

Pseudostate expansions in a simplified model of electron-hydrogen scattering

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A simplified model of electron-hydrogen scattering is considered in which all terms involving nonzero angular momenta are neglected. Elastic scattering and excitation cross sections for the $2s$ and $3s$ states are calculated for this model with the use of close-coupling expansion with four different pseudostate bases. Pseudothreshold structure is observed and removed. It is found that, after removal of this structure, the results agree quite well with each other and with exact results for this model which were given previously by Poet.

I. INTRODUCTION

It has been known for many years that a straightforward close-coupling expansion in which only bound atomic states are included does not yield accurate cross sections for the scattering of electrons by hydrogen and helium atoms. The difficulty is the neglect of contributions from continuum states. The results for hydrogen are greatly improved if some square-integrable functions (pseudostates) are added to the expansion, which, although not exact eigenfunctions of the target, enable an approximate inclusion of continuum contributions.¹

However, the introduction of pseudostates leads to a problem: Unphysical structures in cross section may be produced in the neighborhood of the thresholds for the excitation of the pseudostates. This problem was noted by Burke and Mitchell.² They considered a simple model of electron-hydrogen scattering (the same as is used here), and found that rather broad structures, described as pseudoresonances, were produced when pseudostates were introduced into the expansion. Since this structure can extend over a relatively large range of energies (0.5–1 Ry), it is apparent that caution is required when pseudostates are used in realistic calculations. To some extent, it is possible to alleviate this problem by using different pseudostate bases in different ranges of energy,³ but this procedure is unsatisfactory because of uncertainties concerning the width of the resonances in the different sets, and because the sets represent the continuum in different ways. Recently, other methods of removing pseudoresonance structure from results obtained with a given pseudostate basis have been considered, and seem to produce substantial improvements.^{4,5}

In the meantime, essentially exact results for the model of electron-hydrogen scattering considered by

Burke and Mitchell² have been obtained by Poet⁶ in a range up to 2 Ry above the ionization threshold. These results enable an estimation of the accuracy obtained from different pseudostate expansions, and of the methods for removal of pseudothreshold structure. Such an investigation is reported here. We have considered four different pseudostate expansions applied to this model. In brief, we find that, after the threshold structure is removed, reasonably accurate elastic scattering and excitation cross sections (errors less than 3% for elastic scattering for all bases and less than 8% for excitation for three out of four cases) are obtained. If this standard of accuracy can be maintained in the full electron-hydrogen problem, it should be possible to improve the comparison between theory and experiment for processes such as $2s$ excitation, where uncertainties of the order of 20% still exist.⁷

II. METHOD

The physical model considered here is that of a hydrogen atom which has only s states, and where the total angular momentum of the collision is zero. This is equivalent to replacing the actual Coulomb interaction between electrons, $e^2/|\vec{r}_1 - \vec{r}_2|$ by the leading term in a multipole expansion of this quantity, $e^2/r_>$ (where $r_>$ is the greater of r_1 and r_2). Much of the essential physics of the real hydrogen atom, in particular the degeneracy of states of the same n but different l , is discarded in this model, but there still are an infinite number of discrete bound states and an ionization continuum.

We represent the wave function of the system, $\psi(r_1, r_2)$ (note that r_1 and r_2 are radial variables) as

$$\psi_a(r_1, r_2) = [1 \pm (-1)^S P_{12}] \sum_n R_n(r_1) G_{na}(r_2) \quad (1)$$

TABLE I. Parameters and energies of the four basis sets used in this calculation.

| Basis set | j | n_j | ξ_j | E_n |
|-----------|-----|-------|---------|---------|
| <i>A</i> | 1 | 0 | 1.0 | -1.0 |
| | 2 | 0 | 0.5 | -0.25 |
| | 3 | 1 | 0.5 | -0.1092 |
| | 4 | 0 | 0.8 | 0.0307 |
| | 5 | 1 | 0.2 | 1.7073 |
| <i>B</i> | 1 | 0 | 1.0 | -1.0 |
| | 2 | 0 | 0.5 | -0.25 |
| | 3 | 1 | 0.5 | -0.0523 |
| | 4 | 1 | 1.0 | 0.6810 |
| | 5 | 0 | 1.5 | 6.2674 |
| <i>C</i> | 1 | 0 | 1.0 | -1.0 |
| | 2 | 0 | 0.5 | -0.25 |
| | 3 | 1 | 0.5 | -0.1093 |
| | 4 | 1 | 0.1 | -0.0551 |
| | 5 | 0 | 0.1 | 0.4675 |
| <i>D</i> | 1 | 0 | 1.0 | -1.0 |
| | 2 | 0 | 0.5 | -0.25 |
| | 3 | 1 | 0.5 | -0.1111 |
| | 4 | 0 | 1/3 | -0.0624 |
| | 5 | 1 | 1/3 | -0.0172 |
| | 6 | 2 | 1/3 | 0.1959 |
| | 7 | 0 | 0.2 | 2.0396 |

in which the index a designates the channel containing the incident wave, P_{12} interchanges the coordinates r_1 and r_2 , $R_n(r_1)$ is a member of the basis set of functions describing the target, and G_{na} obeys the usual scattering boundary conditions.

We determine the target functions R_n , which include both exact and pseudostates, by selecting M component functions η_j , Slater orbitals, from which R_n is constructed,

$$R_n(r) = \sum_{j=1}^M \eta_j(r) c_{jn}, \quad (2)$$

where

$$\eta_j(r) = r^{n_j} e^{-\xi_j r}. \quad (3)$$

The parameters n_j, ξ_j specify the functions. The expansion coefficients c_{jn} and energies E_n are determined by simultaneous diagonalization of the Hamiltonian and overlap matrices constructed on the basis of the R_n . Thus one has

$$\int R_n(r) H R_{n'}(r) r^2 dr = E_n \delta_{nn'}, \quad (4)$$

where H is the Hamiltonian for a hydrogen atom with $l=0$,

$$H = -\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \right] - \frac{e^2}{r}. \quad (5)$$

We have considered four sets of functions in this work. The parameters n_j, ξ_j and the energies E_n are listed in Table I. The sets are designated *A, B, C, D* and are discussed briefly below. The first three listed contain five functions; the fourth contains seven.

All sets contain the three component functions required so that the exact 1s and 2s hydrogen atom wave functions are produced in the diagonalization.

Set A. This set is the one used in some calculations of electron-hydrogen scattering.³ In addition to the functions mentioned, we add one long-range function which enables an approximate description of the 3s state, and one medium-range function, which helps the set account for intermediate-range projectile-target electron correlation.

Set B. This set is designed to permit a more accurate description of short-range projectile-target electron correlation. Two relatively short-range orbitals are added to the functions mentioned in *A*. One of the resulting pseudostates is rather high in the continuum (6 Ry).

Set C. A rather open set of pseudostates was considered in order to contrast the results of emphasizing long-range or short-range correlation. Two long-range orbitals were added to the set. The pseudostate energies approximate those of 3s and 4s, and one is at a relatively low continuum energy.

Set D. A set of functions including the exact 3s state was constructed. This now requires specification of six component functions. A seventh, rather long-range function was added. This set of 7s-type functions has also been used in previously reported calculations of electron-hydrogen scattering.³

Thus the basis sets considered are of rather different characters. Comparison of the results using these bases with the exact results enables us to estimate qualitatively the importance of long-range and short-range correlation.

The scattering calculations were performed using the algebraic variational method which has been extensively described elsewhere.³ Since there is no angular momentum in this model, the calculations are simpler than in the full electron-hydrogen problem. We did not notice any serious convergence difficulties.

The pseudothreshold structure that we encountered was surprisingly complicated. We expected, perhaps naively, straightforward resonance structure

TABLE II. Cross sections (in units of πa_0^2) at selected energies for some transitions in the 3S scattering state. The spin weighting factor is included.

| Energy | 1s-1s | 1s-2s | 1s-3s | 2s-3s |
|--------|--------|--------|----------|-------|
| 1.21 | 2.3005 | 0.0035 | 0.000 24 | 0.134 |
| 1.44 | 1.8336 | 0.0048 | 0.000 52 | 0.102 |
| 1.70 | 1.4607 | 0.0055 | 0.000 76 | 0.073 |
| 2.00 | 1.1587 | 0.0058 | 0.000 92 | 0.052 |
| 2.25 | 0.9750 | 0.0057 | 0.000 98 | 0.041 |
| 2.50 | 0.8330 | 0.0056 | 0.001 01 | 0.033 |
| 3.00 | 0.6310 | 0.0051 | 0.001 00 | 0.022 |
| 3.50 | 0.4972 | 0.0046 | 0.000 93 | 0.016 |
| 4.00 | 0.4037 | 0.0041 | 0.000 84 | 0.013 |

of the sort we have found in previous calculations for ionic systems.⁵ Instead, the structure is quite broad, and not easily describable in terms of standard resonance theory. Further, it turned out to be important to remove not only broad resonances but the thresholds as well. We found this to be most efficiently accomplished using the T -matrix averaging technique used by Burke *et al.*⁴ In this procedure, a least-squares fit is made to the transition amplitudes for the physical channels using a low-order polynomial in energy.

Let $T_{ij}(E)$ be an element of the T matrix for a transition between channels i and j . We represent this as

$$T_{ij}(E) = \sum_{m=0}^N a_m E^m, \quad (6)$$

where the coefficients a_m are complex. Quadratic, cubic, and quartic expressions were used, and linear

least-squares fits were made to determine the coefficients a_m . In practice, it is convenient simply to fit the real and imaginary parts of T_{ij} separately.

There are, of course, some obvious problems with this procedure. It is not obvious, for example, exactly what should be the degree of the polynomial in Eq. (6), nor over what range of energies T_{ij} should be fit. In fact, we found that in most cases, a cubic polynomial gave good results; occasionally a quartic expression appeared to give better results, more rarely quadratic was optimal. The best internal criterion we found to determine N was that the cross sections determined from the fits should merge smoothly with those directly calculated at energies far away from the pseudothreshold. Also, because the structure is quite broad, it is necessary to extend the fits over a rather large energy range, typically about 2 Ry.

In spite of the inevitably *ad hoc* elements in this

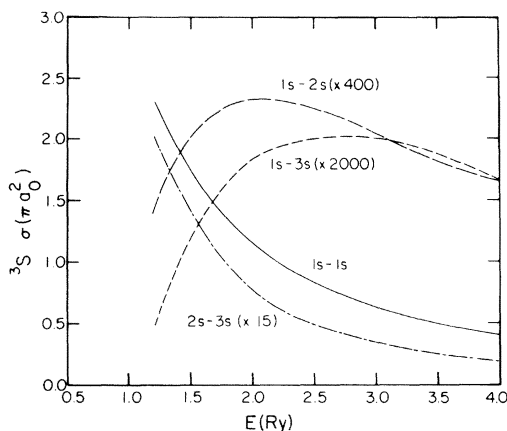


FIG. 1. Cross sections for elastic scattering and for the $1s \rightarrow 2s$, $1s \rightarrow 3s$, and $2s \rightarrow 3s$ transition in the 3S state are shown as a function of incident energy in rydbergs. The scale is as shown for elastic scattering; the cross sections for other transitions have been multiplied by the factors shown to appear on the same graph.

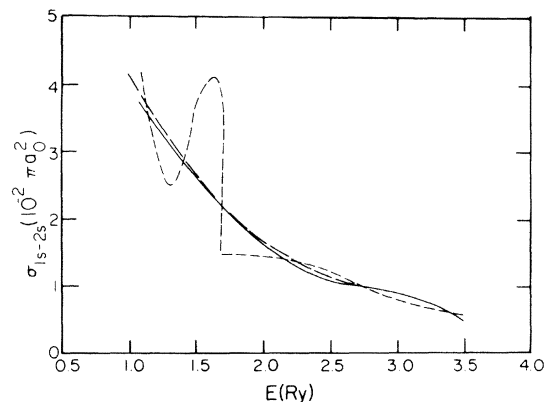


FIG. 2. Cross sections for the $1s \rightarrow 2s$ transition in the 1S state. The short-dashed curve, showing the pronounced pseudothreshold structure is the cross section directly calculated from basis B ; the long-dashed curve is the exact result of Ref. 6; the solid curve is the result of the T -matrix fitting procedure.

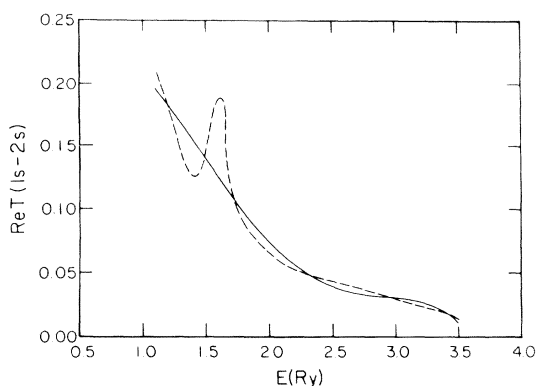


FIG. 3. Real part of the T matrix for the $1s \rightarrow 2s$ transition in the 1S state for basis B : Short dashed curves, directly calculated values; solid line, result of fit.

procedure, highly satisfactory results were obtained. We present these in the next section.

III. RESULTS

The model of electron-hydrogen scattering considered here is, we believe, of considerable importance as a test case for computational methods in atomic scattering theory. It is simple enough so that calculations are not extremely time consuming, but yet far more realistic than other models (the Huck model,⁸ for example) used for test purposes, and some exact results are available. For this reason, we have decided to present numerical results in some detail, in the hope they will be useful to others.

We have considered both singlet and triplet states. Only the singlet-state calculations showed appreciable pseudothreshold structure so that T matrix fitting was not employed for triplet states.

Our results will be compared with those of Poet,⁶ who gives numerical values for the $1s \rightarrow 2s$ excitation in the singlet state at a large number of energies

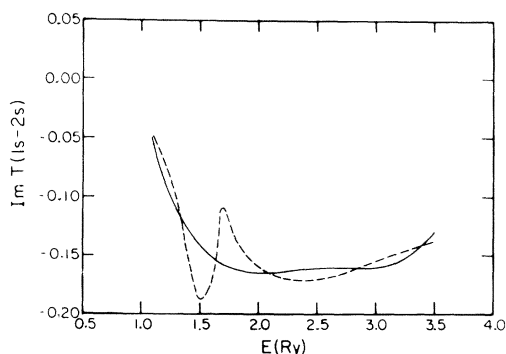


FIG. 4. Imaginary part of the T matrix for the $1s \rightarrow 2s$ (1S) transition. Curves have the same significance as in Fig. 3.

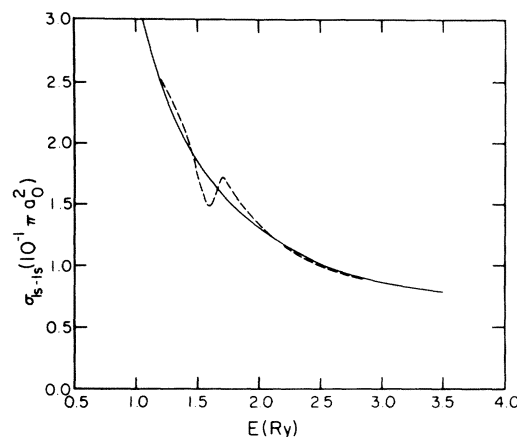


FIG. 5. Cross sections for elastic scattering in the 1S state. The curves have the same significance as in Fig. 2, however the exact (long dashed) curve is not shown as it is indistinguishable from the solid curve.

and for the elastic ($1s \rightarrow 1s$) cross section, also for the singlet state, at a small number of points. Only graphical data are given for other transitions.

We present first the results for the triplet transitions. Cross sections for elastic scattering and the $1s \rightarrow 2s$, $1s \rightarrow 3s$, and $2s \rightarrow 3s$ transitions are given in Table II and are shown graphically in Fig. 1. The specific numbers are obtained from the seven-state basis D but the results for elastic scattering and for $1s \rightarrow 2s$ excitation agree satisfactorily with these values. Our results are indistinguishable from those presented graphically in Ref. 6.

In contrast, the singlet transitions show pronounced structure. An example of this is presented in Fig. 2, in which the $1s \rightarrow 2s$ cross section as computed from basis set B is shown. The directly calculated cross section has a resonancelike structure extending from the lowest energy plotted up to the pseudothreshold at 1.68 Ry. The directly calculated results agree reasonably well with the exact values above about 2.1 Ry. The real and imaginary parts of the T matrix, normalized so that

$$\sigma_{ij} = \frac{1}{k_i^2} |T_{ij}(E)|^2 \quad (7)$$

are shown in Figs. 3 and 4.

A least-squares fit was made to the real and imaginary parts of the T -matrix element using a polynomial of fourth degree in the energy. The solid lines in Figs. 2–4 show the results of this fit. The resulting cross sections agree very well with the exact results of Ref. 6 over the entire energy range. The errors are of the order of 3%.

Corresponding results for the elastic ($1s-1s$) cross section are shown in Figs. 5–7. Comparison of Fig.

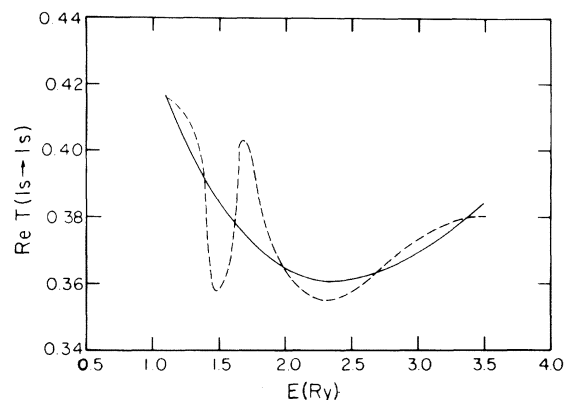


FIG. 6. Real part of the T -matrix element for elastic scattering in the 1S state. The curves have the same significance as in Fig. 3.

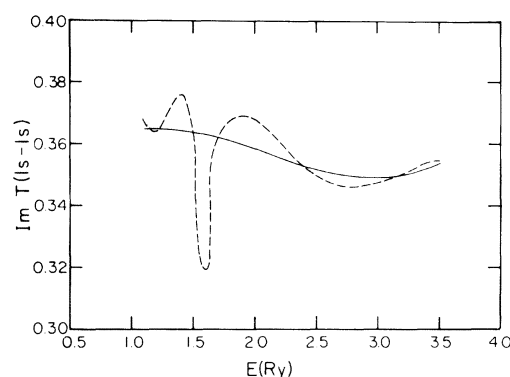


FIG. 7. Imaginary part of the T -matrix element for elastic scattering. The curves have the same significance as in Fig. 3.

5 with Fig. 2 shows that the pseudothreshold structure is much less pronounced for elastic scattering than for $2s$ excitation. The directly calculated cross section (basis B) is adequate (errors less than 5%) except within an interval of about 0.3 Ry on each side of the pseudoresonance. In this case, a least-squares fit was made to the T -matrix element using a cubic polynomial. This fit is compared with the directly calculated elements in Figs. 6 and 7. The cross sec-

tion which results from the fit is indistinguishable from the exact results of Poet on the scale of the graph.

We will not show the results of the other bases for these transitions. These results may be obtained from Table III which summarizes the results of the fitting procedure as applied to the different bases. Numerical results for cross sections are given for all bases at selected energies in Table IV. Exact values

TABLE III. Fitting parameters for T -matrix elements for 1S transitions.

| Basis set | T -matrix element | a_0 | a_1 | a_2 | a_3 | a_4 |
|-----------|---------------------|---------|---------|---------|---------|---------|
| A | $\text{Re}T_{11}$ | 0.7177 | -0.4461 | 0.1858 | -0.0254 | |
| | $\text{Im}T_{11}$ | 0.6419 | -0.4037 | 0.1795 | -0.0253 | |
| | $\text{Re}T_{12}$ | 0.3830 | -0.2013 | 0.0259 | | |
| | $\text{Im}T_{12}$ | 0.0689 | -0.1927 | 0.0398 | | |
| B | $\text{Re}T_{11}$ | 0.6094 | -0.2566 | 0.0831 | -0.0080 | 0 |
| | $\text{Im}T_{11}$ | 0.3326 | 0.0619 | -0.0360 | 0.0058 | |
| | $\text{Re}T_{12}$ | 0.1247 | 0.4107 | -0.4744 | 0.1667 | -0.0192 |
| | $\text{Im}T_{12}$ | 1.1831 | -2.2403 | 1.3810 | -0.3743 | 0.0377 |
| C | $\text{Re}T_{11}$ | 0.6223 | -0.2944 | 0.1153 | -0.0419 | |
| | $\text{Im}T_{11}$ | 0.4892 | -0.1861 | 0.0787 | -0.0101 | |
| | $\text{Re}T_{12}$ | 0.5750 | -0.4904 | 0.1654 | -0.0206 | |
| | $\text{Im}T_{12}$ | 0.5947 | -0.9431 | 0.3783 | -0.0481 | |
| D | $\text{Re}T_{11}$ | 0.7522 | -0.4875 | 0.1982 | -0.0259 | |
| | $\text{Im}T_{11}$ | 0.3414 | 0.0587 | -0.410 | 0.0076 | |
| | $\text{Re}T_{12}$ | 0.4579 | -0.3025 | 0.06721 | -0.0051 | |
| | $\text{Im}T_{12}$ | 0.0687 | -0.2421 | 0.0804 | -0.0080 | |
| | $\text{Re}T_{13}$ | 0.2021 | -0.1075 | 0.0143 | | |
| | $\text{Im}T_{13}$ | 0.0746 | -0.1322 | 0.0268 | | |
| | $\text{Re}T_{23}$ | -1.3913 | 2.1636 | -1.0665 | 0.2381 | -0.0204 |
| | $\text{Im}T_{23}$ | -1.2871 | 2.9422 | -2.0581 | 0.5903 | -0.0608 |

TABLE IV. Numerical values of cross section (units πa_0^2) for 1S transitions according to different bases, and according to Ref. 6 (exact). Numbers in the first row for each energy are the results of pseudostate calculation. Numbers in the second row are corrected for pseudoresonances.

| | Energy | A | B | C | D | Exact |
|-----------------|--------|--------|--------|--------|--------|--------|
| $\sigma(1s-1s)$ | 1.21 | 0.2425 | 0.2501 | 0.2264 | 0.2423 | 0.2469 |
| | | 0.2495 | 0.2465 | 0.2458 | 0.2472 | |
| | 1.44 | 0.1990 | 0.1926 | 0.2138 | 0.1944 | 0.1944 |
| | | 0.1915 | 0.1967 | 0.1944 | 0.1940 | |
| | 1.70 | 0.1625 | 0.1724 | 0.1498 | 0.1570 | 0.1581 |
| | | 0.1533 | 0.1592 | 0.1581 | 0.1562 | |
| | 2.00 | 0.1182 | 0.1340 | 0.1303 | 0.1372 | 0.1314 |
| | | 0.1281 | 0.1305 | 0.1321 | 0.1289 | |
| | 2.25 | 0.1024 | 0.1131 | 0.1184 | 0.1133 | 0.1159 |
| | | 0.1151 | 0.1139 | 0.1178 | 0.1138 | |
| | 3.00 | 0.0839 | 0.866 | 0.0916 | 0.1097 | |
| | | 0.0888 | 0.0862 | 0.0916 | 0.0881 | |
| | 3.50 | 0.0711 | 0.0772 | 0.0774 | 0.0733 | |
| | | 0.0676 | 0.0780 | 0.0772 | 0.0765 | |
| $\sigma(1s-2s)$ | 1.30 | 0.0340 | 0.0247 | 0.0334 | 0.0322 | 0.0323 |
| | | 0.0311 | 0.0311 | 0.0299 | 0.0344 | |
| | 1.70 | 0.0188 | 0.0149 | 0.0273 | 0.0228 | 0.0220 |
| | | 0.0201 | 0.0219 | 0.0215 | 0.0209 | |
| | 2.00 | 0.0212 | 0.0147 | 0.0176 | 0.0145 | 0.0168 |
| | | 0.0159 | 0.0163 | 0.0171 | 0.0159 | |
| | 2.50 | 0.0113 | 0.0123 | 0.0094 | 0.0143 | 0.0113 |
| | | 0.0115 | 0.0111 | 0.0101 | 0.0109 | |
| | 3.00 | 0.0078 | 0.0083 | 0.0060 | 0.0038 | 0.0080 |
| | | 0.0077 | 0.0087 | 0.0057 | 0.0076 | |
| | 3.50 | 0.0063 | 0.0055 | 0.0043 | 0.0058 | |
| | | 0.0042 | 0.0059 | 0.0048 | 0.0053 | |

are included. An interested reader may find the cross section at any other energy within the range considered (1.2–3.5 Ry) simply by using the coefficients in Table III to evaluate the T -matrix elements, and then using Eq. (7). An extrapolation beyond this range may be unreliable.

Comparison of the results obtained from the four different bases leads to the following conclusions.

Rather satisfactory results are obtained from all bases after the pseudothreshold structure is removed as described above. In the case of elastic scattering (1S), at no incident energy (in the range considered) does a quantitative difference between the corrected and exact cross section exceed 3%. This is, we believe, an important conclusion which tends to give one confidence in the result of pseudostate calculations of elastic scattering in the full e -H scattering problem.

The $2s$ excitation cross sections are more basis-set

TABLE V. Table I cross sections for the $1s \rightarrow 3s$ and $2s \rightarrow 3s$ transitions (units πa_0^2) in the 1S state as obtained from basis D . Numbers in the first row for each energy are calculated directly. Numbers in the second row are obtained from the T -matrix fitting procedure.

| Energy | $\sigma(1s-3s)$ | $\sigma(2s-3s)$ |
|--------|-----------------|-----------------|
| 1.30 | 0.007 1 | 0.0701 |
| | 0.007 8 | 0.0683 |
| 1.70 | 0.005 8 | 0.0318 |
| | 0.005 3 | 0.0300 |
| 2.00 | 0.003 6 | 0.0166 |
| | 0.004 4 | 0.0186 |
| 2.50 | 0.004 1 | 0.0118 |
| | 0.003 3 | 0.0110 |
| 3.00 | 0.000 76 | 0.0064 |
| | 0.002 2 | 0.0079 |
| 3.50 | 0.001 5 | 0.0054 |
| | 0.001 0 | 0.0049 |

dependent. Three of the four bases (*A*, *B*, and *D*) yield highly satisfactory results. The best results are obtained with the shortest-range basis *B* (after correction), and the worst with the long-range basis *C*. It appears that in this model, it is most important to incorporate a description of short-range projectile-target electron correlation. In no case do the discrepancies between the present cross sections (using bases *A*, *B*, and *D*) after use of the *T*-matrix fitting procedure, differ from the exact values in the range 1.2–3.5 Ry by more than 8%. The long-range basis *C*, in contrast, produces larger error ($\sim 25\%$) toward the upper end of the range around 3 Ry. We are encouraged to hope that good results for this transition can also be obtained by similar procedures in the full scattering problem.

We have also studied the $1s \rightarrow 3s$ and $2s \rightarrow 3s$ transitions using the seven-state basis *D*. A few numerical results are given in Table V. After the *T*-matrix fit we find also in these cases good agreement with Poet's results (but these are only given graphically). Although our primary interest had been in the calculation of elastic and excitation cross sections in the energy range where ionization is possible, it is

also worth mentioning that the seven-state basis *D* is able to reproduce the exact $2s$ excitation cross section between the $n=2$ and $n=3$ threshold (three significant figures); including the single resonance at 0.8882 Ry.

IV. CONCLUSION

We have shown that different sets of pseudostate bases are capable of giving quite satisfactory cross sections for elastic scattering and for the excitation of the $2s$ state, in a simplified model of electron-hydrogen atom interactions for which exact results are known. Differences of results due to different choices of pseudostates, while not zero, need not be large if the pseudostates are chosen in reasonable ways. Best results for the model considered are obtained by selecting relatively short-range pseudostates. In order to obtain significant results, it is necessary to remove physically meaningless structure associated with pseudostate thresholds. This can be accomplished by making a linear least-squares fit to elements of the *T* matrices using a low-order polynomial in energy.

¹For a review of electron-atom scattering including a discussion of pseudostates, see J. Callaway, *Adv. Phys.* **29**, 771 (1980).

²P. G. Burke and J. F. Mitchell, *J. Phys. B* **6**, 320 (1973).

³J. Callaway, *Phys. Rep.* **45**, 89 (1978).

⁴P. G. Burke, K. A. Berrington, and C. V. Sukumar, *J. Phys. B* **14**, 289 (1981).

⁵N. Abu Salbi and J. Callaway, *Phys. Rev. A* **24**, 2372 (1981).

⁶R. Poet, *J. Phys. B* **11**, 3081 (1978); **13**, 2995 (1980).

⁷J. Callaway and M. R. C. McDowell, *Comments At. Mol. Phys.* (in press).

⁸R. J. Huck, *Proc. Phys. Soc. (London)* **70**, 369 (1957).