Rearrangement Collisions—Electron Excitation of He(2^3s)†

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There are many formal expressions for the T matrix for a rearrangement collision. First-order approximations to the exact wave functions in the different expressions yield different numerical results for the cross section. We have chosen eight forms of the T matrix and have evaluated the eight cross sections for electron excitation of He(2^3s), which is a pure rearrangement collision when spin-dependent forces are neglected. The projection-operator formalism for T yields good agreement with experiment.

I. INTRODUCTION

THE process of rearrangement collision is probably the least understood of any nonrelativistic scattering interaction. This is not surprising in that a rearrangement collision is *intrinsically* at least a three-body problem. One of the reasons for this lack of understanding is the absence of reliable theoretical solutions of meaningful problems and the absence of unambiguously interpretable experiments. Recently, ambitious attempts[1] have been made at a fundamental understanding of the transition matrix elements. We shall not pursue this course here. Instead, we shall be concerned with the practical aspects of getting results from various formulations and testing the assumptions involved against experiments.

We feel that the practical difficulties in obtaining reliable results may be broken into three categories. The first is the ambiguities associated with the different formulations of the T matrix. This will be referred to as the *dynamical problem* and will be discussed more fully below. The second, which is our ignorance of the exact bound-state wave functions in almost all cases, we shall call the *bound-state problem*. Finally, the third is the ignorance of the two-particle interaction in some cases which we call the *interaction problem*.

There exist remarkably thorough and reliable experiments on nuclear rearrangement collisions, but nuclear physics is plagued by real ambiguities in the bound state and the interaction problem—in particular, the latter. These preclude simple comparisons with experiment so that information cannot easily be obtained on the dynamical problem, which is our object here.

Atomic physics is not as badly plagued by the bound-state problem and not at all by the interaction problem. On the other hand, reliable experiments are not as plentiful. In the one reliable electron-scattering situation of which we are aware, elastic scattering of electrons from atomic hydrogen with spin flip, there exist very reliable theoretical calculations[2] and recent confirmatory experiments.[3] These have been analyzed with regard to the dynamical problem[4] with the remarkable result that a "Born approximation" in one of the T-matrix formulations gives the observed resonance exactly.

Our principal aim here is to investigate the ambiguities associated with the dynamical problem. By this we mean the following: The T matrix for a rearrangement collision can be written in a variety of ways, all of which are exact and all of which contain wave functions or operators which we are unable to obtain exactly. When approximations are made on these wave functions or operators, different results are obtained from each of the formulations of the T matrix. Our approximations, in each case, will be to replace a wave function by its unperturbed value, the first Born approximation. We have investigated these differences for the problem of electron excitation of the 2^3s state of helium. This process is a rearrangement collision provided spin-dependent forces are neglected. In that case, the electron spins are individually good quantum numbers and the excitation of a triplet state can come about only by the incident electron replacing one of the bound ones (the one with opposite spin).

There are several experiments[5] giving the 2^3s excitation of helium by electrons which include excitation to higher states with subsequent cascade to 2^3s. These are not easily amenable to analysis. Recently, Schulz and Philbrick[6] have obtained the direct 2^3s population by electron excitation up to about 3 eV above threshold. It is unlikely that any first Born approximation could give a good result at such a low energy. Gabriel and Heddle[7] have obtained the 2^3s excitation cross section after correction for cascade from higher states. They obtained

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* Chargé de Recherches du Fonds National de la Recherche Scientifique, Belgium.
[1] For a comprehensive list of references see C. Lovelace, Phys. Rev. **135**, B1225 (1964).
[2] P. G. Burke and H. Schey, Phys. Rev. **126**, 147 (1962).
[3] G. J. Schulz, Phys. Rev. Letters **13**, 583 (1964).
[4] M. H. Mittleman, Phys. Rev. Letters **9**, 505 (1962).
[5] G. J. Schulz and R. E. Fox, Phys. Rev. **106**, 1179 (1957).
[6] G. J. Schulz and J. W. Philbrick, Phys. Rev. Letters **13**, 477 (1964).
[7] A. H. Gabriel and D. W. O. Heddle, Proc. Roy. Soc. (London) **A258**, 124 (1960).

an absolute measurement at 108 eV where their results agree well with our improved calculation. Maier-Liebnitz[8] has measured the cross section in a lower energy region then Gabriel and Heddle. If the two sets of data are taken at face value then there is a pronounced dip in the cross section at about 5 eV above threshold which is roughly described by one of our forms.

In the next section we shall briefly describe the derivations which yield eight different exact formulations of the T matrix. In each case we shall make first Born approximations for the unknown wave functions thereby obtaining eight different approximate expressions for the T matrix and the cross section. We have used simple variational approximations for the bound state of helium. These could easily be improved and our results indicate that an improvement of the 2^3s wave function is probably worthwhile.

In Sec. III we have presented the results of the eight calculations and compared them with previous calculations and experiments.

II. THEORY

The derivation[9] of the usual T matrix is too common to be repeated in detail here. It will be outlined here only for the purpose of establishing notation. The (unsymmetrized) initial state will be written

$$\lambda_i(0)=\chi_i(0)\alpha(0)(1/\sqrt{2})[\alpha(1)\beta(2)-\alpha(2)\beta(1)], \quad (1)$$

where

$$\chi_i(0)=e^{i\mathbf{p}_i\cdot\mathbf{r}_0}\phi_0(\mathbf{r}_1,\mathbf{r}_2), \quad (2)$$

and ϕ_0 is the spatial part of the ground-state wave function of helium. $\alpha(n)$ ($\beta(n)$) is the spin-up (down) function for the nth electron quantized along some direction in space. The notation $\lambda_i(0)$ and $\chi_i(0)$ indicate that the particle with coordinate $\mathbf{r}_0$ is singled out as the incoming one while the other two are bound. Since ϕ_0 is symmetric, a completely antisymmetrized wave function can be obtained by applying the operator

$$A_0=1-P_{10}-P_{20}, \quad (3)$$

where the P's are operators exchanging the indicated space and spin coordinates. The final state with particle r_1, singled out as the scattering one is

$$\lambda_f(1)=\chi_f(1)\begin{Bmatrix}\beta(1)\alpha(0)\alpha(2)\\ \alpha(1)(1/\sqrt{2})[\alpha(0)\beta(2)+\beta(0)\alpha(2)]\end{Bmatrix}, \quad (4)$$

where

$$\chi_f(1)=e^{i\mathbf{p}_f\cdot\mathbf{r}_1}\phi_1(\mathbf{r}_0,\mathbf{r}_2) \quad (5)$$

and ϕ_1 is the spatial part of the 2^3s state of helium. In Eq. (4) we have written the two possible final spin states which give a nonzero contribution. In Eq. (1) we could also have the state obtained by replacing $\alpha(0)$ by $\beta(0)$ but it is clear that this would lead to two other contributing states in Eq. (4) which would give the same contribution to the cross section as the ones we have chosen. We may therefore consider only those in Eq. (1) and Eq. (4).

The Lippmann-Schwinger equation in which (1) acts as the initial state is

$$\psi_i^{(+)}(0)=\lambda_i(0)+[1/a_i(0)]V_i(0)\psi_i^{(+)}(0), \quad (6)$$

where

$$a_i(0)=E+i\eta-H+V_i(0) \quad (7)$$

and

$$V_i(0)=-2e^2/r_0+e^2/r_{10}+e^2/r_{20} \quad (8)$$

is the interaction of electron "0" with the atom. Here H is the full Hamiltonian and E the total energy. The fully antisymmetrized function is $\psi_i^{(+)}=A_0\psi_i^{(+)}(0)$ which may be written as

$$\psi_i^{(+)}=[i\eta/a_f(1)]A_0\chi_i(0)+[1/a_f(1)]V_f(1)\psi_i^{(+)}, \quad (9)$$

where

$$a_f(1)=E+i\eta-H+V_f(1), \quad (10)$$

and

$$V_f(1)=-2e^2/r_1+e^2/r_{10}+e^2/r_{12} \quad (11)$$

is the interaction of electron (1) with the atom. The T matrix for the reaction may be obtained by projecting $\lambda_f(1)$ on $\psi_i^{(+)}$ and looking for outgoing waves of electron 1. The form, Eq. (9), is particularly suitable for this. The first term contributes nothing[10] (in the physical limit $\eta\to 0$) while the second term yields the standard result

$$T_{fi}=\langle\lambda_f(1)V_f(1)\psi_i^{(+)}\rangle. \quad (12)$$

This may be simplified by using $\psi_i^{(+)}=A_0\psi_i^{(+)}(0)$ and performing all the spin algebra. The result is

$$T_{fi}=\langle\chi_f(1)V_f(1)\hat{\psi}_i^{(+)}(0)\rangle\begin{Bmatrix}-\sqrt{2}\\ 1\end{Bmatrix} \quad (13)$$

where the two results correspond to the two possible final states in Eq. (4). $\hat{\psi}_i^{(+)}(0)$ is just the function $\psi_i^{(+)}(0)$ with the spin dependence removed. It satisfies (6) with $\lambda_i(0)$ replaced by $\chi_i(0)$. The cross section is obtained from T by

$$d\sigma/d\Omega=(m/2\pi\hbar^2)^2(p_f/p_i)\textstyle\sum_f|T_{fi}|^2$$
$$=3(m/2\pi\hbar^2)^2(p_f/p_i)\times|\langle\chi_f(\phi)V_f(1)\hat{\psi}_i^{(+)}(0)\rangle|^2. \quad (14)$$

Henceforth we shall make no more reference to spins and use the reduced T matrix (without spins) in Eq. (14) to obtain the cross section.

We are, of course, unable to obtain $\hat{\psi}_i^{(+)}(0)$ exactly. The simplest approximation is to replace it by its unperturbed value $\chi_i(0)$ yielding the first Born approximation for T

$$T_1=\langle\chi_f(1)V_f(1)\chi_i(0)\rangle. \quad (15)$$

[8] H. Maier-Liebnitz, Z. Phys. **95**, 499 (1936).

[9] M. L. Goldberger and K. M. Watson, in *Collision Theory* (John Wiley & Sons, Inc., New York, 1964).

[10] M. H. Mittleman, Phys. Rev. **126**, 373 (1962).

The forms, Eqs. (14) and (15), are the "post" forms. The analogous "prior" forms are

$$T=\langle\hat{\psi}_f^{(-)}(1)V_i(0)\chi_i(0)\rangle, \tag{16}$$

where

$$\hat{\psi}_f^{(-)}(1)=\chi_f(1)+\hat{\psi}_f^{(-)}(1)V_f(1)/a_f(1). \tag{17}$$

Again $\hat{\psi}_f^{(-)}(1)$ must be approximated. The leading term yields

$$T_2=\langle\chi_f(1)V_i(0)\chi_f(0)\rangle. \tag{18}$$

Equation (15) and (18) yield identical results provided the exact functions ϕ_0 and ϕ_1 are available.[11] The actual difference between T_1 and T_2 is usually considered to be a measure of the effect of our ignorance of these functions.

An alternative form of T can be obtained by using a distorted wave rather than the plane wave in the final state. The potential which is absorbed into this distortion is then removed from the interaction appearing n T. The result is

$$T=\langle\chi_f^{(-)}(1)(V_f(1)-\mathcal{U}_f(1))\hat{\psi}_i^{(+)}(0)\rangle, \tag{19}$$

where

$$\chi_f^{(-)}(1)=\chi_f(1)+\chi_f^{(-)}(1)\mathcal{U}_f(1)/a_f(1). \tag{20}$$

If we define $\mathcal{U}_f(1)=-2e^2/r_1$, the interaction with the nucleus and

$$\hat{V}_f(1)=V_f(1)+2e^2/r_1=e^2/r_{10}+e^2/r_{12}, \tag{21}$$

then $\chi_f^{(-)}$ is a Coulomb wave and the effective interaction has a long-range $(1/r_1)$ part. If we again make the approximation $\psi_i^{(+)}(0)\rightarrow\chi_i(0)$ the result is a matrix element which gives significant exchange contributions from large distances and is probably in error. We conclude that the exact form, Eq. (19) with the definition of Eq. (21), is probably a poor one upon which to make approximations. At high energies $\chi_f^{(-)}(1)$ may be replaced by $\chi_f(1)$, its Born approximation. Therefore, we make this further approximation in Eq. (19). The result is

$$T_3=\langle\chi_f(1)\hat{V}_f(1)\chi_i(0)\rangle. \tag{22}$$

Again we may make the analogous approximations in the prior form. If we chose the distortion potential $\mathcal{U}_i(0)=-2e^2/r_0$, the interaction with the nucleus, and

$$\hat{V}_i(0)=V_i(0)-\mathcal{U}_i(0)=e^2/r_{01}+e^2/r_{02}, \tag{23}$$

the result is

$$T_4=\langle\chi_f(1)\hat{V}_i(0)\chi_i(0)\rangle. \tag{24}$$

A variety of distortion potentials could be chosen here but rather than pursue the matter further in this way we turn to another approach.

If the distortion potential is chosen to be the exact equivalent potential then T may be written[12]

$$T=\langle\psi_f^{(-)}(1)[\pi_f(1),V_f(1)]\psi_i^{(+)}\rangle, \tag{25}$$

where the projection operator onto the final state is given by

$$\pi_f(1)=\delta(\mathbf{r}_1-\mathbf{r}_1')\phi_1(\mathbf{r}_0,\mathbf{r}_2)\phi_i^*(\mathbf{r}_0',\mathbf{r}_2'). \tag{26}$$

Removal of the spin dependence yields

$$T=\langle\hat{\psi}_f^{(-)}(1)[\pi_f(1),V_f(1)]\hat{\psi}_i^{(+)}(0)\rangle. \tag{27}$$

In this form there is no longer any mention of the "distortion potentials." Indeed, the identity of Eqs. (25) and (12) (in the physical limit $\eta\rightarrow 0$) may be established without any recourse to "distortion potentials." The Born approximation here results from the two replacements $\hat{\psi}_i^{(+)}(0)\rightarrow\chi_i(0)$ and $\hat{\psi}_f^{(-)}(1)\rightarrow\chi_f(1)$. The result is

$$T_5=\langle\chi_f(1)[\pi_f(1),V_f(1)]\chi_i(0)\rangle. \tag{28}$$

The analogous exact prior form is

$$T=\langle\hat{\psi}_f[V_i(0),\pi_i(0)]\hat{\psi}_i^{(+)}(0)\rangle, \tag{29}$$

where the projection operator on the initial state is

$$\pi_i(0)=\delta(\mathbf{r}_0-\mathbf{r}_0')\phi_0(\mathbf{r}_1,\mathbf{r}_2)\phi_0^*(\mathbf{r}_1',\mathbf{r}_2'). \tag{30}$$

Again the first-order approximation yields

$$T_6=\langle\chi_f(1)[V_i(0),\pi_i(0)]\chi_i(0)\rangle. \tag{31}$$

We may obtain two additional forms from Eqs. (25) and (29) by noting that in both forms the unperturbed Hamiltonian commutes with the projection operator, Then

$$[\pi_f(1),V_f(1)]=[\pi_f(1),H] \tag{32a}$$

and

$$[V_i(0),\pi_i(0)]=[H,\pi_i(0)]. \tag{32b}$$

These forms may be more useful in situations where it is difficult to define the perturbation.[13] These result in

$$T_7=\langle\chi_f(1)|[\pi_f(1),H]|\chi_i(0)\rangle \tag{33}$$

and

$$T_8=\langle\chi_f(1)|[H,\pi_i(0)]|\chi_i(0)\rangle. \tag{34}$$

These will of course yield the same results as Eqs. (28) and (31) if the exact bound states are known, but since they are not, the results are expected to be different and will give another measure of the importance of the bound state problem. The first four forms suffer from the difficulty that the initial and final states are not orthogonal, so that a poor choice of the approximation can yield spurious results. The commutators in the last four forms of T eliminate this difficulty.[10] Additional exact forms of T can be obtained by generalizing the projection operators to project onto additional bound states. In the one case where this has been tried, spin exchange in electron hydrogen scattering,[4] the method gave results which were worse than those of Eqs. (28) and (31). Moreover, the excited-state wave functions of helium are not known so the method will not be pursued here.

[11] B. A. Lippmann, Phys. Rev. **102**, 264 (1956).
[12] M. H. Mittleman, Phys. Rev. **122**, 1930 (1961).
[13] E. Bauer and T. Y. Wu, Can. J. Phys. **34**, 1436 (1956).

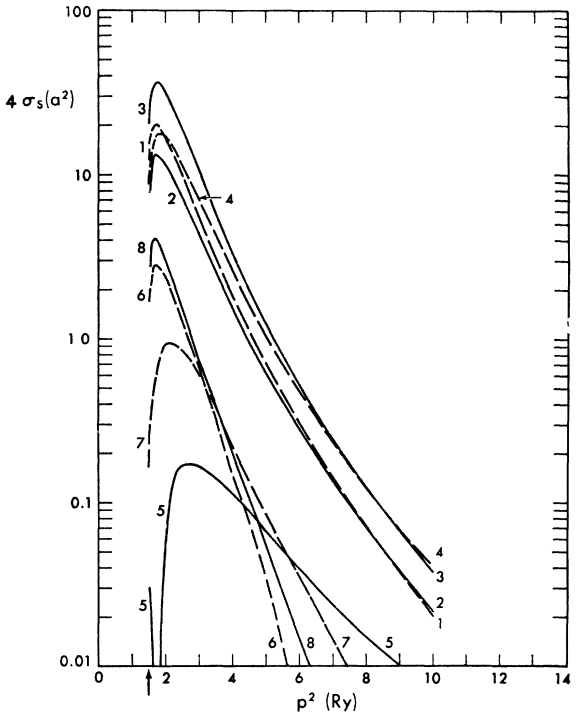

FIG. 1. Four times the s-wave contribution to the section (units a^2) versus energy (units 13.6 eV).

III. RESULTS AND DISCUSSION

We have evaluated the forms T_i, $i=1\cdots8$ by using the following simple variational forms for the helium wave functions. The ground state is a product of two is wave functions

$$\phi_0(r_1,r_2)=(\alpha^3/\pi)e^{-\alpha(r_1+r_2)}, \tag{35}$$

where α is a variational parameter given by $\gamma=27/16$.[14] The 2^3s state is assumed to be an antisymmetrized product of a $1s$ and a $2s$ state

$$\phi_1(r_0,r_2)=[(\beta\gamma)^{3/2}/\pi N](1-P_{02})e^{-\beta r_0-\frac{1}{2}\gamma r_2}(\tfrac{1}{2}\gamma r_2-1), \tag{36}$$

with

$$N^2=1-\frac{8(\beta\gamma)^3(\gamma-\beta)^2}{(\beta+\frac{1}{2}\gamma)^8}.$$

The parameters are determined variationally,[14] $\beta=2.01$, $\gamma=1.53$, and the initial and final momenta are related by

$$p_f^2=p_i^2-1.457. \tag{37}$$

The eight different T-matrix approximations are then obtained as

$$T_i=I+\Lambda_i, \quad i=1\cdots8, \tag{38}$$

where I and the Λ_i are matrix elements between $\chi_f(1)$ and $\chi_i(0)$ of the operators given in Table I and where

TABLE I. Notation for matrix elements of certain operators.

I	$2/r_{10}$
Λ_1	$2/r_{12}-4/r_1$
Λ_2	$2/r_{02}-4/r_0$
Λ_3	$2/r_{12}$
Λ_4	$2/r_{02}$
Λ_5	$2/r_{12}-v_f(r_1)$
Λ_6	$2/r_{02}-v_i(r_0)$
Λ_7	$0.096+2\alpha/r_1+(2\alpha-4)/r_2-4/r_0+2/r_{12}+2/r_{02}-v_f(r_1)$
Λ_8	$(2\alpha-4)(1/r_1+1/r_2)+2/r_{02}+2/r_{12}-v_i(r_0)$

$$v_i(r_0)=4\int d^3x_1d^3x_2\phi_0^2(\mathbf{x}_1,\mathbf{x}_2)\frac{1}{|\mathbf{x}_2-\mathbf{r}_0|}, \tag{39}$$

$$v_f(r_1)=4\int d^3x_0d^3x_2\phi_1^2(\mathbf{x}_0,\mathbf{x}_2)\frac{1}{|\mathbf{x}_2-\mathbf{r}_1|}. \tag{40}$$

The Λ_i integrals can all be performed analytically. It proved to be simpler to do I numerically after reducing it to a one-dimensional integral.

We have obtained the differential cross section

$$d\sigma^{(i)}/d\Omega=(3/16\pi^2)[(p^2-\epsilon)/p^2]^{1/2}[I(\mu)+\Lambda_i]^2, \tag{41}$$

the total cross section

$$\sigma_T{}^{(i)}=(3/8\pi)[(p^2-\epsilon)/p^2]^{1/2}[\bar{I}^2+2\Lambda_i\bar{I}+2\Lambda_i{}^2], \tag{42}$$

and the s-wave part of the total cross section

$$\sigma_s{}^{(i)}=(3/4\pi)[(p^2-\epsilon)/p^2]^{1/2}[\tfrac{1}{2}\bar{I}+\Lambda_i]^2 \tag{43}$$

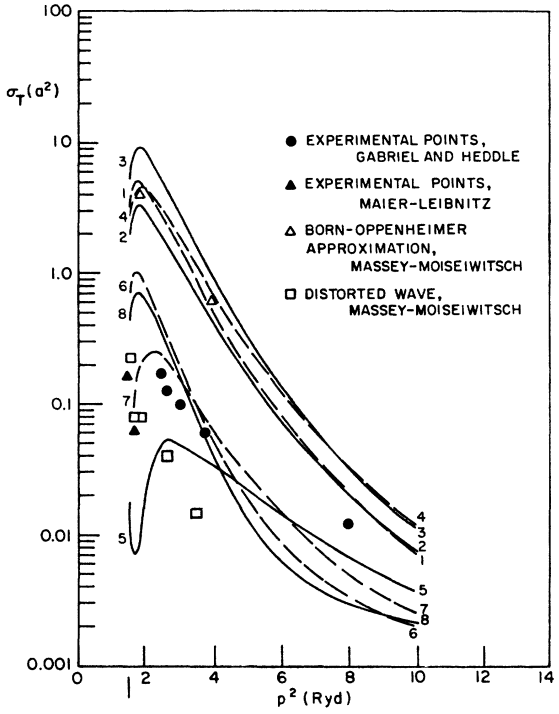

FIG. 2. Total cross section versus energy.

[14] H. Bethe and E. Salpeter, in *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1957).

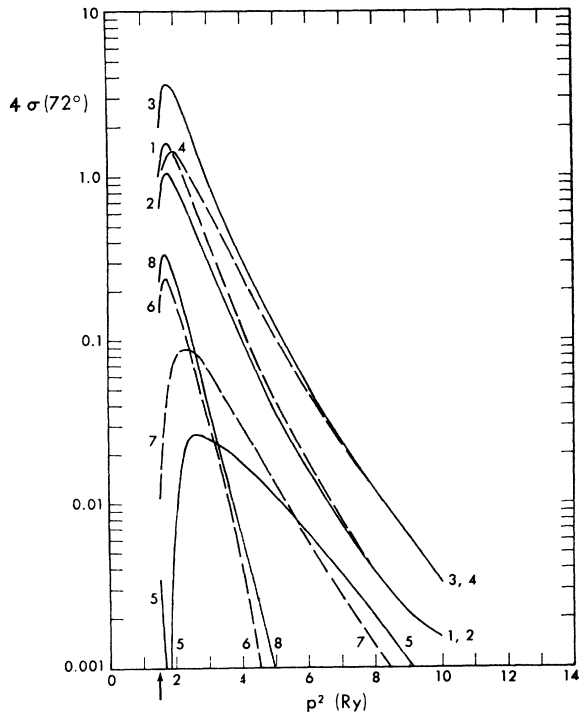

FIG. 3. Four times the cross section at 72° versus energy.

all in units of $a^2=0.28\times10^{-16}$ cm^2. Here μ is the cosine of the angle between the initial and final momenta and a bar over a function indicates the integral over μ over its entire range, -1 to $+1$.

We note that the Λ_i are all independent of the scattering angle so that the eight cross sections will differ only in their s-wave part. In Fig. 1 we have displayed four times the s-wave part of the total cross section in units of a^2 versus incident energy in rydbergs. As is expected, curves 3 and 4 lie above the Born approximations. The post-prior discrepancy, the difference between the Born forms 1 and 2 due to the errors in the bound-state wave functions, is small at high energies growing slightly larger with decreasing energy. This might be interpreted as an indication of good bound-state wave functions. This is not the case as we shall see below. σ_s^5 goes through zero at about 2.7 eV above threshold. A similar effect was noticed in the analogous form for spin exchange in electron-hydrogen elastic scattering.[4] In that case it was due to a resonance in the singlet scattering. A similar explanation may apply here. Curves 6, 7, and 8 also each have a zero but at higher energies. Figure 2 shows the total cross section. It is evident by comparison of σ_s with σ_T that the higher partial waves start to be important at about $p^2=3$, 21 eV above threshold. In Fig. 2 we have shown two points of the Born-Oppenheimer-approximation calculation of Massey and Moisewitsch.[15] This is identical with our curve 1 or 2 except that they used a slightly more general wave function for the 2^3s state of He. The difference between curves 5 and 7 is due solely to inaccuracies in the wave function of the excited state. The errors are sizeable indicating that this wave function is a poor one. Thus we feel that the smallness of the post-prior discrepancy between 1 and 2 is not evidence of good wave functions. That is, a large post-prior discrepancy is evidence of poor wavefunctions, but the converse is not necessarily true. The difference between 6 and 8 is due solely to inaccuracies of the ground-state wave function. It is seen that these are not serious. Given no other criteria, we feel that 5 and 6 are probably more trustworthy than 7 and 8. The reason for this is the appearance of the kinetic-energy operators in H which probably emphasize the errors in the approximate wave functions. We have also shown some experimental points of Gabriel and Heddle[7] and Maier-Liebnitz.[3] The Gabriel and Heddle curve is normalized at 108 eV, $p^2\simeq8$, where an absolute measurement was performed. Curve 5 is about the same amount too high. The general shape of the experimental curve at lower energies seems to favor 5. If the Maier-Liebnitz and the Gabriel and Heddle experiments are taken at face value there is an indication of a sharp dip in σ_T as in curve 5. Further experiments in this energy range are clearly desirable. We have also shown several points of the extremely elaborate exchange-distorted wave calculation of Massey and Moisewitsch.[15]

We feel that there is some *a priori* reason for favoring 5 over 6. If we view them as "distorted-wave" calculations then 5 accounts for the distortion in the final channel while 6 accounts for the distortion in the initial channel. The final state is more loosely bound than the initial one and so we might expect that its interaction with the free electron would be more important.

In Fig. 3 we have shown four times the cross section at 72° versus energy. Schulz and Philbrick[6] have measured this cross section up to about 3 eV above threshold (i.e., up to about $p^2=1.7$). Their cross section exhibits complex structure but there is one pronounced dip which might be associated with the low-energy dip in our curve 5.

In summary it is clear that the commutator forms are much preferable to the forms 1–4 and they involve little extra effort. We think that the difference between the forms with H and V is a better indication of errors due to bound-state inaccuracies than the usual post-prior discrepancies. Finally, we feel that at least in this case, there are physical reasons for selecting either the post or prior commutator forms when they differ.

ACKNOWLEDGMENT

We would like to thank Professor K. M. Watson for useful discussions throughout this work.

[15] H. S. W. Massey and B. L. Moisewitsch, Proc. Roy. Soc. (London) **A227**, 38 (1950).