PHYSICAL REVIEW A VOLUME 4, NUMBER 5 NOVEMBER 1971

Further Calculations of s-Wave Elastic e-H Scattering above the Ionization Threshold by the Complex-Energy Method*

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(Received 9 June 1971)

The method of extrapolation from complex energies is used to calculated s-wave electron–hydrogen-atom elastic scattering from the ground state at energies in the region ranging from 1.21 to 2.25 Ry.

I. INTRODUCTION

This paper gives the results of some further calculations of s-wave electron–hydrogen-atom elastic scattering in the energy region above the ionization threshold, using the method of extrapolation from complex energies proposed previously.[1] We have increased the number of trial functions and calculated at five energies from 1.21 to 2.25 Ry. The results agree well with other calculations for the triplet state, but differ from some previous estimates in the singlet case.

II. METHOD OF CALCULATION

We briefly recapitulate the idea of the method using the notation of Ref. 1. In order to determine the s-wave elastic scattering amplitude for an electron of momentum k incident on the ground state of the hydrogen atom, we first calculate the function $T(p)$ for several values of the complex momentum p (with positive imaginary part) and then extrapolate these results to $p=k$. The amplitude $T(p)$ is defined as

$$T(p)=\langle Q\phi_0|QV\phi_0\rangle+\langle QV\phi_0|(E-H)^{-1}|QV\phi_0\rangle\,, \tag{1}$$

where

$$\phi_0=\frac{e^{-r_2}\sin kr_1}{2\pi kr_1}\,,\quad V=-\frac{2}{r_1}+\frac{2}{r_3}\,,\quad Q=\frac{1\pm P_{12}}{\sqrt{2}}\,,$$

with $E=p^2-1$ and the Hamiltonian H given by

$$H=-\nabla_1^2-\nabla_2^2-2/r_1-2/r_2+2/r_3\,. \tag{2}$$

We obtain $T(p)$ by characterizing it as the stationary value of $[T]$,

$$[T]=\langle Q\phi_0|QV\phi_0\rangle+\langle\chi_t'|QV\phi_0\rangle+\langle QV\phi_0|\chi_t\rangle-\langle\chi_t'|(E-H)\chi_t\rangle\,, \tag{3}$$

as the trial functions χ_t and $\chi_t'=\chi_t^*$ are varied. The fundamental advantage in using complex p is that the exact $|\chi\rangle=(E-H)^{-1}|QV\phi_0\rangle$ is a function that falls off rapidly enough at large distances to be square-integrable. Thus we expand χ_t as a linear combination of Hylleraas functions

$$\chi_t=(4\pi)^{-1}Q\sum_{l+m+n\leq M}C_{lmn}e^{-(\kappa/2)(r_1+r_2)}r_3^l r_1^m r_2^n\equiv\sum_{l+m+n\leq M}C_{lmn}u_{lmn}(r_1,r_2,r_3)\,. \tag{4}$$

Although it has not been proved, we believe that the estimates of T derived by varying the coefficients C_{lmn} in (4) converge to $T(p)$ as $M\to\infty$. [A proof would follow if it could be shown that the set of functions $\{(E-H)\,u_{lmn}\}$ was dense for E complex.]

A theory of the rate of convergence of such a procedure is slowly being developed,[2] and, while we are not yet able to treat the present case on a rigorous basis, it seems likely that it is those parts of χ which fall off slowest at infinity that dominate the asymptotic convergence rate. For each two-body channel χ will contain a term that, for large distances, has the form

$$Qf_{nl}(\hat{r}_1)(e^{ip_nr_1}/r_1)\,\Psi_{nl}(\vec{r}_1)\,, \tag{5}$$

where Ψ_{nl} is a hydrogen bound-state wave function for binding energy B_n, and $p_n^2=E+B_n$. Those channels with largest B_n have smallest $\mathrm{Im}p_n$, and are expected to have most effect on the convergence rate. Consequently, to accommodate this behavior, we have added to (4) three trial functions corresponding to $1s$, $2s$, and $2p$ states. They are

$$\begin{aligned}\theta_{1s}&=Q\,e^{-r_2}(e^{ip_1r_1}/r_1)\,g\,,\\ \theta_{2s}&=Q\,(2-r_2)\,e^{-r_2/2}(e^{ip_2r_1}/r_1)\,g\,,\\ \theta_{2p}&=Q\,r_2\,e^{-r_2/2}\,\frac{e^{ip_2r_1}}{r_1}\left(1+\frac{ig}{p_2r_1}\right)g^2\,,\end{aligned} \tag{6}$$

with $g=1-e^{-\kappa r_1/2}$. It is found that the inclusion of these functions, especially θ_{1s}, markedly improves the apparent rate of convergence of the method.

A study[3] of the close-coupling equations indicates that, in addition to (5), there may be terms in χ

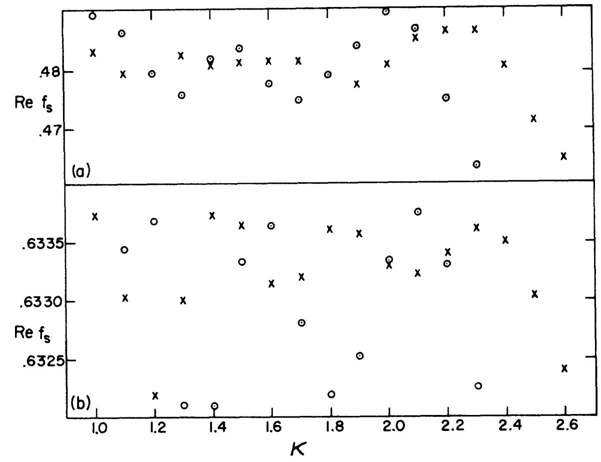

FIG. 1. Dependence of Re$f_s(p)$[where $f_s(p) = -kT(p)$ for the singlet spin state] on the nonlinear parameter κ, for $M = 7$ (circles) and $M = 8$ (crosses), and $k = 1.1$. (a) $p = 1.1 + 0.1\,i$; (b) $p = 1.1 + 0.25\,i$.

that do not fall off exponentially, even for complex E, but behave like

$$Q r_1^{-m} e^{\pm i k r_1} \Psi_n(\vec{r}_2)\,. \tag{7}$$

These terms are present as a result of the long-range character of the interactions. However since the value of m is at least 3, these terms may not be too important. It would be interesting to include trial functions of this sort in the calculation and see what the effect is.

For each value of p and M, we carried out the calculation for a range of values of κ. The results always oscillated with varying κ with an amplitude that decreased with increasing M. There appeared to be a value of κ, κ_0, near which the relative amplitude of the oscillations was smaller than elsewhere, suggesting better convergence. The value of κ_0 increased as Imp increased, roughly following the formula $\kappa_0 = 1.1 + 4\,\mathrm{Im}p$ at $k = 1.1$, with Re$p = 1.1$. This type of behavior is to be expected, since generally speaking χ falls off faster for larger Imp, requiring a larger decrease in the trial functions u_{lmn}. The above statements are illustrated by the results shown in Fig. 1.

From all the results for a given p, we estimated the value of $T(p)$. These estimates for values of p given by Re$p = k$, Im$p = 0.05$–0.55 in steps of 0.05 were plotted, and the value of $T(k)$ obtained by extrapolation of smooth curves through the points.

It should be pointed out that $T(p)$ is singular at $p = k$, which raises questions about the meaning of the extrapolation described above. However, from the close-coupling equations we deduce that for 1s elastic scattering, in the s state, the singularity is quite weak since an expansion of $T(p)$ about $p = k$ has the form

$$T(p) \simeq T(k) + (p-k) \times \lfloor(\text{function analytic at } p=k) + a(p-k)^2 \ln(p-k)\rfloor + \cdots\,, \tag{8}$$

so that the first two derivatives of $T(p)$ exist at $p = k$. In the present work, we have made no use of this information, but it is possible to envisage a more sophisticated technique which would adjust parameters in a function with a singularity of this nature, until the function passed through or near the points we have calculated.

III. RESULTS

Physically, there is a great deal of difference between s-wave elastic scattering in the triplet and singlet spin states. The space part of the triplet wave function must be antisymmetric, which keeps the incident electron away from the atom. There is therefore little chance that the atom will be excited from its ground state, and the scattering is well described by a model in which the incident electron moves in the average potential of the atom.

This picture of the triplet state is borne out by our results, given in Table I. Even when Im$p = 0$ our calculations with $M = 8$ appear to converge to better than 2% accuracy for the range of k considered, $k = 1.1\,(0.1)\,1.5$. The results for Im$p = 0$ always lie within a few percent of smooth curves passing through other values of Imp, and thus seem fairly reliable. If there was a difference between the extrapolated value and the value at Im$p = 0$, we have given the extrapolated value. Applying the optical theorem to these results, we deduce that probably at least 98% of the total cross section at all k considered comes from elastic scattering, which fits in with our picture. It seems most likely that the reason for the apparent convergence of our calculations at Im$p = 0$ is the smallness of the coefficients of terms such as (5), which should be included for all n at Im$p = 0$.

Our results at $k = 1.1$ are close to the results of various close-coupling calculations,[4] one involving correlations.[5] Even a three-state close-coupling calculation gives a result for the partial cross section only 1% smaller than ours. A plot using our results and those of others[5,6] (Fig. 2) shows that $k \cot(\mathrm{Re}\,\delta)$ is close to a linear function of k^2 as

TABLE I. Estimates from this calculation of the triplet and singlet s-wave elastic e-H scattering amplitudes $f = -kT(k)$.

k	Ref_t	Imf_t	Ref_s	Imf_s
1.1	0.232	0.939	0.37	0.47
1.2	0.298	0.893	0.35	0.45
1.3	0.350	0.845	0.34	0.43
1.4	0.386	0.795	0.33	0.42
1.5	0.422	0.749	0.33	0.41

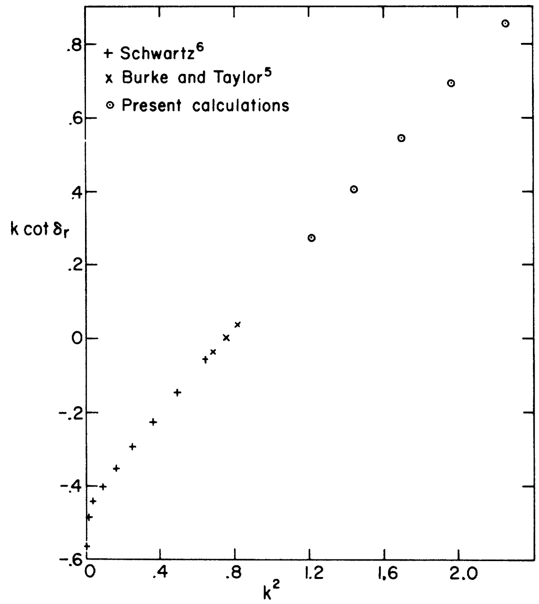

FIG. 2. Calculated values of $k\cot(\mathrm{Re}\delta)$ for triplet s-wave elastic e-H scattering.

far as $k = 1.5$. The situation is very similar to that occurring in the quartet s-wave state of neutron-deuteron scattering.[7,8] The conclusion is that the triplet s-wave elastic scattering is easy to calculate, and that it is indeed a poor method which does not give good results for this case.

The singlet state is another matter. There is no sign of convergence at $\mathrm{Im}p = 0$. At $\mathrm{Im}p = 0.05$, with $M = 8$, errors range from 2% at $k = 1.1$ to 10% at $k = 1.5$. By the time $\mathrm{Im}p$ has increased to 0.15, these errors have decreased by a factor of 10. The values of $T(p)$ that can be calculated with reasonable precision lie on smooth curves as $\mathrm{Im}p$ is varied. Examples of the curves, with their extrapolation to $\mathrm{Im}p = 0$, are shown in Fig. 3.

At $k = 1.1$, the present calculation predicts a value of 0.30 (in units of π) for the singlet partial cross section. This compares with values of 0.17 and 0.19 for close-coupling calculations in the $1s - 2s - 2p$ and $1s - 2s - 2p - 3s - 3p$ approximations,[4] respectively. Burke and Taylor[5] have carried out a $1s - 2s - 2p$ close-coupling calculation with 16 correlation functions added, and have obtained a result of 0.23 for the singlet partial cross section. However, their result varies rapidly with κ, as do our results for real p, and it is hard to know what weight to place on their calculation.

It will be seen from Table I that our predictions for the singlet amplitude do not vary rapidly with energy over the range considered. The elastic cross section is roughly $\frac{2}{3}$ of the total s-wave cross section. Following the trend of our results, we would estimate a value of 0.40 for the singlet s cross section at $k = 1.0$, which compares to a value of 0.47 obtained with the polarized orbital method by Temkin and Lamkin.[9] However, the meaning of their result is a little unclear, since their method does not seem to allow for inelastic scattering.

IV. DISCUSSION

The principle of the method used in this paper may be extended to processes other than elastic scattering, such as excitation and ionization.[10] We do not know if such calculations are feasible at the present time.

The extrapolation procedure introduces errors of unknown size. It would be very helpful if our results could be compared with those of another method, however cumbersome, that did not involve extrapolation. The Kohn variational method would be one such method, but this is likely to require some very lengthy computations.

ACKNOWLEDGMENTS

For the provision of CDC 6600 computing facilities, we wish to thank the University of Texas at Austin Computation Center, Major W. A. Whitaker of the Air Force Weapons Laboratory, Kirtland Air Force Base, and Los Alamos Scientific Laboratory. We are grateful to Dr. S. Ormonde and Dr. G. M. Hale for their assistance.

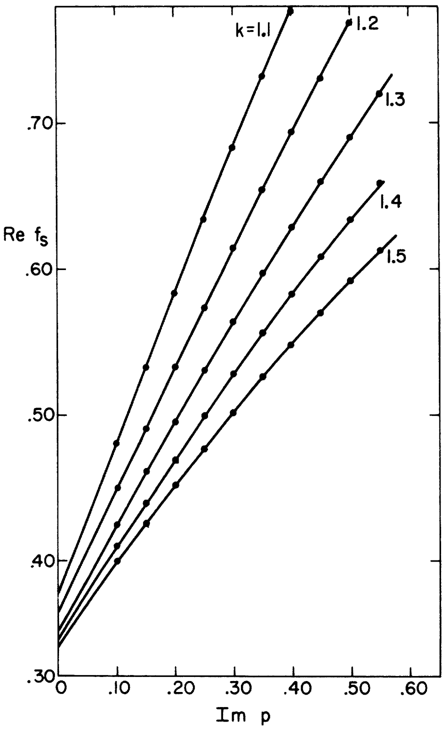

FIG. 3. Extrapolations of $\mathrm{Re}f_s$ from the values calculated at $p = k + i\,\mathrm{Im}p$, shown by the solid circles. Note that the size of these circles does not indicate the expected error (see text).

*Work supported in part by the U.S. Air Force Office of Scientific Research, Office of Aerospace Research under Grant No. 71-1979, in part by the National Science Foundation, Institutional Grant for Science, Southern Methodist University, and in part performed under the auspices of the A.E.C. at Los Alamos Scientific Laboratory.

[1] F. A. McDonald and J. Nuttall, Phys. Rev. Letters 23, 361 (1969).

[2] C. Schwartz, *Methods in Computational Physics* (Academic, New York, 1963), Vol. 2; L. M. Delves and K. O. Mead (unpublished).

[3] R. W. Stagat and J. Nuttall, Bull. Am. Phys. Soc. 16, 528 (1971).

[4] P. G. Burke, Proc. Phys. Soc. (London) 82, 443 (1963).

[5] P. G. Burke and A. J. Taylor, Proc. Phys. Soc. (London) 88, 549 (1966).

[6] C. Schwartz, Phys, Rev. 124, 1468 (1961).

[7] F. A. McDonald and J. Nuttall, Bull. Am. Phys. Soc. 15, 1588 (1970).

[8] M. G. Fuda (unpublished).

[9] A. Temkin and J. C. Lamkin, Phys. Rev. 121, 788 (1961).

[10] G. D. McCartor and J. Nuttall, Phys. Rev. (to be published).

PHYSICAL REVIEW A VOLUME 4, NUMBER 5 NOVEMBER 1971

Charge Transfer in Na$^+$-O$^-$ Collisions at Low Relative Energy

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(Received 5 November 1970; revised manuscript received 7 June 1971)

Total cross sections have been measured for electron transfer from O$^-$ to Na$^+$, resulting in optically allowed transitions to Na(^2S) ground state. A merged-beam technique was used to study the collisions in the energy range 0.1–7 eV. Structure in the curves of cross sections vs relative energy indicates that the excitation of oxygen plays an important role in the charge-transfer process. Cross sections for an endoergic process, giving Na(4p), are of order 10^{-14} cm^2; cross sections for the exoergic processes leading to production of Na(3d) and Na(3p) are of order 10^{-13} cm^2. Production of Na(3d) is nearly a resonant process; production of Na(3p) is apparently due to a cascade from Na(3d).

I. INTRODUCTION

The study of ion-ion mutual neutralization processes in the collision energy range between 0 and 10 eV is of particular interest because this range encompasses those internal states of the neutralized atoms most frequently observed in optical spectra. If the end result of a charge-transfer collision is to leave one or both atoms in excited states, and if the excitation energy arises from the collisional interaction, then the intensity of photon emission from the excited atoms should show a dependence upon the relative translational energy of the ions. The nature and significance of that dependence will be reflected in the individual cross sections associated with specific final states of the neutralized atoms.

The experimental difficulties inherent in working in this range of energies are well known.[1] Crossed-beam techniques (intersecting beam angle, greater than, say, 10°) are difficult to apply at relative energies less than about 50 eV. Low-energy beams of ionized gases suffer in particular from spreading due to space charge.

A means of obtaining well-collimated beams with useable intensities and low relative energies is to merge two high-energy ion beams which have a low *relative* energy. Space-charge problems are largely overcome and standard beam techniques developed for crossed-beam studies can be employed. Thus, for example,[2] for two beams of equal masses and laboratory energies of 1250 and 1350 eV, the relative energy is only 1 eV. In addition, the merged-beam approach has the asset that, in converting from laboratory coordinates to relative coordinates, there is a reduction of the dispersion of kinetic energies, which increases the relative energy resolution of the experiments. Suppose, in the example just given, the ion-source energy spread is about 5 eV in the laboratory frame. This corresponds to an energy uncertainty of about 0.1 eV in the center-of-mass system.

To date, merged beams have been used to study charge transfer and charge rearrangement in ion-neutral reactions,[3] charge transfer and rearrangement in neutral-neutral collisions,[4] and total mutual neutralization cross section in ion-ion collisions.[5] The experiment described here is apparently the first to combine the high collision-energy resolution of the merged-beam technique with the high *photon*-energy resolution of spectroscopy. With this arrangement it is possible to measure individual charge-transfer cross sections leading to specific final states as functions of energy for those channels which result in optically allowed transitions. The object of this experiment, then, is to