$$

We may evaluate c by returning to the deflection function, expanding (to first order only) around $b_0{}^{*}$

$$\theta(b^{*})=(b^{*}-b_0{}^{*})\cdot\theta_0{}'+\cdots, \qquad (18)$$

where $\theta_0{}'$ is the slope evaluated at $b_0{}^{*}$, $\theta_0{}'\equiv(d\theta/db^{*})_{b_0{}^{*}}$; then making use of Eq. (7),

$$\phi=\frac{A}{2}\int_{\beta_2}^{\beta_m}\theta d\beta=\frac{A}{16}\theta_0{}'(\beta_2-\beta_1)^2=\frac{A\theta_0{}'\alpha_0{}^2}{4}, \qquad (19)$$

so that

$$c=A\theta_0{}'/4. \qquad (20)$$

Substituting Eqs. (17) in (15) we obtain, after some manipulation,

$$X=\tfrac{1}{2}\{1-f_1(\phi)\cos2\zeta-f_2(\phi)\sin2\zeta\}, \qquad (21)$$

where

$$f_1(\phi)\equiv1-\tfrac{2}{5}\phi^2+\tfrac{2}{27}\phi^4-\tfrac{4}{585}\cdot\phi^6+\tfrac{2}{53355}\cdot\phi^8-\cdots,$$

and

$$f_2(\phi)\equiv\tfrac{2}{3}\phi-\tfrac{4}{21}\phi^3+\tfrac{4}{165}\phi^5-\tfrac{8}{47125}\phi^7+7.43\times10^{-5}\phi^9-\cdots.$$

It is instructive to carry out a preliminary analysis, as follows. As a first trial, we arbitrarily assume $\zeta=(N-\frac{1}{4})\pi$. For simplicity, we confine our attention to a

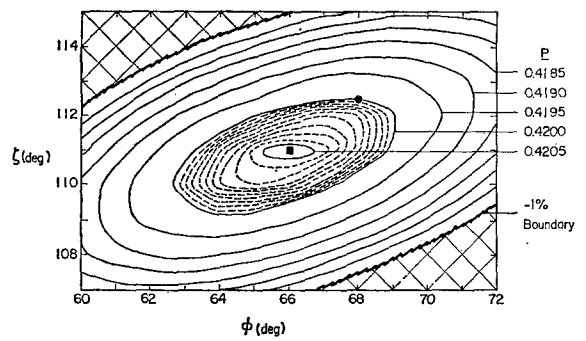

FIG. 6. Topographical plot: $P[\equiv\phi^{\frac{1}{2}}(X-\frac{1}{2})]$ as a function of ϕ and ζ. The squared point represents the maximum in P, the circle is chosen for application (see text).

maximum in ΔQ^*; thus N is an integer, and since only principal values of angles are needed we may take $\zeta=3\pi/4$ rad $=135°$.

Then we find $X=\frac{1}{2}(1+\frac{2}{3}\phi-\frac{4}{21}\phi^3+\cdots)$; this function goes through a maximum at $\phi\cong\pi/2$, yielding $X_{\max}\cong\frac{3}{4}$. Substituting back into Eq. (14), employing Eq. (19), we obtain

$$\Delta Q_{\max}{}^*\cong\beta_2{}^2-\beta_1{}^2=4\alpha_0\beta_m$$
$$=[4(2\pi)^{\frac{1}{2}}/(A\theta_0')^{\frac{1}{2}}]\beta_m\cong 10\beta_m/(A\theta_0')^{\frac{1}{2}}. \quad (22)$$

Since[1] $Q_{MM}{}^*=3.170\,D^{\frac{1}{2}}$, we can evaluate the desired maximum fractional deviation, i.e., the "undulation amplitude," U:

$$U\equiv\frac{\Delta Q_{\max}{}^*}{Q_{MM}{}^*}=\frac{4(2\pi)^{\frac{1}{2}}}{3.170}\frac{\beta_m}{(\theta_0')^{\frac{1}{2}}}K^{-1/20}B^{-9/20}=G_1(K)B^{-0.45}, \quad (23a)$$

where G_1 is a function only of K, evaluated from a knowledge of $\beta_m(K)$ (e.g., Fig. 4) and $\theta_0'(K)$, from the tabulated[7] deflection functions.

A more accurate and less arbitrary procedure, however, is as follows. We consider *both* ζ and ϕ as disposable parameters, and evaluate ΔQ^* as a function of ζ and ϕ. We must locate the set of values (ζ_m, ϕ_m) such that ΔQ^* is maximized with respect to both variables ζ and ϕ, i.e., such that, simultaneously

$$\partial\Delta Q^*/\partial\zeta=\partial\Delta Q^*/\partial\phi=0.$$

This is a proper criterion for an extremum in the deviation function, $\Delta Q_{\max}{}^*$.

From Eqs. (14) and (19) we note that $\Delta Q^*=32\beta_m P/(A\theta_0')^{\frac{1}{2}}$, where $P=\phi^{\frac{1}{2}}(X-\frac{1}{2})$. Using Eq. (21) for X, and allowing ζ and ϕ to be varied independently over a wide range, P was computed and plotted. The topography in the region of the maximum is shown in Fig. 6. The maximum is seen to be very broad; $P_{\max}=0.4205$ deg$^{\frac{1}{2}}$ (and $X_{\max}=0.892$) for the squared point at $\phi=66°$, $\zeta=111°$. For the circled point at $\phi=68°$, $\zeta=112.5°$ ($5\pi/8$ rad), P is only 0.1% smaller.

It is noted that our tentative criterion for a maximum deviation ($\zeta=3\pi/4$) has now been superseded and that the proper value of ζ (i.e., yielding the greatest deviation $\Delta Q_{\max}{}^*$) lies in the range $111\pm2°$. For simplicity (and with negligible loss of accuracy) we choose $\zeta=112.5°=5\pi/8$ rad.

Thus we obtain the revised form of Eq. (6):

$$\eta_m=(N-\tfrac{3}{8})\pi. \quad (24)$$

As a consequence, in place of Eq. (23a), we have, more properly

$$\Delta Q_{\max}{}^*=13.5\beta_m/(A\theta_0')^{\frac{1}{2}}, \quad (22')$$

and

$$U=G(K)B^{-0.45}. \quad (23b)$$

Figure 7 shows a plot of $G(K)$, evaluated numerically by the procedure mentioned in connection with $G_1(K)$. In the region near $K=1$, Eq. (23b) suggests that, as a very rough approximation, the undulation amplitude can be estimated by the relation

$$U\approx 2.7/B^{\frac{1}{2}}. \quad (23c)$$

The inverse dependence on B of Eqs. (23) implies that the extrema will be easily detectable only for systems with low B (e.g. $B\lesssim 10\,000$). Equation (23b) (together with Fig. 7) also suggests (at least for $K<4$) a small isotope effect in U.

Returning to the general question of the undulation amplitude, the symmetry of the problem is such that a maximum in P (for any given value of ϕ) occurs at an angle $\zeta_{\max}$, a minimum in P is found at an angle $\zeta_{\min}=\zeta_{\max}-90°$; also $(X-\frac{1}{2})_{\max}+(X-\frac{1}{2})_{\min}=0$, so that $X_{\max}+X_{\min}=0$. These relations afforded a check on the computations. They also imply that positive and negative deviations should be symmetrical; more properly, Eq. (23b) should be written

$$U_N=(-1)^{2N}G(K)B^{-0.45}, \quad (23d)$$

where N is the previously employed[1] index of the extremum. (The sign of U had been disregarded earlier.)

As an illustration of the applicability of the procedures developed for the locations and magnitudes of

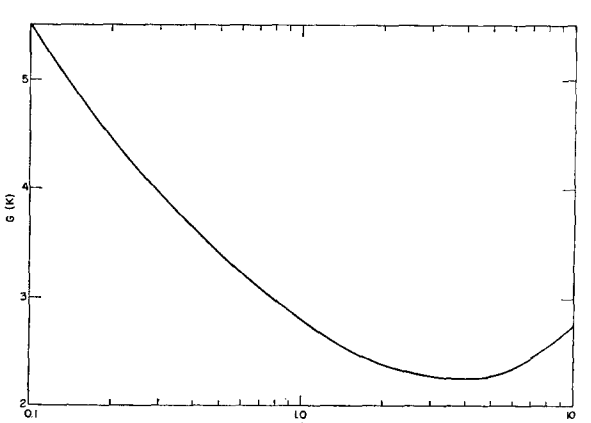

FIG. 7. The amplitude function $G(K)$; [LJ (12,6) potential].

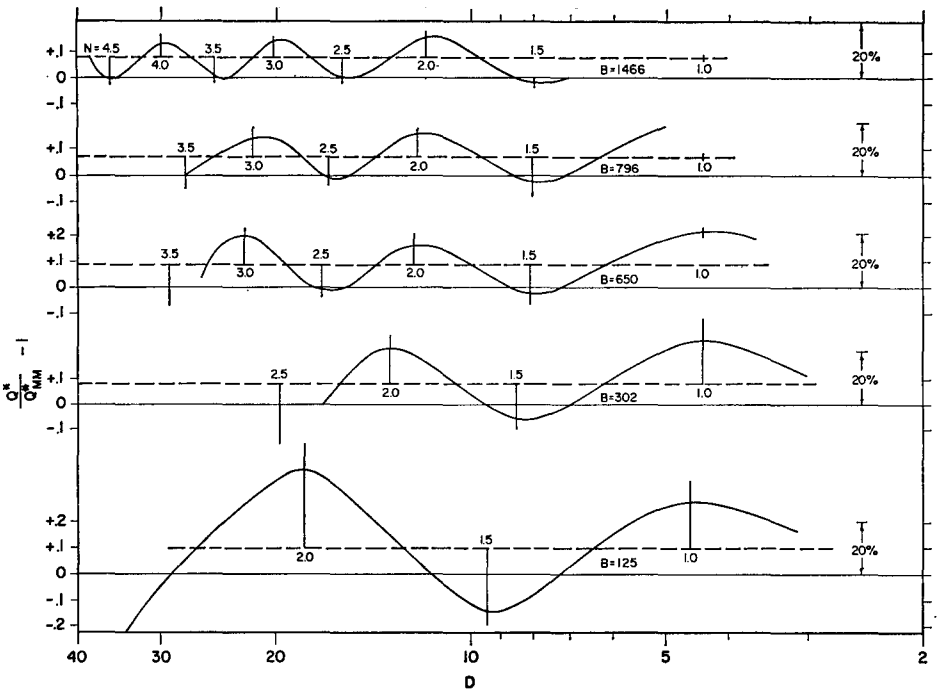

FIG. 8. Deviation function ($\Delta Q/Q_{MM}$) as a function of D; [LJ (12,6) potential]. Calculated (partial-wave procedure), from reference 8. Vertical lines are predictions from Eqs. (12) and (23d). The horizontal dashed lines are drawn through the mean of the undulations (see text for further details).

the extrema, Fig. 8 shows plots of the elastic atom–atom impact spectra, i.e., the function $\Delta Q^*/Q_{MM}{}^*$ vs D, for various values of B, obtained from partial-wave calculated values of the cross sections[8]; these are compared with extrema predictions based on Eqs. (12) and (23d). The vertical lines are located at D_N values in accord with Eq. (12), indexed as shown. The lengths of the lines were obtained via Eq. (23d) [using $G(K)$ from Fig. 7]; they have been placed relative to a dashed line passing through the mean of the undulations. It has already been noted[6,8] that the MM formulation for the case of the $s=6$ attractive potential introduces a bias of about 7% relative to the exact calculated Q; this is the main source of the shift between the dashed lines and the "zero" lines drawn.

Figure 8 shows that the extrema velocities (or D_N values) are very well represented by Eq. (12), but that the extrema amplitudes (U_N) are less accurately predicted by Eq. (23d).[9]

One notes that the repulsion in the interaction potential acts only as a perturbing influence on the behavior of $Q(v)$ which is dominated by the long-range attraction, to produce undulatory deviations (whose magnitude decreases with increasing B).

This suggests that impact spectra in the thermal energy region should be displayed in the following way. The product $v^{\frac{1}{3}}Q(v)$ [or, better,[6] $C_{app}{}^{(6)}$(erg cm^6) $= 5.68\times10^{-30}vQ^{\frac{1}{3}}$] should be plotted as a function of $1/v$, yielding an undulatory curve (symmetrical about a horizontal "mean" line), in which the extrema are fairly uniformly spaced [cf. Eq. (12)]. [As a measure of the resolution, we note from Eq. (12) that for an LJ (12,6) potential the limiting high-velocity spacing between successive maxima on such a $1/v$ plot is $\sim3.50\times10^{-27}(\epsilon\sigma)^{-1}$ sec cm^{-1}]. From such a plot the extrema velocities v_N (characteristic for any given colliding system) can be accurately located and the desired graph of $N-\frac{3}{8}$ vs $1/v_N$ prepared for comparison with Fig. 5.

In concluding this section it should be re-emphasized that the extrema phenomenon in the total elastic cross section $Q(v)$ should be quite general,[10–13] subject only to the conditions mentioned in the Introduction. The present computational procedures are easily adaptable to any of the several realistic potential functions for which classical deflection functions are available.

RELATION BETWEEN EXTREMA AND DIATOM BOUND STATES

Starting with a given interatomic potential, assuming the validity of the Born–Oppenheimer approximation,

[8] E. W. Rothe, P. K. Rol, and R. B. Bernstein, Phys. Rev. (to be published).

[9] One source of the inaccuracy may be in the use of the parabolic approximation for $\eta(\beta)$ near η_m; the range $\beta_2-\beta_1$ was found to be slightly greater than that for which the assumption is valid. Also, there is some uncertainty in the factor $G(K)$ whose evaluation requires numerical differentiation of $\theta(K)$, to yield θ_0'.

[10] It is interesting to note that, in addition to definite observations of such extrema in the case of atom–atom collisions[11,12], there is the possibility that small undulations appearing on graphs of $Q(v)$ for certain charge-changing ion–atom (and ion–molecule) collisions[13] may originate from similar considerations.

[11] H. U. Hostettler and R. B. Bernstein, Phys. Rev. Letters **5**, 318 (1960).

[12] (a) E. W. Rothe, P. K. Rol, S. M. Trujillo, and R. H. Neynaber, Phys. Rev. **128**, 659 (1962); (b) P. K. Rol and E. W. Rothe, Phys. Rev. Letters **9**, 494 (1962).

[13] See, for example, E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **29**, 361 (1958) and references cited therein.

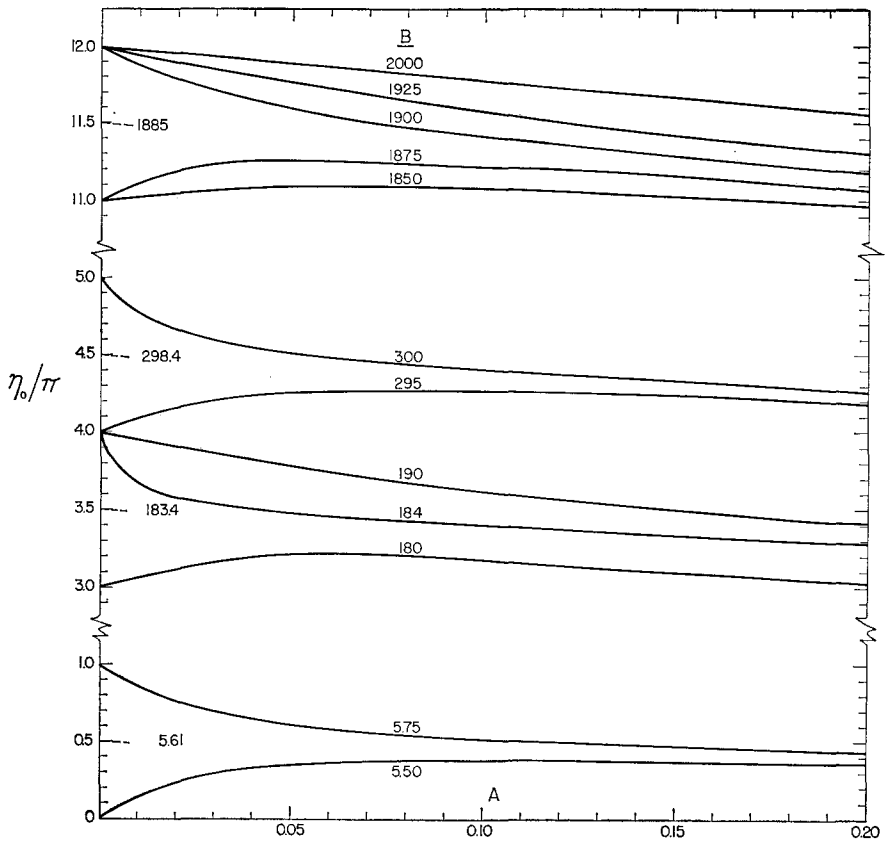

FIG. 9. Application of Levinson's theorem: $\eta_0(A)/\pi$ vs A for various values of B; [LJ (12,6) potential]. Critical values of B taken from reference 14(a). Intercepts yield the number of bound states of zero angular momentum.

it is a straightforward computational task[14] to obtain the eigenvalues and eigenfunctions corresponding to all the discrete (vibration–rotation) states of the diatom. Conversely, from spectroscopic observations of the optical transitions between these levels the potential may be readily adduced. Such observations, however, have usually been limited, for reasons of intensity (i.e., concentration), to a familiar family of relatively stable gaseous molecules[15] (those for which D_e/k exceeds some minimum temperature, corresponding to an adequate vapor pressure) and radicals produced in abundance by dissociation of polyatomic molecules. Obviously, a large class of diatoms (i.e., weakly bound or "van der Waals" molecules) exists for which the stability requirement is not met, and for which it would still be of interest to ascertain the interatomic potential and the number of bound states. The relation between the extrema velocities and the potential has been established in the previous section. In what follows it is shown that the extrema also serve as "counters" of the vibrational states[16] of the diatom or "collision complex."

We make use of Levinson's theorem,[17] which states that

$$\lim_{k\to 0}\eta_l(k)=n_l\pi, \tag{25}$$

where n_l is the number of discrete levels of angular momentum l (we can now identify l with the conventional molecular-rotational quantum number j). We recognize also that

$$n_l\leq n_0. \tag{26}$$

We shall be concerned here primarily with the rotationless states (thus we will be interested in the relation between the maximum phase and the s-wave phase).

It is illustrative to re-examine Fig. 1. As the velocity

[14] (a) See, for example, H. Harrison and R. B. Bernstein, J. Chem. Phys. **38**, 2135 (1963). The analogous nuclear problem has been studied by (b) R. S. Caswell, National Bureau of Standards Technical Note No. 159 (1962), and (c) A. E. S. Green, Phys. Rev. **99**, 772, 1410 (1955).

[15] However, note that N. Bernardes and H. Primakoff [J. Chem. Phys. **30**, 691 (1959)] have suggested the possibility of observing the Raman spectra of certain van der Waals molecules (rare-gas dimers) in the liquid state.

[16] Before proceeding, it should be pointed out, in all fairness, that the number of bound states is completely determined from the potential, so that no *new* information can come from the extrema-counting procedure. For example, for the LJ (12,6) potential the number (n_0) of vibrational states is a function only of the single parameter B.[14a] For approximation purposes the following simplified formula can be used: $n_0-\frac{1}{2}=0.27\,B^{\frac{1}{2}}$; this equation predicts n_0 within ± 1. More exact formulas, for various potentials of interest, are given in reference 14(a).

[17] (a) P. Swan, Proc. Roy. Soc. (London) **A228**, 10 (1955). Pauli-excluded states are not involved here; (b) N. Levinson, Kl. Danske Videnskab. Selskab. Mat.-Fys. Medd. **25**, No. 9 (1949).

parameter is decreased, the maximum phase approaches progressively closer to the s-wave phase, which in turn, increases toward its zero-velocity limit (12π, in this example). The curve $\eta_0(A)$ is a plot (*with abscissa* A) of the velocity dependence of the s-wave phase itself [data taken from the $\eta_l(A)$ curves and additional computations for $A<1$]. This *suggests* that

$$\lim_{k\to 0}\eta_{\max}\cong\lim_{k\to 0}\eta_0(=n_0\pi). \tag{27}$$

If the approximate equality above could be strengthened, Eq. (27) would yield the simple rule[1]

$$M=n_0, \tag{28}$$

where M is the total number of maxima in $Q(v)$ (each maximum occurring as $\eta_{\max}$ passes through $(N-\frac{3}{8})\cdot\pi$, where N is an integer) and n_0 is the number of vibrational levels of zero angular momentum for the diatom.

Before proceeding further it is instructive to examine the low-velocity behavior of the s-wave phases and the applicability of Levinson's theorem to the LJ (12, 6) potential. Figure 9 shows the results of partial-wave computations[18] of $\eta_0(A)/\pi$ for various values of B. In every case the extrapolation to $A=0$ yields the correct[14a] number n_0 of bound states for the given B.[19] Presumably, curves calculated at precisely the critical values of B (the "resonance" cases) would pass through half-integral intercepts, indicated by the short dashed lines. (Similar results are expected for other realistic potential functions.) We note that, depending upon B, $\eta_0(A)$ may or may not possess a maximum at some $A_{\max}>0$.

We designate the maximum value of the s-wave phase shift $\eta_0(k_{\max}{}^{(0)})$; $k_{\max}{}^{(l)}$ is that value of k for which η_l is a maximum (for a given potential well). We see that, in general,

$$\eta_0(k_{\max}{}^{(0)})\leq\eta_0(0)+\tfrac{1}{2}\pi. \tag{29}$$

From Eqs. (25) and (26) we have

$$\eta_l(0)\leq\eta_0(0). \tag{30}$$

We define

$$\eta_{\max}(0)\equiv\lim_{k\to 0}\eta_{\max}(k), \tag{31}$$

where $\eta_{\max}$ is the usual maximum phase at a given k. (The order $l_{\max}$ of the maximum phase varies, of course, with k, in a stepwise manner.) Since Eq. (30) applies to any l, including $l_{\max}$, we have

$$\eta_{\max}(0)\leq\eta_0(0). \tag{32}$$

We now *assume* (see discussion below) the following inequality for any potential involving a repulsive core:

$$\eta_l(k_{\max}{}^{(l)})\leq\eta_0(k_{\max}{}^{(0)}). \tag{33}$$

Then we have

$$\eta_{\max}\leq\eta_0(k_{\max}{}^{(0)})\leq\eta_0{}^{(0)}+\tfrac{1}{2}\pi=(n_0+\tfrac{1}{2})\pi. \tag{34}$$

Thus,

$$\pi(N-\tfrac{3}{8})\leq(n_0+\tfrac{1}{2})\pi, \tag{35a}$$

i.e.,

$$N\leq n_0+\tfrac{7}{8}. \tag{35b}$$

Since both N and n_0 are integers, this implies

$$N\leq n_0, \tag{35c}$$

so that M, the total number of maxima in $Q(v)$ (i.e., the largest value of the index N) is equal to n_0, the number of vibrational bound states.

Unfortunately this result must be regarded only as an approximation, since it hinges on the applicability of Eq. (24) down to very low velocities where only few phases differ from multiples of π and the semiclassical "statistics" are poor.

Returning to the question of the validity of Eq. (33), one notes from standard scattering-length theory that

$$\lim_{k\to 0}[\tan\eta_l(k)]=-a_l k^{2l}, \tag{37}$$

where a_l is the lth-order scattering length, independent of k. This implies that

$$\lim_{k\to 0}[d\eta_l(k)/dk]=0 \qquad (l>0). \tag{38}$$

Thus, for the s-wave phases the initial slopes of $\eta(k)$ are finite, whereas for *all* other l, they are zero. For the cases when $a_0<0$, $\eta_0(k)$ exhibits an initial increase, reaching a maximum at $k_{\max}{}^{(0)}$, when the strong negative influence of the repulsion begins to dominate (note from Fig. 9 that this maximum, when present, occurs at very low A, i.e. $A_{\max}{}^{(0)}<0.1$; see also reference 19). For all higher-order phases an appreciable range of k is required before the curve of $\eta_l(k)$ can possibly cross and exceed $\eta_0(k)$, so that when there is a maximum in $\eta_l(k)$ it is expected to lie below the corresponding maximum in $\eta_0(k)$, and at larger k. At somewhat higher k, of course, all the curves become monotonic, decreasing with increasing k (with the vertical spacing between successive low-order phases limited, semiclassically, to be $\leq\pi/2$). Thus we may regard Eq. (33) as plausible but not rigorously proved.

Because of this and the previously mentioned uncertainty associated with the use of semiclassical approximation in the very low velocity region, we must acknowledge the possibility that in special circumstances, the number of maxima *may* exceed the number of bound

[18] Computations were carried out by the "exact" numerical integration (Runge–Kutta–Gill) procedure of reference 4(a), slightly modified to deal with the very small values of A.

[19] See R. A. Buckingham and J. W. Fox, Proc. Roy. Soc. (London) **A267**, 102 (1962) for similar results for a square-well potential bounded by the long-range r^{-6} attraction.

TABLE I. Diatom electronic states: unlike atoms.

Atom 1 \ Atom 2								
		Group: I	II, VIII	III A	IV A	V A	VI A	VII A
Group	State	State: $^2S_{\frac{1}{2}}$	$^1S_0$	$^2P_{\frac{1}{2}u}$	$^3P_0$	$^4S_{\frac{3}{2}u}$	$^3P_2$	$^2P_{\frac{1}{2}u}$
I	$^2S_{\frac{1}{2}}$	$^1\Sigma^+$, $^3\Sigma^+$.						
II, VIII	$^1S_0$	$^2\Sigma^+$.	$^1\Sigma^+$.					
III A	$^2P_{\frac{1}{2}u}$	$^1\Sigma^+$, $^1\Pi$, $^3\Sigma^+$, $^3\Pi$.	$^2\Sigma^+$, $^2\Pi$	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, $^3\Sigma^+(2)$, $^3\Sigma^-$, $^3\Pi(2)$, $^3\Delta$.				
IV A	$^3P_0$	$^2\Sigma^-$, $^2\Pi$, $^4\Sigma^-$, $^4\Pi$.	$^3\Sigma^-$, $^3\Pi$	$^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, also triplets and quintets of above.			
V A	$^4S_{\frac{3}{2}u}$	$^3\Sigma^-$, $^5\Sigma^-$.	$^4\Sigma^-$.	$^3\Sigma^-$, $^3\Pi$, $^5\Sigma^-$, $^5\Pi$.	$^2\Sigma^+$, $^2\Pi$, $^4\Sigma^+$, $^4\Pi$, $^6\Sigma^+$, $^6\Pi$.	$^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$, $^7\Sigma^+$.		
VI A	$^3P_2$	$^2\Sigma^-$, $^2\Pi$, $^4\Sigma^-$, $^4\Pi$.	$^3\Sigma^-$, $^3\Pi$.	$^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, also triplets and quintets of above.	$^2\Sigma^+$, $^2\Pi$, also $^4(\ )$ and $^6(\ )$.	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, also $^3(\ )$ and $^5(\ )$ of above.	
VII A	$^2P_{\frac{1}{2}u}$	$^1\Sigma^+$, $^1\Pi$, $^3\Sigma^+$, $^3\Pi$.	$^2\Sigma^+$, $^2\Pi$.	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, $^3\Sigma^+(2)$, $^3\Sigma^-$, $^3\Pi(2)$, $^3\Delta$.	$^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.	$^3\Sigma^-$, $^3\Pi$, $^5\Sigma^-$, $^5\Pi$.	$^2\Sigma^+$, $^2\Sigma^-(2)$, $^2\Pi(2)$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-(2)$, $^4\Pi(2)$, $^4\Delta$.	$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, also $^3(\ )$ and $^5(\ )$ of above.

states. Thus the rule $M=n_0$ must be considered only as an approximation.[20]

However, there remains a direct correlation between the low-index (high-velocity) extrema and the low-lying vibrational states, as follows. Consider the well "capacity" parameter B to be increased in a continuous manner; we note that when B exceeds its first "critical" value, i.e., $B_{\text{crit}}(0)$, the first discrete level ($v=0$) appears. This level then moves down in energy (i.e., its binding energy increases) with increasing B; one maximum is expected in $Q(v)$. Eventually, as B exceeds the second critical value $[B_{\text{crit}}(1)]$ the second level ($v=1$) appears, and a second maximum in $Q(v)$ is generated, etc. This implies a one-to-one correlation[21] between the extrema index and vibrational quantum number: $(N-1)\leftrightarrow v$.

We conclude this section by a somewhat weakened restatement of our rule [Eq. (28)], suitable for application in any practical situation (where measurements are confined to a limited velocity range)[20]:

The observation of m maxima in the elastic atom–atom impact spectrum implies the existence of at least m discrete levels of zero angular momentum for the composite system.

POSSIBLE EXTENSION TO MOLECULAR SCATTERING

Although the extrema phenomenon has not yet been reported in connection with the scattering of molecules,[22] it is quite reasonable to expect it. However, some reservation must be retained because of the possible deleterious effect ("washing-out" of the detail) due to the inelastic (rotational excitation) contribution to the observed total cross section, which may be appreciable.[23] Even assuming successful resolution of extrema in the elastic cross section, a question still remains regarding the interpretation of the "new" vibrational states for the composite system, the "collision complex."

[20] From a practical point of view, of course, the point is a moot one, since experimental limitations preclude measurements down to the very low velocity range under discussion.

[21] For an LJ (12,6) well of high capacity (e.g., $B>2000$), it is possible to develop quantitative relations such as the following:

$$\Delta E_{0\to1}\equiv h\nu\cong 10.7\,\epsilon/B^{\frac{1}{2}};\qquad E_1=\tfrac{1}{2}\mu v_1^2\cong 0.0581\,\epsilon B,\qquad \text{so that}$$

$\Delta E_{0\to1}/E_1\cong 184\ B^{-\frac{1}{2}}$, where v_1 is the velocity of the $N=1$ extremum and ν is the classical fundamental frequency of the diatom (calculated from the curvature of the well at the minimum). Thus for $B=2000$, the ratio $\Delta E_{0\to1}/E_1$ is about 0.2%, i.e., the collision energy at the $N=1$ maximum is about 500 times the $v=0\to1$ excitation energy for the diatom.

Also, by combining (the very approximate) Eq. (23c) with the relation given in footnote 16, one may estimate directly from the undulation amplitude the number of bound states: $n_0\approx 0.73/U$.

[22] H. Pauly [Z. Naturforsch **15a**, 277 (1960)] examined the K–N_2 system (high B?) and did not resolve extrema. However, unexplained (and quite possibly unrelated) undulations appear in some of the $Q(T)$ curves for CsCl scattering, by H. Schumacher, R. B. Bernstein, and E. W. Rothe, J. Chem. Phys. **33**, 584 (1960).

[23] (a) R. B. Bernstein, Bull. Am. Phys. Soc. **7**, 217 (1962); (b) R. B. Bernstein, A. Dalgarno, H. S. W. Massey, and I. C. Percival, Proc. Roy. Soc. (London) (to be published).

TABLE II. Diatom electronic states: like atoms.

Group	State	Diatom states
I	$^2S_{\frac{1}{2}}$	$^1\Sigma_g^+$, $^3\Sigma_u^+$.
II, VIII	$^1S_0$	$^1\Sigma_g^+$.
III A, VII A	$^2P_{\frac{1}{2}u}$, $^2P_{\frac{3}{2}u}$	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$, $^3\Sigma_u^+(2)$, $^3\Sigma_g^-$, $^3\Pi_g$, $^3\Pi_u$, $^3\Delta_u$.
IV A, VI A	$^3P_0$, $^3P_2$	$^1\Sigma_g^+(2),\cdots{}^3\Delta_u$; $^5\Sigma_g^+(2)$, $^5\Sigma_u^-$, $^5\Pi_g$, $^5\Pi_u$, $^5\Delta_g$.
V A	$^4S_{\frac{3}{2}u}$	$^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$.

ACKNOWLEDGMENTS

The author thanks Mr. A. Flank, Mr. A. Graube, and Mr. F. Parker for their help with the numerical work, and acknowledges valuable comments from Dr. H. Harrison, Dr. E. A. Mason, and Dr. E. W. Rothe.

APPENDIX

Enumeration of Possible Diatom Electronic States

We consider first the scattering of unlike atoms in their electronic ground states. Table I lists the possible molecular electronic states, following standard procedures[24] for obtaining the term manifold from the states of the separated atoms. The left-hand column lists the group designation of one of the two atoms in the periodic system and its ground state; the top row lists the same information for the other atom. Listed in the body of the table are the diatom states, with multiplicities specified (important in scattering of state-unselected beams; see footnote 3). All groups in the periodic table are represented except for the B subgroups of Groups III–VII, inclusive. It is noted that for any combination of atoms from Groups I, II, and/or VIII, there are never more than four molecular states involved. Obviously, most suited for experiment are the combinations I+II, I+VIII, II+II, II+VIII, VIII+VIII, II+VA, and VIII+VA, where only a single potential function is involved.

Table II summarizes the same information for the scattering of like atoms. Inspection of the table suggests that here Groups II and VIII would be favorable for study.

[24] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules* (D. Van Nostrand, Inc., New York, 1950), 2nd Ed.