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SEMI-EMPIRICAL METHOD OF CALCULATING THE CROSS SECTION FOR ELASTIC SCATTERING OF SLOW ELECTRONS BY ATOMS

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A method is proposed by which the scattering length and effective range of elastic scattering of electrons by a neutral atom can be determined by isoelectronic extrapolation with respect to the quantum defects of the electron in the ion fields. The model potential parameters employed for the extrapolation are chosen to correspond to quantum defects known from experiments. The extrapolation is not performed with respect to Z but with respect to zero values of the quantum defects. By way of example the method is used to determine the cross sections for the elastic scattering of electrons by Ar and Ne atoms at energies up to 1 eV. The results obtained are in satisfactory agreement with available data.

PUBLISHED data on elastic scattering of slow electrons by atoms are relatively scanty. Theoretical investigations, as a rule, are confined to an examination of scattering by the hydrogen atom. Calculations for more complicated atoms entail great difficulties. Experiments were made for a limited number of atoms, and as a rule the measurements did not cover the very important region of incident-electron energy, on the order of a fraction of an electron volt. It is therefore of interest to devise semi-empirical methods by which to calculate the elastic scattering of slow electrons.

Theoretical estimates of the ionization potentials of negative ions are made for the most part by the method isoelectronic extrapolation[1-4]. This method does not claim high accuracy, but is relatively simple, permits analysis of the ions of all elements, and, as shown by comparison with the experimental data, gives sensible values for the affinity energies.

A similar extrapolation procedure can be used also to calculate the cross section for elastic scattering of slow electrons by atoms. In fact, the quantum defect method proposed by Seaton[5,6] enables us to find the phase shifts of elastic scattering of slow electrons by positive ions. Consequently, we can, by calculating the elastic scattering of electrons by the ions of the isoelectronic sequence, attempt to extrapolate these data and thus determine the scattering by the atom. For example, we can determine the scattering by the Ne atom from the scattering by the ions Na^+, Mg^{++}, Al^{+++} etc.

We must note immediately, however, that the quantum defect method in the form proposed by Seaton does not make it possible to choose directly a quantity that can be extrapolated for our purposes. It is meaningless to extrapolate the phase shift (or the quantum defect), if for no other reason, because of the elastic scattering of the electron by the atom at zero energy is already known from general considerations: it is equal to an integral multiple of π. At the same time, the parameters customarily used in scattering theory, such as the scattering length and the effective radius, are missing from Seaton's exposition of the quantum-defect method. It must also be noted that there are some unjustified assumptions in Seaton's cumbersome arguments. Therefore, the first step was to reconsider the scattering of an electron in the ion field by applying the effective-radius theory[7] to the Coulomb attraction field. The result was a rigorous justification of the quantum-defect method and establishment of its connection with the effective-radius theory[8][1].

In the present paper we first apply effective-radius theory to the extrapolation problem, and then propose an extrapolation method. The results obtained with its aid for Ar and Ne are compared with the experimental data.

EFFECTIVE RADIUS THEORY FOR A COULOMB ATTRACTION FIELD

The radial part $u(r)/r$ of the wave function of the electron in the ion field satisfies the equation (we are considering only the s-wave)

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[1] Similar work was done a year later by Moiseiwitsch[9].

$$[d^2/dr^2 + k^2 + 2Z/r + 2V(r)]\,u(r) = 0, \tag{1}$$

where k^2 is the energy of the electron, Z the ion charge, and V(r) takes into account the difference between the potential and Coulomb energies at small r. The asymptotic form of U(r) for large r is described by a function $\varphi(r)$ which satisfies the equation

$$(d^2/dr^2 + k^2 + 2Z/r)\,\varphi(r) = 0. \tag{2}$$

Using arguments similar to those used by Bethe [7] for a Coulomb repulsion field, we obtain, confining ourselves as usual to two terms in the expansion in powers of the energy,

$$2Z\left[\frac{\pi \operatorname{ctg}\delta(k^2)}{1-\exp(-2\pi\gamma)} - h\left(\frac{1}{\gamma^2}\right)\right] = -\frac{1}{a} + \frac{1}{2}r_0k^2,$$
$$h(\gamma^{-2}) = \operatorname{Re}\psi(i\gamma) - \ln|\gamma|, \tag{3}^*$$

where $\delta(k^2)$ is the phase shift of the electron wave function, characterizing the difference between the field and a Coulomb field, $\gamma = Z/k$, $\psi(x)$ is the logarithmic derivative of the Γ-function, a is the scattering length (in atomic units), and r_0 is the effective radius:

$$r_0 = 2\int_0^\infty (\varphi_0^2 - u_0^2)\,dr \tag{4}$$

(φ_0 and u_0 are the solutions of (1) and (2) for $k^2 = 0$). The function $h(\gamma^{-2})$ can be expressed, according to Hartree and Johnston [10], in the form

$$h(\gamma^{-2}) = \psi(i\gamma) + (2i\gamma)^{-1} - \ln(i\gamma) - i\pi\,[\exp(2\pi\gamma) - 1]^{-1}.$$

Expression (3) is valid also for negative energies, provided we make the substitutions

$$i\gamma \to n^*, \qquad \operatorname{ctg}\delta(k^2) \to i.$$

The first substitution follows from the fact that the energy k^2 is replaced by the negative electron energy E in the bound state, expressed in terms of the effective quantum number n*: $E = -Z^2/n^{*2}$. The second substitution follows from the fact that the scattering amplitude has poles at the points corresponding to the bound states. We thus obtain

$$[1 - \exp(-2\pi\gamma)]^{-1}\operatorname{ctg}\delta(k^2) + i\,[\exp(2\pi\gamma) - 1]^{-1}$$
$$\to i\operatorname{cth}(-i\pi n^*) = \operatorname{ctg}\pi\mu(E),$$
$$2Z\,[\pi\operatorname{ctg}\pi\mu(E) - h(n^{*-2})] = -a^{-1} + 0.5r_0E,$$
$$h(n^{*-2}) = \psi(n^*) + (2n^*)^{-1} - \ln n^*. \tag{5}^\dagger$$

We have introduced the quantum defect $\mu = n - n^*$. This quantity is calculated from the term energy, which is known from the experimental data. We represent (5) directly in the form of the energy dependence of the quantum defect:

$$\mu(E) = \mu_0 - \frac{\alpha}{n^{*2}}, \qquad \alpha = -\frac{\sin^2\pi\mu_0}{\pi}\left(\frac{Zr_0}{4\pi} + \frac{1}{12\pi}\right). \tag{6}$$

We have used here the fact that $h(n^{*-2}) \approx -1/12n^{*2}$ [10], and also introduced μ_0, the quantum defect at zero energy, which determines the scattering length:

$$2\pi Z\operatorname{ctg}\pi\mu_0 = -a^{-1}. \tag{7}$$

Thus, by calculating $\mu(E)$ from the spectrum of the energy levels of the atom, we can, as is usually done in the quantum-defect method, determine the elastic scattering of an electron by an ion. For example, from the spectrum of NaI we can determine the scattering by the ion Na^+, from the spectrum of Mg II we can determine the scattering by Mg^{++}, from the spectrum of Al III we can determine the scattering by Al^{+++}, etc. We note that it turns out actually that $\delta(k^2) = \pi\mu(k^2)$, where $\mu(k^2)$ is the quantum defect extrapolated to positive energies k^2.

EXTRAPOLATION METHOD

Letting $Z \to 0$ in (3), we obtain the known expression

$$k\operatorname{ctg}\delta(k^2) = -a^{-1} + 0.5\,r_0k^2. \tag{8}$$

We can thus extrapolate the scattering length. However, the quantity a, defined by (7), has a highly irregular behavior and does not lend itself to dependable extrapolation. We can attempt to do this analytically, by regarding μ_0 in (7) as a function of Z and recognizing that μ_0 tends to an integer as $Z \to 0$. We obtain

$$a = -\tfrac{1}{2}\,d\mu_0(Z)/dZ\,\big|_{Z=0}. \tag{9}$$

However, it must be taken into account here that the transition to the limit from (3) to (8) is made for $k \neq 0$, and the transition to the limit from (7) to (9) is made already after we put $k = 0$ in (3) [and thus obtain (7)]. However, for a function of type (3), the second limit, generally speaking, can depend on the sequence with which the transitions to the limit were made. Indeed, calculations by means of (9) give patently incorrect results. In particular, the scattering length for any sensible approximation of the function $\mu_0(Z)$ always turns out to be positive. We therefore discard (9) as erroneous.

We use for the extrapolation the quantity V(r), which can be determined from model considerations. Indeed, we know μ_0 and α from experiment. We can therefore specify a model potential which depends on two parameters, and determine these

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*ctg = cot.

†cth = coth.

Table I

	μ_0	$(-\alpha)$	x	y	qb
Na I	1,3480 [12]	0.0614	8.6993	4.5190	6.9071
Mg II	1.0674 [13]	0.0986	8.7760	5.5006	5.8452
Al III	0,8960	0.11	8.8052	6,0616	5.0986
Si IV	0.7746 [14]	0,1229	8.8412	6,4768	4.5272
P V	0,6856	0,125	8,8586	6.7680	4,0836
K I	2.1802 [12]	0,136	11.8986	5.1934	14,3257
Ca II	1,8024 [15]	0.238	11.9794	6.4710	12.7040
Sc III	1.560	0.336	12,0522	7.3055	11.4856
Ti IV	1,3826	0.448	12,1345	7.9449	10.5156
V V	1.238	0.50	12.1741	8,4261	9.6512

parameters for each ion from the condition that the corresponding values of μ_0 and α be equal to the experimental values. It can be hoped that the parameters obtained in this manner vary smoothly along the isoelectronic sequence and that we can obtain by extrapolation the effective model potential for scattering by a neutral atom. We can then calculate the scattering length and effective radius of interest to us.

We have chosen V(r) in the form

$$V(r) = \begin{cases} q/r, & r < b \\ 0 & r > b, \end{cases} \tag{10}$$

where q and b are unknown parameters. Solving now Eq. (1) with $k^2 = 0$ and with a potential (10), we obtain from the boundary condition an expression for μ_0:

$$\operatorname{tg} \pi\mu_0 = \frac{xJ_0(x)J_1(y) - yJ_0(y)J_1(x)}{xJ_0(x)Y_1(y) - yY_0(y)J_1(x)}, \tag{11*}$$

where J_n and Y_n are Bessel functions of the first and second kind, $y^2 = 8Zb$, and $x^2 = 8(Z+q)b$. Expression (11), together with the condition that μ_0 be a continuous function of x and y and that $\mu_0(x=y) = 0$, determines μ_0 uniquely.

Further, calculating (4) and using (6), we get

$$\alpha = \frac{y^4 \sin^2 \pi\mu_0}{192 J_1^2(x)} \{J_2^2(x)[J_1(y) \operatorname{ctg} \pi\mu_0 - Y_1(y)]^2 - J_1^2(x)[J_2(y) \operatorname{ctg} \pi\mu_0 - Y_2(y)]^2\} \tag{12}$$

Equations (11) and (12) enable us to determine x and y for each member of the isoelectronic sequence from the known values of μ_0 and α, and determine by the same token the model-potential parameters that can be extrapolated.

By way of an example we have attempted to obtain the cross sections for the scattering of slow electrons by Ne and Ar atoms. The experimental data on these cross sections are available, so that such a calculation can be regarded as a check on the proposed method. It is important that the energy dependence of the cross sections for the scattering by these atoms differs greatly.

The isoelectronic sequences for the scattering by Ne and Ar are all the ions containing 11 and 19 electrons, respectively. The results of a graphical solution of the system (11) and (12) for these isoelectronic sequences are listed in Table I. The quantities μ_0 and α were chosen from the data given in [11], or were taken from the original papers.

The extrapolation was carried out not with respect to Z but with respect to μ_0. This yielded smoother relations. The sought values of the parameters were obtained for $\mu_0 = 2$ for Ne and for $\mu_0 = 3$ for Ar[16].

We have attempted to achieve linear extrapolation. Such extrapolation could be carried out for the quantities q (Fig. 1) and $\ln(qb/\mu_0)$ (Fig. 2). In choosing the latter quantity we took account of the fact that $qb = 0$ for $\mu_0 = 0$, since this point corresponds to $Z = \infty$. The straight line was drawn through five points by least squares.

The extrapolated values of q and b determine the scattering length and the effective radius for the scattering of an electron by a neutral atom.

$$\frac{a}{b} = -\frac{J_2(\sqrt{8qb})}{J_0(\sqrt{8qb})}, \quad \frac{r_0}{b} = \frac{2}{3}\left(2 - \frac{1}{2qb} - \frac{b}{a}\right). \tag{13}$$

DISCUSSION OF RESULTS

The results obtained for Ar and Ne are shown in Table II. The scattering length was found to be negative for argon and positive for neon. This corresponds precisely to the fact that the Ramsauer effect is observed for argon but not for neon.

We note that (13) are quite sensitive to small changes in qb. Nonetheless, we were able to use the same extrapolation methods for two atoms, argon and neon, which have greatly differing scattering cross sections. This is evidence in favor of the chosen extrapolation method.

In constructing the elastic scattering cross section, we used an expression derived by O'Malley,

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*tg = tan.

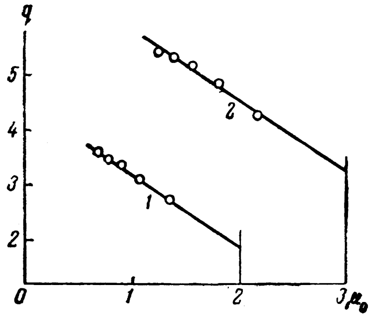

FIG. 1. Extrapolation of the quantity q: 1 – for the NaI isoelectronic sequence, 2 – for KI sequence.

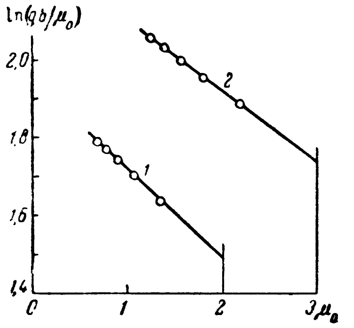

FIG. 2. Extrapolation of $\ln(qb/\mu_0)$: 1 – for the NaI isoelectronic sequence 2 – for the KI sequence.

Table II

	qb	q	a	r_0
Ne	8.846	1,86	0.10	−140
Ar	16,994	3,26	—1,6	18

Rosenberg, and Spruch[17,18], which takes account of the polarization potential β^2/r^4:

$$k^{-1}\operatorname{tg}\delta(k^2) = -a - \tfrac{1}{3}\pi\beta^2 k - \tfrac{4}{3}\alpha\beta^2 k^2 \ln 1,23\beta k - a^2\left(\tfrac{1}{2}r_0 + \tfrac{1}{3}\pi\beta - \pi\beta^3/3a^2\right)k^2. \tag{14}$$

With respect to polarization, it must be stated that in the present investigation it is taken into account only "effectively": the calculation is based on the experimental values of μ_0 and α; the quantity μ_0 is used to perform the extrapolation itself; formula (14) is used to calculate the cross sections of interest to us. However, in the derivation of (6) and in selecting the model potential (10), no account was taken of the polarization. A correct account of the polarization should make the extrapolation more dependable 2)

The scattering length and the polarizability coefficient are sufficient to determine the phase shifts by means of formula (14) only at energies up to several hundredths of an electron volt. At higher energies it is necessary to know also the effective radius. The simultaneous determination of both a and r_0 is therefore an advantage of the proposed extrapolation method.

The obtained cross sections are shown in Figs. 3 and 4. We see that they are in satisfactory agreement with the experimental data.

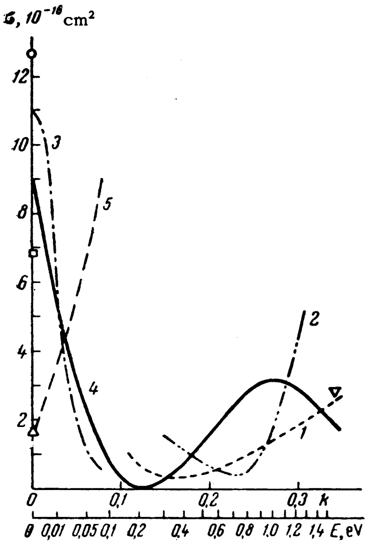

FIG. 3. Cross section for the elastic scattering of electrons by the argon atom. Experimental data: curve 1 – from[21], 2 – from[22], 3 – from[23]; □ – point obtained by measuring the shift of the higher levels of the alkali metals in inert gases[16]. We note with respect to this that it is indicated in[23], with reference to a private communication by Baranger, that the reduction of these measurements should be made more precise. The cross section obtained must be referred apparently not to zero energy, but to an energy on the order of several hundredths of an electron volt, i.e., the point on the plot should be shifted somewhat to the right; ○ – point obtained in[24] by extrapolating the data from[21] with the aid of formula (14); curve 4 – present work; △ – point obtained by Moiseiwitsch[25,26]; ▽ – experimental point[27] with which Moiseiwitsch compared his results; 5 – curve plotted from the scattering length calculated by Moiseiwitsch.

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2)It must be noted that even the very formulation of the problem of allowing for polarization is not clear in all respects. The polarization appears in two ways: first, a long-range potential β^2/r^4 appears; second, the short-range potential also becomes deformed. In recent investigations by Veklenko, Novobrantsev, and Starostin of the scattering of slow electrons by the hydrogen atom[19,20], only the second factor was taken into account, and good results were obtained nonetheless. The deformation of the short-range potential can, generally speaking, depend on the electron energy. This in turn produces in the expansion (14) additional terms that depend on the derivatives of the potential with respect to the energy. The foregoing ideas are due to Starostin.

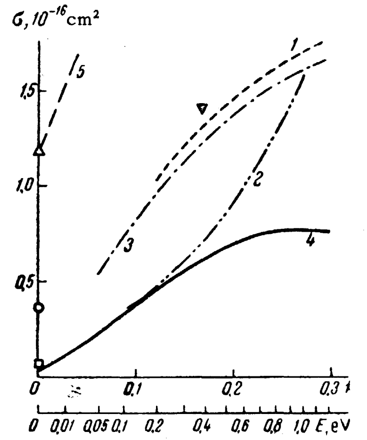

FIG. 4. Cross section for the elastic scattering of electrons by the neon atom. Experimental data: curve 1 – from[21], 2 – from[28], 3 – from[29]; □, ○, △, ▽, curve 5 – the same as in Fig. 3; 4 – present work.

Let us make a few remarks with respect to two communications by Moiseiwitsch[25,26], with which we became acquainted as the present work was being completed. Moiseiwitsch also called attention to the fact that the extrapolation procedure can be applied to the calculation of elastic scattering. However, he carried out the extrapolation in accordance with formula (9), and obtained for argon and neon scattering lengths of 0.62 and 0.73 respectively (in accordance with the foregoing, both values are positive). These numbers do not agree with the experimental data. The discrepancy becomes even sharper if these values of the scattering lengths and the first two terms of expansion (14) are used to plot the cross sections in the region of several hundredths of an electron volt (to plot the cross sections at higher energies it is necessary to know the parameter r_0, which Moiseiwitsch did not calculate). The curves obtained are also shown in Figs. 3 and 4. An utter disagreement with experiment can be noted. It must be emphasized in particular that Moiseiwitsch did not note the specific nature of the atoms, namely that the cross sections of argon and neon turned out to be almost the same, and no Ramsauer effect was obtained for argon. All this confirms that formula (9) is erroneous. The method used by Moiseiwitsch for comparison with experiment is surprising. His figures, which correspond to zero energy, were compared by him with the cross section measured for argon at 1.6 eV and for neon at 0.4 eV. In view of the fact that the cross section is strongly dependent on the energy in this range, such a comparison is utterly meaningless.

The extrapolation method proposed in the present paper can be employed, if suitable spectroscopic data are available, for atoms of any element. Obviously, we can determine separately here the scattering for states with different multiplicities (in general with different values of the momentum).

It should be noted that in addition to direct isoelectronic extrapolation, we can use, as for negative ions[3], "horizontal" extrapolation based on comparison of atoms which are in the same row of the periodic table. In this connection, we make several general remarks, analogous to those we made earlier[30] for a different problem. The quantum defects increase gradually with increasing atomic number. The difference between the quantum defects of neighboring elements is determined by the difference in the structure of the residual ions. Therefore an atom of an inert gas and the atom of the alkali metal which follows it will have nearly equal quantum defects. To the contrary, the alkaline-earth atom alongside will have a noticeably different quantum defect. Consequently, using isoelectronic extrapolation, we can assume that nearly equal scattering cross sections should be obtained, for example, for the atoms Ne and F, Ar and Cl, etc. The corresponding cross sections of the elements of the sixth column of the periodic table will likewise not differ by much. Indeed, the measured cross section for O[31,32] was found to resemble the cross section for Ne.

The proposed extrapolation can also be used, generally speaking, to determine the phase shifts of p- or d-scattering, etc. The calculation of the higher phases makes it possible to extend the region for which the cross sections can be determined at least to several electron volts. The proposed extrapolation method can apparently be used also to determine the energy of the affinity of the electron to the atom.

In conclusion we express our gratitude to A. Kh. Mnatsakanyan and A. N. Starostin for many interesting discussions.

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[1] G. Glockler, J. Chem. Phys. **32**, 708 (1960).

[2] B. Edlen, J. Chem. Phys. **33**, 98 (1960).

[3] J. W. Edie and F. Rohrlich, J. Chem. Phys. **36**, 623 (1962).

[4] Scherr, Silverman, and Matsen, Phys. Rev. **127**, 830 (1962).

[5] M. J. Seaton, Compt. rend. **240**, 1317 (1955).

[6] M. J. Seaton, Monthly Notices Roy. Astron. Soc. **118**, 504 (1958).

[7] H. Bethe, Phys. Rev. **76**, 38 (1949).

[8] G. E. Norman, Optika i spektroskopiya **12**, 333 (1962).

[9] B. L. Moiseiwitsch, Proc. Phys. Soc. **79**, 1166 (1962).

[10] D. R. Hartree and S. Johnston, Quart. J. Mech. and Appl. Math. **1**, 29 (1948).

[11] Ch. Moore, Atomic Energy Levels. **1**, NBS, Washington (1949).

[12] P. Risberg, Ark. Fysik **10**, 583 (1956).

[13] P. Risberg, Ark. Fysik **9**, 483 (1955).

[14] Y. G. Torresson, Ark. Fysik **17**, 179 (1960).

[15] B. Edlen and P. Risberg, Ark. Fysik **10**, 553 (1956).

[16] H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Oxford Univ. Press, 1952.

[17] O'Malley, Spruch, and Rosenberg, J. Math. Phys. **2**, 491 (1961).

[18] O'Mally, Rosenberg, and Spruch, Phys. Rev. **125**, 1300 (1962).

[19] B. A. Veklenko and I. V. Novobrantsev, JETP **43**, 919 (1962), Soviet Phys. JETP **16**, 652 (1963).

[20] B. A. Veklenko and A. N. Starostin, JETP **45**, 260 (1963), Soviet Phys. JETP **18**, 182 (1964).

[21] C. Ramsauer and R. Kollath, Ann. Physik **3**, 536 (1929).

[22] M. Rusch, Ann. Physik **80**, 707 (1926).

[23] J. L. Pack and A. N. Phelps, Phys. Rev. **121**, 798 (1961).

[24] T. F. O'Malley and L. Spruch, Bull. Amer. Phys. Soc. **7**, 69 (1962).

[25] B. L. Moiseiwitsch, 2-nd International Conference on the Physics of Electronic and Atomic Collisions. Abstract of Papers. W. A. Benjamin, Inc. New York.

[26] B. L. Moiseiwitsch, Proc. Phys. Soc. **81**, 35 (1963).

[27] J. C. Bowe, Phys. Rev. **117**, 1416 (1960).

[28] M. Rusch, Physik Z. **26**, 748 (1925).

[29] A. L. Gilardini and S. C. Brown, Phys. Rev. **105**, 31 (1957).

[30] Biberman, Norman, and Ul'yanov, Astronom. zh. **39**, 107 (1962), Soviet Astronomy **6**, 77 (1962).

[31] S. C. Lin and B. Kivel, Phys. Rev. **114**, 1026 (1959).

[32] Neynaber, Marino, Rothe, and Trujillo, Phys. Rev. **123**, 148 (1961).

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