temperature unit cell in chloranil in good agreement with that of Chu *et al.*[14] except for a c axis of twice the length. Other workers[20] have obtained a cell in agreement with that of Chu *et al.* While it is possible that a degree of ordering may persist to room temperature—that is, in oscillating in the wells $V(\theta_x)$, the molecules might spend a measurably smaller fraction of a period at the center of the well than they would in the absence of the barrier—it is puzzling that only the sample of Chorghade[19] would show it.

[20] I. Ueda (private communication with Chu *et al.*). G. Gafner and F. H. Herbstein (private communication with Chu *et al.*).

ACKNOWLEDGMENTS

The author gratefully acknowledges the advice of Dr. C. Dean during this work. The single crystal was kindly furnished by Dr. Shirley Chu. His special thanks go to Tosio Sakurai for many helpful discussions.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 38, NUMBER 2 15 JANUARY 1963

High-Velocity Molecular Beam Scattering: Total Elastic Cross Sections for L-J(n, 6) and Exp-6(α) Potentials*

RICHARD B. BERNSTEIN
Chemistry Department, University of Michigan, Ann Arbor
(Received 2 October 1962)

Explicit expressions are derived for the total elastic scattering cross sections in the high-velocity region for molecules interacting according to L-J (n, 6) and exp-6(α) potentials. Cross sections are presented in tabular and graphical form.

INTRODUCTION

PREVIOUS papers[1] in this series have dealt with (a) the evaluation of radial wavefunctions, phase shifts, reduced phases, and differential elastic cross sections for scattering by a L-J (12, 6) potential; (b) the resulting velocity dependence of the differential and total scattering cross sections, with attention given to the Jeffreys–Born (JB) approximation for the higher-order phases; (c) the applicability of the semiclassical equivalence principle to the calculation of the phase shifts from the classical deflection function; and (d) an analysis of the undulatory velocity dependence of the total cross section in terms of bound states. The present paper presents an explicit treatment of the velocity dependence of the JB phases and the total elastic scattering cross sections in the high-velocity region (e.g., in the eV-energy range) for molecules interacting according to the L-J (n, 6) and exp-6(α) potentials. A criterion is given for estimating the lower limit of velocity for which the treatment is valid.

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

[1] R. B. Bernstein, (a) J. Chem. Phys. **33,** 795 (1960); (b) **34,** 361 (1961); (c) **36,** 1403 (1962); (d) **37,** 1880 (1962). Errata are as follows: (1a) Table III: $\eta_1(3)$ and $\eta_{16}(20)$ should both be positive. Fig. 13: For the lowest curve, $\beta'=3.3$. (1b) p. 365: BA^4 should be 2.00×10^7. (1c) Equation (5) was not in fact, obtained from Eq. (4), but rather was derived from the integral using an alternate boundary condition appropriate to this special case, i.e., $\eta_0=-A$. In example 3, for $b^*>2$, the sign of η^* should be positive. (1d) The symbol $\eta^{\rm m}\equiv\eta^{\rm max}$ (i.e., the superscript m is *not* an exponent).

METHOD

The procedure to be followed makes use of the random-phase approximation introduced by Massey and Mohr[2] (MM) for the low-order phases and the JB approximation[1b] for the higher-order phases, evaluated for the potentials of interest. The present treatment also takes advantage of certain of the methods and results of Dalgarno *et al.*[3] and Mason and Vanderslice.[4]

The potentials considered are (A) the Lennard-Jones (n, 6) and (B) the modified Buckingham exp-6(α) type, here expressed in the usual "reduced" forms[5]:

$$V_{\rm A}^*(z)=[n/(n-6)][(6/n)z^{-n}-z^{-6}], \qquad (1a)$$

$$V_{\rm B}^*(z)=[\alpha/(\alpha-6)][(6/\alpha)e^{\alpha(1-z)}-z^{-6}], \qquad (1b)$$

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

[3] A. Dalgarno and M. R. McDowell, Proc. Phys. Soc. (London) **A69,** 615 (1956); A. Dalgarno, M. R. McDowell, and A. Williams Phil. Trans. Roy. Soc. (London) **A250,** 411 (1958).

[4] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **29,** 361 (1958). These authors employ a reduced velocity parameter v^* which is closely related to D_z: $v^*=2D_z^{-1}$.

[5] In reference 1 attention was limited to the L-J (12, 6) potential, and the notation involved σ [the first zero of $V(r)$] and $x\equiv r/\sigma$; for the purpose of generalizing to other potentials, it is advantageous to change to the notation which makes use of r_m and $z\equiv r/r_m$.

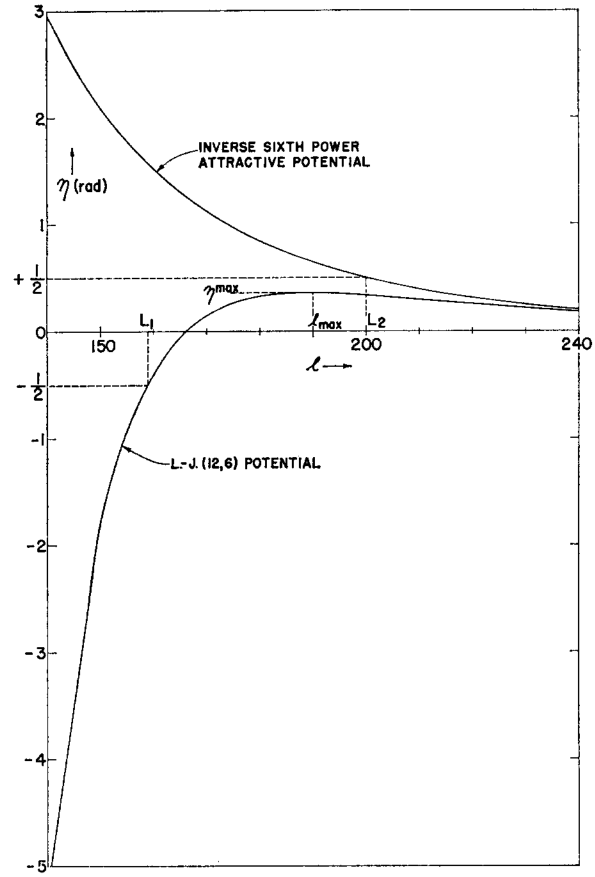

FIG. 1. Comparison of behavior of high-velocity phases: inverse sixth power attraction vs L–J (12, 6) potential with same attractive constant. Note the significantly smaller value of L for the latter potential (i.e., $L_1 < L_2$). For this example v has been assumed greater than $v_{\min}$ (Eq. 17).

where $V^* = V/\epsilon$, with ϵ the depth of the potential well; and $z = r/r_m$, where r_m is the value of r at the minimum in the potential; and the other symbols have their usual meaning. For the purposes of the present paper it is convenient to restrict both n and α to be greater than 6.

The reduced cross section Q_z^* is defined in terms of Q, the total elastic cross section:

$$Q_z^* \equiv Q/\pi r_m^2, \tag{2}$$

with

$$Q = (4\pi/k^2) \sum_{l=0}^{\infty} (2l+1) \sin^2 \eta_l(k), \tag{3}$$

where $k = 2\pi/\lambda = \mu v/\hbar$ and $\eta_l(k)$ is the phase shift for the lth order partial wave, defined in the standard[6] way.

In the MM treatment[2] a purely attractive potential (inverse s power) was assumed, for which all phases are positive, decreasing monotonically with increasing l. However, for a realistic intermolecular potential both repulsive and attractive terms are involved. In fact (cf. reference 1), the short-range repulsion gives rise to substantial negative contributions to the lower order phases and thus to a broad maximum in η_l. Figure 1 shows an example of phase shifts for a purely attractive ($s=6$) potential compared with those for a L-J (12, 6) potential. The symbol $\eta^{\max}(k)$ is used to designate the maximum phase at the given k. For the purpose of the *present paper* we assume that k is sufficiently large that

$$\eta^{\max}(k) < \tfrac{1}{2}. \tag{4}$$

This inequality ensures the validity of the JB approximation for all the net positive phases. This condition incidentally sets a lower limit on the relative velocity for which the treatment is valid. This matter is further discussed below. The velocity region for which $\eta^{\max}(k) > \frac{1}{2}$ (cf. reference 1d) is to be analyzed in detail in a subsequent paper.

Following a procedure analogous to that of MM, we may define a characteristic value of l, say $L(k)$, such that $\eta_L = -\frac{1}{2}$ and $|\eta_l| \leq \frac{1}{2}$ for $l \geq L$. The sum in Eq. (3) is conveniently divided into two parts:

$$Q_z^* = Q_<^* + Q_>^*, \tag{5}$$

where the two terms denote the contribution from $l \leq L$ and from $l > L$, respectively.

To evaluate $Q_<^*$ and $Q_>^*$ we employ the Massey-Mohr[2] random phase and JB approximations, respectively; in addition, we make use of the usual[2] small-phase approximation: $\sin \eta_l \cong \eta_l$ for $|\eta_l| \leq \frac{1}{2}$.

In the semiclassical notation,[1c] Eq. (5) then becomes

$$Q_z^* = 2\beta_L^2 \cdot \left\{ 1 + 4\beta_L^{-2} \cdot \int_{\beta_L}^{\infty} \beta \eta_{JB}^2 d\beta \right\}, \tag{6}$$

where η_{JB} is the phase according to the JB approximation and $\beta = (l+\frac{1}{2})/A_z$ is the "reduced angular momentum function" or "reduced impact parameter," defined so as to be analogous to (but not identical with) β' from reference 1a, b^* of reference 1c, and β of reference 1d. Here $A_z = kr_m$, by analogy with the parameter $A = k\sigma$ of reference 1. For the present case we are concerned with large values of l, so we may take $\beta \sim l/A_z$; thus $\beta_L \sim L/A_z$ (analogous to β_1 of reference 1d).

It remains to derive expressions for η_{JB} and then to evaluate β_L from the condition

$$\eta_{JB}(\beta_L) = -\tfrac{1}{2}. \tag{7}$$

JB PHASES

By an extension of the procedures of MM and reference 1b, we note that for any potential expressible as the sum of repulsive and attractive terms

$$V(r) = V_{\text{rep}}(r) + V_{\text{attr}}(r) \tag{8}$$

[6] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1949), 2nd ed.

(where V_{rep} is taken to be positive and V_{attr} negative), one may express the JB phase as a similar sum

$$\eta_{JB}(l,k)=\eta_{JB}^{rep}+\eta_{JB}^{attr}. \quad (9)$$

Here the repulsive and attractive JB phases are calculated separately from V_{rep} and V_{attr} in the usual way, yielding negative values for η_{JB}^{rep} and positive values for η_{JB}^{attr}.

For the L-J (n, 6) potential [Eq. (1a)], generalizing from reference 1b, one obtains the following result for the JB phase:

$$\eta_{JB(A)}=(3\pi/32)[n/(n-6)]D_z\beta^{-5} \times\{1-[32f(n)/\pi n]\beta^{-n+6}\}, \quad (10a)$$

where $D_z=B_z/A_z=2\epsilon r_m/\hbar v$; $B_z=2\mu\epsilon r_m^2/\hbar^2$ (in obvious analogy with the symbols of reference 1). The function $f(n)$ is that of MM

$$f(n)=\frac{(n-3)(n-5)\cdots(1)}{(n-2)(n-4)\cdots(2)}\frac{\pi}{2} \quad (n \text{ even})$$

$$=\frac{(n-3)(n-5)\cdots(2)}{(n-2)(n-4)\cdots(3)}1 \quad (n \text{ odd}); \quad (11)$$

in general, $f(n)=\frac{1}{2}\sqrt{\pi}\Gamma\frac{1}{2}(n-1)/\Gamma\frac{1}{2}n$; $f(n)$ is tabulated for $n=7(1)28$ in Table I.

For the special case of $n=12$, Eq. (10a) reduces to

$$\eta_{JB}^{(12,6)}=\tfrac{3}{16}\pi D_z\beta^{-5}(1-\tfrac{21}{64}\beta^{-6}), \quad (12)$$

which is identical with the results of reference 1b, Eqs. (13), (17), (18) (after taking into account the new nomenclature).

For the exp-6(α) potential [Eq. (1b)], the repulsive JB phase is evaluated by making use of the results of Dalgarno *et al.*[3] for a simple exponential potential. The Jeffreys phase is expressible in terms of a first-order

TABLE I. The function $f(n)$.

n	$f(n)$	n	$f(n)$
7	0.53333	18	0.30847
8	0.49087	19	0.29954
9	0.45714	20	0.29134
10	0.42951	21	0.28377
11	0.40635	22	0.27677
12	0.38656	23	0.27026
13	0.36941	24	0.26419
14	0.35435	25	0.25851
15	0.34099	26	0.25318
16	0.32904	27	0.24817
17	0.31826	28	0.24344

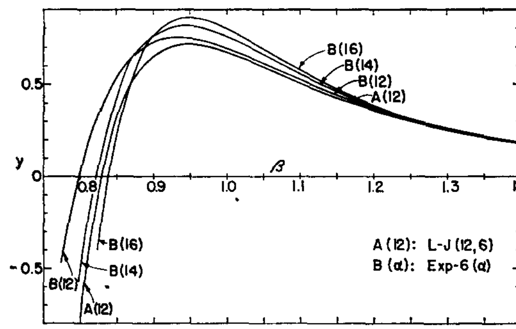

FIG. 2. Behavior of the JB phases: y_{JB} vs β for $n=12$ and $\alpha=12$, 14, 16.

modified Bessel function of the second kind, while the Born phase may be written in terms of a Legendre polynomial of the second kind. In the limit of large l and high velocity (using the present nomenclature: for $\alpha\beta\gtrsim5$ and $\alpha/A_z\ll1$), the Jeffreys and Born expressions become identical; it is this limiting behavior for the repulsive JB phase which is used in the present application. (Mason and Vanderslice[4] have considered the influence of higher-order terms in the expansions needed for the Jeffreys phases; however, these were not found to alter the final results significantly.)

In the present notation we obtain for the exp-6(α) potential [Eq. (1b)]:

$$\eta_{JB(B)}=(3\pi/32)[\alpha/(\alpha-6)]D_z\beta^{-5} \times\{1-[32/(2\pi)^{\frac{1}{2}}](\beta^{11/2}/\alpha^{\frac{1}{2}})e^{\alpha(1-\beta)}\}. \quad (10b)$$

Appendix I describes an application to a classical scattering problem.

Figure 2 shows a comparison of the dependence upon β of the two JB results [Eqs. (10a) and (10b)]. Plotted are quantities proportional to η_{JB}

$$y_A\equiv(32/3\pi)[(n-6)/n]D_z^{-1}\eta_{JB(A)} \quad (13a)$$

and

$$y_B\equiv(32/3\pi)[(\alpha-6)/\alpha]D_z^{-1}\eta_{JB(B)} \quad (13b)$$

for the special cases of $n=12$ and $\alpha=12$, 14, and 16.

The difference is most pronounced at low β. The JB phase associated with the exponential, $\alpha=16$, repulsion is more negative than the one for $\alpha=12$, as it must be. The latter is, in turn, *less* negative than the one calculated for the inverse power ($n=12$) repulsion. This is expected since the exponential repulsion is "softer" for a given $\alpha=n$. [Matching of first derivatives $(dV/dr)_{r_0}$ requires $\alpha=nr_m/r_0$, so that for $r_0<r_m$, $\alpha>n$.]

Total Cross Sections

Substitution of Eqs. (10a) and (10b), respectively, into Eq. (6) yields, after some manipulation, the

TABLE II. Q_A^* and Q_B^* as a function of D_z. Parameters: n for L−J $(n,6)$; α for exp-6(α).

	$n=8$		$n=10$		$n=11$		$n=12$		$n=13$		$n=14$		$n=15$		$n=16$		$n=20$	
β_L	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*	D_z	Q_A^*
0.400	0.00150	0.3433	0.00043	0.3392	0.00022	0.3374	0.00011	0.3358	0.00005	0.3345	0.00003	0.3333	0.00001	0.3323	0.00001	0.3314	...	...
0.410	0.00181	0.3605	0.00054	0.3563	0.00028	0.3544	0.00014	0.3528	0.00007	0.3514	0.00004	0.3502	0.00002	0.3491	0.00001	0.3482	...	...
0.420	0.00218	0.3780	0.00068	0.3738	0.00036	0.3719	0.00019	0.3702	0.00010	0.3687	0.00005	0.3674	0.00002	0.3663	0.00001	0.3654	0.000001	0.3626
0.430	0.00262	0.3960	0.00085	0.3917	0.00046	0.3897	0.00025	0.3880	0.00013	0.3865	0.00007	0.3851	0.00003	0.3840	0.00002	0.3830	0.000001	0.3801
0.440	0.00314	0.4143	0.00105	0.4100	0.00058	0.4080	0.00032	0.4062	0.00017	0.4046	0.00009	0.4032	0.00005	0.4021	0.00002	0.4010	0.000001	0.3980
0.450	0.00375	0.4331	0.00130	0.4287	0.00073	0.4266	0.00041	0.4248	0.00022	0.4232	0.00012	0.4218	0.00006	0.4205	0.00003	0.4194	0.000002	0.4162
0.460	0.00447	0.4522	0.00160	0.4478	0.00092	0.4457	0.00052	0.4438	0.00029	0.4422	0.00016	0.4407	0.00008	0.4394	0.00004	0.4383	0.000003	0.4350
0.470	0.00532	0.4717	0.00196	0.4672	0.00115	0.4652	0.00066	0.4633	0.00037	0.4616	0.00021	0.4600	0.00011	0.4587	0.00006	0.4575	0.000005	0.4541
0.480	0.00631	0.4915	0.00239	0.4871	0.00143	0.4850	0.00084	0.4831	0.00048	0.4813	0.00027	0.4798	0.00015	0.4784	0.00008	0.4772	0.000007	0.4736
0.490	0.00748	0.5118	0.00291	0.5074	0.00177	0.5053	0.00106	0.5033	0.00062	0.5015	0.00036	0.5000	0.00020	0.4985	0.00012	0.4973	0.00001	0.4935
0.500	0.00884	0.5324	0.00354	0.5281	0.00218	0.5260	0.00133	0.5240	0.00079	0.5222	0.00047	0.5205	0.00027	0.5191	0.00016	0.5178	0.00002	0.5139
0.510	0.01044	0.5534	0.00429	0.5491	0.00269	0.5470	0.00166	0.5450	0.00101	0.5432	0.00061	0.5415	0.00036	0.5400	0.00021	0.5387	0.00002	0.5346
0.520	0.01231	0.5747	0.00518	0.5705	0.00330	0.5684	0.00207	0.5664	0.00128	0.5646	0.00078	0.5629	0.00047	0.5613	0.00028	0.5600	0.00003	0.5558
0.530	0.01449	0.5965	0.00625	0.5923	0.00403	0.5902	0.00257	0.5882	0.00162	0.5864	0.00100	0.5846	0.00062	0.5831	0.00037	0.5817	0.00005	0.5774
0.540	0.01705	0.6185	0.00752	0.6145	0.00493	0.6124	0.00319	0.6104	0.00204	0.6086	0.00129	0.6068	0.00080	0.6052	0.00050	0.6038	0.00007	0.5994
0.550	0.02004	0.6409	0.00904	0.6370	0.00600	0.6350	0.00394	0.6330	0.00255	0.6311	0.00164	0.6294	0.00104	0.6278	0.00065	0.6263	0.00009	0.6218
0.560	0.02354	0.6637	0.01084	0.6599	0.00729	0.6579	0.00485	0.6560	0.00320	0.6541	0.00208	0.6524	0.00134	0.6507	0.00086	0.6492	0.00013	0.6446
0.570	0.02765	0.6868	0.01299	0.6832	0.00884	0.6812	0.00596	0.6793	0.00398	0.6775	0.00264	0.6757	0.00173	0.6741	0.00112	0.6726	0.00019	0.6678
0.580	0.03247	0.7103	0.01555	0.7068	0.01070	0.7049	0.00731	0.7030	0.00496	0.7012	0.00333	0.6994	0.00222	0.6978	0.00146	0.6963	0.00026	0.6914
0.590	0.03815	0.7342	0.01860	0.7307	0.01294	0.7289	0.00895	0.7271	0.00615	0.7253	0.00419	0.7236	0.00283	0.7219	0.00190	0.7204	0.00036	0.7454
0.600	0.04483	0.7585	0.02223	0.7550	0.01563	0.7533	0.01094	0.7515	0.00761	0.7498	0.00526	0.7481	0.00360	0.7464	0.00245	0.7449	0.00049	0.7399
0.610	0.05274	0.7831	0.02656	0.7797	0.01886	0.7780	0.01335	0.7763	0.00940	0.7746	0.00658	0.7729	0.00458	0.7713	0.00316	0.7698	0.00067	0.7647
0.620	0.06212	0.8083	0.03173	0.8047	0.02275	0.8031	0.01628	0.8014	0.01160	0.7998	0.00822	0.7981	0.00579	0.7966	0.00406	0.7951	0.00092	0.7899
0.630	0.07329	0.8339	0.03792	0.8300	0.02744	0.8285	0.01983	0.8269	0.01429	0.8253	0.01025	0.8237	0.00732	0.8222	0.00520	0.8207	0.00125	0.8156
0.640	0.08666	0.8602	0.04535	0.8558	0.03309	0.8542	0.02415	0.8527	0.01759	0.8512	0.01277	0.8497	0.00923	0.8482	0.00664	0.8467	0.00169	0.8416
0.650	0.1027	0.8873	0.05431	0.8819	0.03992	0.8803	0.02939	0.8789	0.02163	0.8774	0.01587	0.8759	0.01161	0.8745	0.00846	0.8731	0.00227	0.8680
0.660	0.1222	0.9154	0.06513	0.9085	0.04821	0.9068	0.03579	0.9054	0.02659	0.9040	0.01972	0.9026	0.01459	0.9012	0.01075	0.8998	0.00305	0.8948
0.670	0.1461	0.9449	0.07829	0.9356	0.05830	0.9337	0.04362	0.9322	0.03269	0.9309	0.02449	0.9295	0.01831	0.9282	0.01365	0.9269	0.00407	0.9220
0.680	0.1755	0.9765	0.09438	0.9634	0.07065	0.9611	0.05322	0.9595	0.04021	0.9581	0.03040	0.9568	0.02297	0.9555	0.01732	0.9543	0.00543	0.9495
0.690	0.2123	1.011	0.1142	0.9920	0.08585	0.9890	0.06506	0.9872	0.04952	0.9857	0.03776	0.9845	0.02880	0.9832	0.02194	0.9820	0.00722	0.9774
0.700	0.2589	1.051	0.1388	1.022	0.1047	1.018	0.07974	1.015	0.06110	1.014	0.04696	1.012	0.03613	1.011	0.02780	1.010	0.00957	1.006
0.710	0.3193	1.098	0.1698	1.053	0.1283	1.047	0.09808	1.044	0.07557	1.042	0.05849	1.041	0.04537	1.040	0.03522	1.039	0.01266	1.034
0.720	0.3994	1.159	0.2092	1.088	0.1581	1.079	0.1212	1.074	0.09380	1.071	0.07304	1.070	0.05708	1.068	0.04468	1.067	0.01673	1.063
0.730	0.5091	1.246	0.2604	1.126	0.1963	1.112	0.1506	1.105	0.1170	1.101	0.09154	1.099	0.07199	1.098	0.05678	1.096	0.02208	1.093
0.740	0.6663	1.385	0.3283	1.173	0.2461	1.149	0.1887	1.138	0.1468	1.133	0.1153	1.129	0.09114	1.128	0.07235	1.126	0.02914	1.122
0.750	0.9065	1.641	0.4211	1.233	0.3127	1.193	0.2388	1.175	0.1857	1.166	0.1461	1.161	0.1160	1.158	0.09258	1.156	0.03849	1.152
0.755	1.080	1.863	0.4809	1.272	0.3546	1.219	0.2699	1.195	0.2096	1.184	0.1650	1.177	0.1312	1.174	0.1049	1.172	0.04425	1.167
0.760	...	...	0.5530	1.321	0.4042	1.249	0.3063	1.218	0.2374	1.203	0.1869	1.195	0.1487	1.190	0.1191	1.187	0.05091	1.182
0.765	...	...	0.6414	1.385	0.4635	1.285	0.3491	1.243	0.2698	1.223	0.2122	1.212	0.1689	1.207	0.1355	1.203	0.05862	1.198
0.770	...	...	0.7516	1.471	0.5354	1.330	0.4001	1.272	0.3079	1.245	0.2417	1.232	0.1923	1.224	0.1545	1.220	0.06756	1.213
0.775	...	...	0.8924	1.594	0.6238	1.388	0.4614	1.307	0.3532	1.271	0.2765	1.252	0.2198	1.242	0.1766	1.237	0.07796	1.229
0.780	...	...	1.078	1.780	0.7346	1.466	0.5362	1.351	0.4074	1.300	0.3177	1.275	0.2521	1.262	0.2025	1.255	0.09008	1.245
0.785	...	...	...	...	0.8770	1.579	0.6291	1.408	0.4733	1.336	0.3670	1.301	0.2904	1.284	0.2330	1.274	0.1043	1.260
0.790	...	...	...	...	1.066	1.750	0.7467	1.486	0.5546	1.381	0.4268	1.332	0.3363	1.308	0.2693	1.294	0.1209	1.277
0.795	...	...	...	...	...	...	0.8995	1.599	0.6566	1.440	0.5003	1.370	0.3919	1.335	0.3128	1.317	0.1406	1.293
0.800	...	...	...	...	...	...	1.105	1.776	0.7879	1.524	0.5923	1.419	0.4602	1.369	0.3656	1.343	0.1640	1.311
0.805	...	...	...	...	...	...	...	...	0.9618	1.650	0.7099	1.486	0.5456	1.411	0.4306	1.373	0.1920	1.328
0.810	...	...	...	...	...	...	...	...	1.202	1.854	0.8644	1.584	0.6544	1.468	0.5117	1.412	0.2258	1.347
0.815	...	...	...	...	...	...	...	...	...	...	1.075	1.739	0.7969	1.550	0.6152	1.462	0.2669	1.368
0.820	...	...	...	...	...	...	...	...	...	...	...	...	0.9901	1.676	0.7507	1.534	0.3175	1.391
0.825	...	...	...	...	...	...	...	...	...	...	...	...	1.264	1.892	0.9341	1.644	0.3807	1.418
0.830	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.194	1.829	0.4612	1.451
0.835	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.5658	1.494
0.840	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.7060	1.556
0.845	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.9012	1.653
0.850	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.188	1.824

Table II (*continued*)

β_L	$\alpha=10$ D_z	$\alpha=10$ $Q_B{}^*$	$\alpha=11$ D_z	$\alpha=11$ $Q_B{}^*$	$\alpha=12$ D_z	$\alpha=12$ $Q_B{}^*$	$\alpha=13$ D_z	$\alpha=13$ $Q_B{}^*$	$\alpha=14$ D_z	$\alpha=14$ $Q_B{}^*$	$\alpha=15$ D_z	$\alpha=15$ $Q_B{}^*$	$\alpha=16$ D_z	$\alpha=16$ $Q_B{}^*$	$\alpha=20$ D_z	$\alpha=20$ $Q_B{}^*$
0.400	...	...	...	...	0.00529	0.3620	0.00285	0.3574	0.00166	0.3538	0.00099	0.3510	0.00060	0.3488	0.00008	0.3426
0.410	...	...	...	...	0.00584	0.3789	0.00320	0.3742	0.00188	0.3705	0.00114	0.3677	0.00070	0.3656	0.00010	0.3593
0.420	...	...	...	...	0.00645	0.3962	0.00360	0.3914	0.00214	0.3875	0.00131	0.3848	0.00081	0.3827	0.00012	0.3764
0.430	...	...	...	...	0.00715	0.4138	0.00405	0.4088	0.00244	0.4050	0.00151	0.4024	0.00094	0.4003	0.00014	0.3938
0.440	...	...	...	...	0.00794	0.4318	0.00457	0.4264	0.00278	0.4229	0.00174	0.4203	0.00110	0.4182	0.00017	0.4117
0.450	...	...	...	...	0.00884	0.4502	0.00515	0.4445	0.00317	0.4411	0.00200	0.4387	0.00128	0.4366	0.00021	0.4300
0.460	...	...	...	...	0.00985	0.4688	0.00582	0.4631	0.00362	0.4598	0.00231	0.4574	0.00148	0.4553	0.00025	0.4487
0.470	...	...	0.02080	0.4959	0.01100	0.4873	0.00658	0.4819	0.00414	0.4789	0.00266	0.4765	0.00173	0.4744	0.00031	0.4678
0.480	...	...	0.02282	0.5157	0.01230	0.5061	0.00745	0.5012	0.00474	0.4984	0.00307	0.4961	0.00201	0.4939	0.00037	0.4872
0.490	...	...	0.02511	0.5360	0.01378	0.5254	0.00845	0.5209	0.00542	0.5183	0.00355	0.5160	0.00235	0.5138	0.00045	0.5071
0.500	...	...	0.02771	0.5566	0.01546	0.5451	0.00958	0.5410	0.00621	0.5386	0.00410	0.5362	0.00274	0.5341	0.00054	0.5274
0.510	...	...	0.03066	0.5753	0.01737	0.5652	0.01088	0.5616	0.00712	0.5592	0.00475	0.5569	0.00319	0.5547	0.00066	0.5480
0.520	...	...	0.03403	0.5946	0.01956	0.5857	0.01238	0.5827	0.00817	0.5802	0.00550	0.5779	0.00373	0.5758	0.00080	0.5691
0.530	...	...	0.03786	0.6144	0.02205	0.6066	0.01409	0.6040	0.00938	0.6016	0.00637	0.5993	0.00436	0.5972	0.00097	0.5905
0.540	...	...	0.04223	0.6346	0.02490	0.6279	0.01607	0.6258	0.01079	0.6234	0.00738	0.6211	0.00510	0.6190	0.00117	0.6123
0.550	0.1021	0.7004	0.04724	0.6554	0.02818	0.6500	0.01834	0.6479	0.01242	0.6454	0.00857	0.6432	0.00597	0.6412	0.00142	0.6346
0.560	0.1121	0.7155	0.05298	0.6765	0.03194	0.6725	0.02097	0.6704	0.01431	0.6679	0.00995	0.6657	0.00699	0.6638	0.00172	0.6572
0.570	0.1239	0.7322	0.05958	0.6982	0.03627	0.6954	0.02401	0.6932	0.01651	0.6907	0.01158	0.6886	0.00819	0.6867	0.00209	0.6802
0.580	0.1376	0.7503	0.06721	0.7202	0.04128	0.7187	0.02754	0.7164	0.01908	0.7138	0.01348	0.7119	0.00962	0.7101	0.00254	0.7036
0.590	0.1536	0.7696	0.07605	0.7427	0.04709	0.7423	0.03163	0.7398	0.02208	0.7374	0.01571	0.7355	0.01130	0.7337	0.00309	0.7274
0.600	0.1726	0.7903	0.08633	0.7674	0.05384	0.7664	0.03641	0.7635	0.02559	0.7613	0.01834	0.7595	0.01329	0.7578	0.00376	0.7515
0.610	0.1951	0.8124	0.09837	0.7928	0.06172	0.7909	0.04200	0.7877	0.02971	0.7855	0.02145	0.7839	0.01565	0.7822	0.00457	0.7761
0.620	0.2221	0.8361	0.1125	0.8190	0.07096	0.8159	0.04857	0.8122	0.03456	0.8102	0.02511	0.8086	0.01846	0.8069	0.00557	0.8010
0.630	0.2547	0.8620	0.1293	0.8461	0.08186	0.8411	0.05630	0.8371	0.04029	0.8352	0.02946	0.8336	0.02180	0.8320	0.00679	0.8263
0.640	0.2947	0.8908	0.1493	0.8743	0.09476	0.8667	0.06545	0.8625	0.04709	0.8606	0.03464	0.8590	0.02580	0.8575	0.00829	0.8519
0.650	0.3442	0.9237	0.1733	0.9040	0.1102	0.8928	0.07634	0.8882	0.05518	0.8864	0.04082	0.8848	0.03059	0.8833	0.01012	0.8779
0.660	0.4069	0.9803	0.2026	0.9359	0.1286	0.9199	0.08937	0.9147	0.06486	0.9127	0.04822	0.9109	0.03636	0.9095	0.01239	0.9043
0.670	0.4879	1.053	0.2386	0.9708	0.1511	0.9479	0.1051	0.9418	0.07651	0.9394	0.05714	0.9375	0.04332	0.9360	0.01517	0.9311
0.680	0.5958	1.155	0.2835	1.010	0.1785	0.9775	0.1242	0.9698	0.09062	0.9666	0.06794	0.9644	0.05176	0.9630	0.01862	0.9582
0.690	0.7451	1.310	0.3407	1.054	0.2125	1.009	0.1475	0.9988	0.1078	0.9944	0.08111	0.9919	0.06207	0.9903	0.02290	0.9856
0.700	0.9630	1.577	0.4152	1.108	0.2553	1.044	0.1765	1.029	0.1290	1.023	0.09728	1.020	0.07472	1.018	0.02823	1.013
0.710	1.307	2.108	0.5149	1.181	0.3101	1.084	0.2129	0.162	0.1554	1.053	0.1173	1.049	0.09037	1.046	0.03489	1.041
0.720	...	...	0.6538	1.290	0.3820	1.133	0.2595	1.098	0.1887	1.084	0.1424	1.079	0.1099	1.075	0.04326	1.070
0.730	...	...	0.8582	1.473	0.4792	1.199	0.3202	1.140	0.2312	1.119	0.1742	1.110	0.1345	1.105	0.05384	1.099
0.740	...	...	1.184	1.838	0.6158	1.294	0.4014	1.192	0.2869	1.157	0.2151	1.143	0.1660	1.137	0.06732	1.128
0.750	...	...	...	...	0.8189	1.455	0.5142	1.261	0.3615	1.203	0.2690	1.181	0.2070	1.170	0.08464	1.158
0.755	...	...	...	...	0.9614	1.585	0.5880	1.309	0.4087	1.231	0.3025	1.201	0.2321	1.188	0.09515	1.173
0.760	...	...	...	...	1.147	1.778	0.6783	1.369	0.4648	1.263	0.3416	1.224	0.2613	1.207	0.1072	1.188
0.765	...	...	...	...	...	...	0.7909	1.451	0.5324	1.303	0.3878	1.250	0.2953	1.227	0.1209	1.204
0.770	...	...	...	...	...	...	0.9346	1.567	0.6149	1.353	0.4429	1.281	0.3352	1.250	0.1368	1.220
0.775	...	...	...	...	...	...	1.124	1.741	0.7174	1.418	0.5095	1.317	0.3827	1.276	0.1552	1.236
0.780	...	...	...	...	...	...	...	...	0.8476	1.510	0.5911	1.363	0.4397	1.305	0.1766	1.253
0.785	...	...	...	...	...	...	...	...	1.018	1.644	0.6930	1.423	0.5091	1.342	0.2017	1.270
0.790	...	...	...	...	...	...	...	...	...	...	0.8231	1.507	0.5948	1.387	0.2312	1.289
0.795	...	...	...	...	...	...	...	...	...	...	0.9941	1.631	0.7030	1.448	0.2663	1.308
0.800	...	...	...	...	...	...	...	...	...	...	1.227	1.827	0.8428	1.534	0.3085	1.330
0.805	...	...	...	...	...	...	...	...	...	...	...	...	1.029	1.664	0.3597	1.354
0.810	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.4226	1.383
0.815	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.5013	1.417
0.820	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.6019	1.463
0.825	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.7336	1.526
0.830	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.9123	1.621
0.835	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.166	1.779

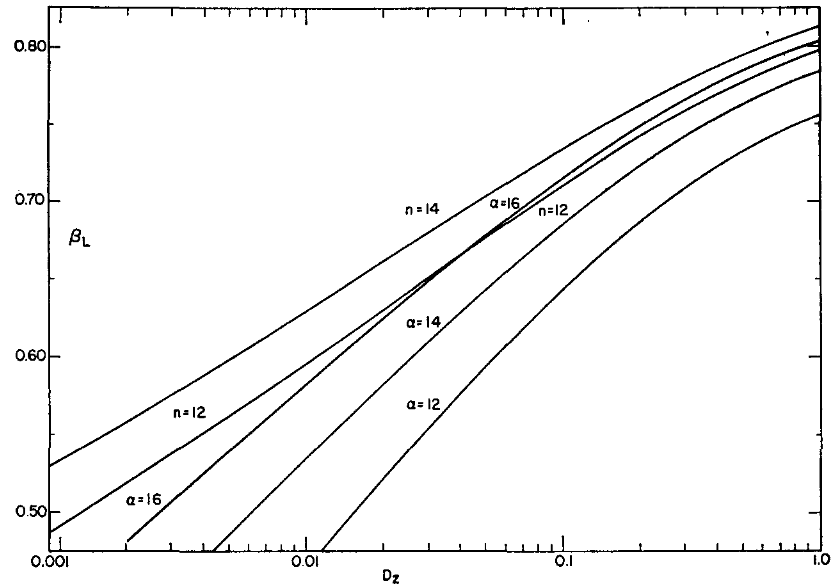

FIG. 3. Velocity dependence of β_L: β_L vs D_z.

following expressions[7] for the reduced cross sections Q_z^* in terms of β_L, for potentials A and B:

$$Q_A^* = 2\beta_L^2\left\{1+\left[\frac{3\pi}{32}\frac{n}{(n-6)}\right]^2 \tfrac{1}{2}D_z^2\left[\beta_L^{-10}-\frac{512f(n)}{\pi n(n+2)}\beta_L^{-n-4} + (n-2)^{-1}\left[\frac{64f(n)}{\pi n}\right]^2\beta_L^{-2n+2}\right]\right\} \quad (14a)$$

and

$$Q_B^* = 2\beta_L^2\left\{1+\left[\frac{3\pi}{32}\frac{\alpha}{(\alpha-6)}\right]^2 \tfrac{1}{2}D_z^2 \times\left[\beta_L^{-10}-\frac{512X\beta_L^{-11/2}e^{\alpha(1-\beta_L)}}{(2\pi)^{\frac{1}{2}}\alpha^{5/2}}+\frac{2048Y}{\pi\alpha^4}e^{2\alpha(1-\beta_L)}\right]\right\}, \quad (14b)$$

where

$$X \equiv 1-(7/2x)+[7\cdot 9/(2x)^2]-[7\cdot 9\cdot 11/(2x)^3]+\cdots$$

(the series is semiconvergent; the error is less than the term of smallest absolute magnitude[7]),

$$Y \equiv 1+x^{-1}+(2x^2)^{-1},$$

and $x \equiv \alpha\beta_L$.

Application of the condition of Eq. (7) to Eqs. (10a) and (10b), respectively, yields the dependence (albeit implicitly) of β_L upon D_z

$$\text{(A)}\quad D_z = (16/3\pi)[(n-6)/n]\beta_L^5 \times\{[32f(n)/\pi n]\beta_L^{-n+6}-1\}^{-1} \quad (15a)$$

and

$$\text{(B)}\quad D_z = (16/3\pi)[(\alpha-6)/\alpha]\beta_L^5 \times\{[32\beta_L^{11/2}e^{\alpha(1-\beta_L)}/(2\pi)^{\frac{1}{2}}\alpha^{\frac{3}{2}}]-1\}^{-1}. \quad (15b)$$

Figure 3 shows a comparison of $\beta_L(D_z)$ for the two potentials. Table II presents calculated values of $D_z(\beta_L)$ for the various values of n and α.

Having established the relationship $\beta_L(D_z)$, the velocity dependence of the cross section may be obtained directly, using Eqs. (14). $Q_{A,B}^*$ is a function only of the mass-independent variable $D_z = (2\epsilon r_m/\hbar)v^{-1}$. Table II summarizes the results of the computations of $Q_{A,B}^*(D_z)$ for a wide range of n and α.

Figure 4 is a log–log plot of Q_A^* vs D_z for various values of n, while Fig. 5 is a similar plot of Q_B^*, with parameter α. In Appendix II the limiting high-velocity form of Eq. (14a) is presented, with special reference to the L-J (12, 6) potential.

VELOCITY RANGE FOR VALIDITY OF RESULTS

In order to satisfy the condition [Eq. (4)] for validity of the present MM–JB treatment, D_z cannot exceed some maximum value, say $D_z^{\max}$, obtained from Eqs. (10a) and (10b) for potentials (A) and (B), respectively.

For the L-J (n, 6) potential one finds

$$D_z^{\max} = \tfrac{5}{6}[f(n)]^{5/(n-6)}\{(32/5\pi)[(n-1)/n]\}^{(n-1)/(n-6)}. \quad (16)$$

[7] Equation (14a) follows exactly from Eqs. (10a) and (6). However, in deriving Eq. (14b) from Eqs. (10b) and (6), an approximation was introduced, since the integral yielding the term in $e^{\alpha(1-\beta_L)}$ is not expressible in simple form. It was convenient to transform it to one involving Erf $(x^{\frac{1}{2}})$, which was then expanded for large x in a semiconvergent series (the first few terms of which disappeared by cancellation). In computation, the series is terminated when the $(n+1)$th term exceeds the nth; a residue of half the nth term is then applied. The error in X introduced by this procedure is $<2\%$ for $x>10$, but increases to $\sim 30\%$ at $x=5$. Fortunately, this has a negligible influence on the resulting Q_B^* since the entire second term in the braces of Eq. (14b) is in the range 5–10%, compared to unity. The principal factor governing Q^* is the quantity $2\beta_L^2$, where β_L is, of course, strongly dependent on D_z.

Substitution shows that for the cases of practical interest ($7 \leq n \leq 28$), $D_z^{\max} > 1$; thus if $D_z \leq 1$, the present treatment should be valid. This condition is equivalent to requiring that $v > v_{\min}$, where

$$v_{\min} = 2\epsilon r_m / \hbar. \tag{17}$$

For the exp-6(α) potential the analysis is more complicated but approximately the same lower limit of velocity obtains. However, for this potential a complication ensues from the well-known "spurious" maximum in $V(r)$ at small r, which gives rise to a divergence in $\beta_L(D_z)$ at the origin, so that at *extremely* high velocities the treatment gives unphysical results. However, this is not of serious practical concern.

Note added in proof: The accuracy of the present results for Q^* is, of course, limited by the accuracy of the MM random-phase approximation. Work is in progress to explore the validity of this assumption and the possibility of a small (velocity-independent) bias in the resulting MM cross sections.

ACKNOWLEDGMENTS

The author appreciates valuable discussions with Dr. Halstead Harrison, and acknowledges with thanks the assistance of Miss Doris Kitson, who checked a number of the equations, and of Mr. Frank Parker and Mr. Arnold Flank, who aided in plotting and computing the numerical results. In addition, the author wishes to thank Professor I. Amdur for his valuable comments on the manuscript.

APPENDIX I. SMALL-ANGLE DEFLECTION FUNCTION

Amdur and co-workers[8] have measured the velocity dependence of the low-resolution total cross section $S(\theta_1)$ for elastic scattering of high-energy molecular beams. Here θ_1 is a constant, i.e., the limiting effective angular aperture of the apparatus (calculated from the geometry) in the center-of-mass coordinate system. Assuming a repulsive potential $V(r) = Ar^{-n}$, one evaluates the small-angle classical deflection function $\theta(b)$ and thus the cross section $S(\theta_1) = \pi b_{\theta 1}^2$, where b is the impact parameter. The slope of a plot of $\log S(\theta_1)$ vs $\log E$ (where $E = \frac{1}{2}\mu v^2$) is $-2/n$; the intercept, which is a function of θ_1, yields A.

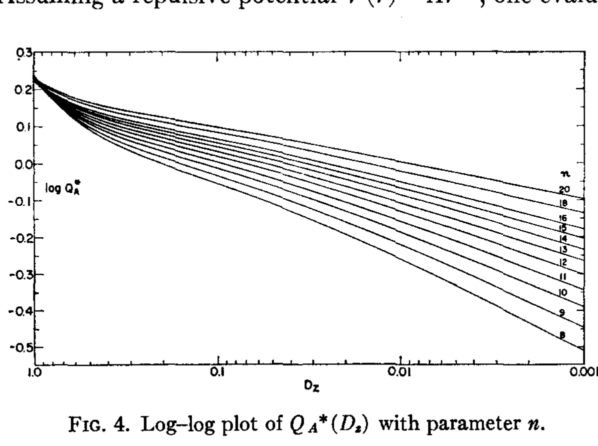

FIG. 4. Log–log plot of $Q_A^*(D_z)$ with parameter n.

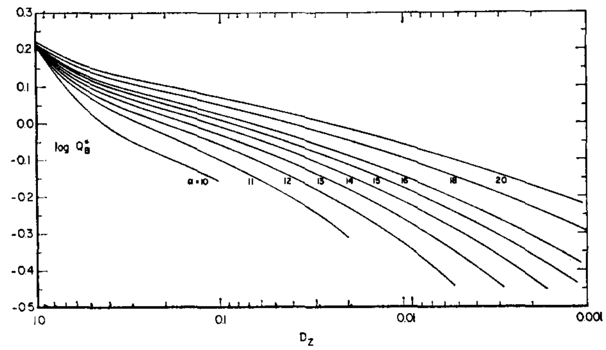

FIG. 5. Log–log plot of $Q_B^*(D_z)$ with parameter α.

For an exponential repulsion the analysis is more complicated due to the fact that the small-angle deflection function has not yet been expressed in simple terms. Amdur and Pearlman[8a] developed an implicit, asymptotic series formulation from which the potential constants may be calculated from the energy dependence of $S(\theta_1)$; this method was further exploited by Mason and Vanderslice.[9] In this Appendix we derive a compact formula for the small-angle deflection function for a simple exponential potential and for the exp-6(α) potential [Eq. (1b)], making use of the semiclassical equivalence principle.[1c]

For the exponential potential $V(r) = Ae^{-cr}$, the Jeffreys phase is $\eta_J = -(Al/2E)K_1(cb)$, where $l \sim kb$ and $K_1(x)$ is the first-order modified Bessel function of the second kind.[10] From the relation $\theta = 2d\eta/dl$ we obtain

$$\theta = -(A/E)(d/dx)[xK_1(x)], \tag{18}$$

where $x \equiv cb$. From the properties of the Bessel function this yields, without approximation, the desired formula for the small-angle deflection function

$$\theta = (Acb/E)K_0(cb), \tag{19}$$

where $K_0(x)$ is the zero-order modified Bessel function,[10] available in tabular form, which may be represented for large x by

$$K_0(x) \sim (\pi/2x)^{\frac{1}{2}} e^{-x} \{1 - \tfrac{1}{8}x^{-1} + \tfrac{9}{128}x^{-2} - \cdots\}. \tag{20}$$

For most practical cases of interest here, $x > 5$, so that we may ignore the terms in x^{-1} in braces [Eq. (20)] and obtain the simple approximate form:

$$\theta \sim (A/E)(\pi cb/2)^{\frac{1}{2}} e^{-cb} = (\pi cb/2)^{\frac{1}{2}} V(b)/E. \tag{21}$$

[8] I. Amdur and H. Pearlman, J. Chem. Phys. **9**, 503 (1941); I. Amdur, J. E. Jordan, and S. O. Colgate, *ibid.* **34**, 1525 (1961) and other papers in the series.

[9] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **27**, 917 (1957).

[10] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, England, 1944), 2nd ed., pp. 78, 79, 202.

[This *approximate* form of Eq. (19) can also be obtained via the Amdur procedure, as a first approximation.] Replacing b by $[S(\theta_1)/\pi]^{\frac{1}{2}}$, Eq. (21) yields

$$S^{\frac{1}{2}}=[(\pi)^{\frac{1}{2}}/c]\ \ln[\pi^{\frac{1}{4}}(c/2)^{\frac{1}{2}}(A/\theta_1)]+(\pi^{\frac{1}{2}}/c)\ \ln[S^{\frac{1}{2}}/E], \tag{22}$$

[where $S\equiv S(\theta_1)$], so that a plot of $S^{\frac{1}{2}}$ vs $\ln[S^{\frac{1}{2}}/E]$ should be linear. The slope yields c; from the intercept *and* the slope, A may then be obtained, provided θ_1 is known. Since $S^{\frac{1}{2}}$ is a slowly varying function of E, a simple plot of $S^{\frac{1}{2}}$ vs $\log E$ is expected to be nearly linear, in accord with the empirical finding of Mason and Vanderslice.[9]

Repeating and extending the above procedure for the exp-6(α) potential, using Eq. (10b), we obtain the following result for the small-angle deflection function [valid in the limit of large $\alpha\beta$, analogous to Eq. (21)]:

$$\theta\sim[(\alpha-6)K]^{-1}\{6(\pi\alpha\beta/2)^{\frac{1}{2}}e^{\alpha(1-\beta)}-(15\pi/16)\alpha\beta^{-6}\}, \tag{23}$$

where $K=E/\epsilon=A_z/D_z$ and $\beta=l/A_z$ as usual.

APPENDIX II. LIMITING HIGH-VELOCITY BEHAVIOR

It is of interest to evaluate the limiting high-velocity behavior of the total cross section. For the L-J (n, 6) potential, Eq. (14a) yields, in the limit $D_z\rightarrow 0$ (concurrently, $\beta_L\rightarrow 0$):

$$Q_A^*\sim 2\beta_L^2\{1+[3f(n)/(n-6)]^2[2D_z^2/(n-2)]\beta_L^{-2n+2}\} \tag{24}$$

and

$$D_z\sim[(n-6)/6f(n)]\beta_L^{n-1}, \tag{25}$$

so that

$$Q_A^*\sim 2[(2n-3)/(2n-4)]\beta_L^2$$
$$=\{2[(2n-3)/(2n-4)][6f(n)/(n-6)]^{2/(n-1)}\}D_z^{2/(n-1)}. \tag{26}$$

Thus a curve[1d] of $\log Q^*$ vs $\log v$ would be asymptotic to a line with a slope of $-2/(n-1)$, in the limit $v\rightarrow\infty$. For $n=12$, Eq. (26) becomes:

$$Q_A^*\sim[\tfrac{21}{10}(63\pi/512)^{2/11}]D_z^{2/11}\qquad (n=12), \tag{27}$$

or in the "x notation" of reference 1,

$$Q_{(12,6)}^*\sim[\tfrac{21}{10}(63\pi/128)^{2/11}]D^{2/11}, \tag{28}$$

where $Q^*\equiv Q/\pi\sigma^2$ and $D=2\epsilon\sigma/\hbar v$.

For the exp-6 potential, the spurious high-velocity behavior mentioned earlier gives rise to an unphysical solution. However, for a simple exponential $V=Ae^{-cr}$, the limiting high-velocity dependence of the cross section may be evaluated, approximately, using the procedures already outlined. One obtains the result:

$$Q\sim 2\pi b_L^2\{1+(2cb_L)^{-1}+[2(cb_L)^2]^{-1}-[2(cb_L)^3]^{-1}\}, \tag{29}$$

where b_L is defined by the implicit equation

$$e^{-cb_L}=(E/Ak)(2c/\pi b_L)^{\frac{1}{2}}. \tag{30}$$

For $cb_L>5$,

$$Q^{\frac{1}{2}}\sim(2\pi)^{\frac{1}{2}}b_L=[(2\pi)^{\frac{1}{2}}/c]\ \ln\{[Ak/(2c)^{\frac{1}{2}}](\pi/2)^{\frac{1}{4}}\}$$
$$+[(2\pi)^{\frac{1}{2}}/c]\ \ln(Q^{\frac{1}{4}}/E). \tag{31}$$

Thus a plot of $Q^{\frac{1}{2}}$ vs $\ln(Q^{\frac{1}{4}}/E)$ would be linear with a slope of $(2\pi)^{\frac{1}{2}}/c$. The analogy with the result of Appendix I is evident.