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J-matrix method: Application to s-wave electron-hydrogen scattering

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The method of the preceding paper is here applied to s-wave electron-hydrogen collisions. A pseudo-state model is developed and applied to elastic and inelastic scattering above and below the ionization threshold where we compare with the results of Burke and Mitchell. Additional calculations show the effect of Kato correction, the effect of the closed-channel asymptotic forms, and include a comparison with the results of Schwartz.

I. INTRODUCTION

In this paper, we consider several applications of the theory given in the preceding paper,[1] hereafter called I, to a model s-wave electron-hydrogen scattering problem. In Sec. II, we present the most straightforward applications of the method. To illustrate the utility of the method for small basis sets, we give results for static-exchange scattering using a 3×3 potential matrix. In Sec. II B, we present an approximate Kato[2] correction scheme involving only bound-bound matrix elements of the potential which demonstrates, for the case of static hydrogen scattering, the improvement in accuracy which results from this correction.

The main numerical results of this work deals with s-wave "radial limit" (i.e., only s-symmetry allowed for each electron) cross sections above and below the ionization threshold, using a model pseudo-state target Hamiltonian. The model is introduced in Sec. III. Applications of the model begin in Sec. IV. In Sec. IV A the effect of including closed-channel asymptotic forms in both the elastic- and inelastic-scattering regions is shown. In Sec. IV B we present results for the cross sections $\sigma(1s, 1s)$, $\sigma(1s, 2s)$, and $\sigma_{\text{tot}}(1s, ns)$ $n \neq 1, 2$, comparing our results with the work of Burke and Mitchell. Section IV C contains correlated elastic electron-hydrogen scattering results, which we compare with the results of Schwartz.

II. SIMPLE APPLICATIONS

A. e-H static exchange scattering

To show the utility of the method presented in Paper I even for small basis sets, we consider first the scattering of an electron from the static $1s$ ground state of hydrogen, including exchange. The basis set used was

$$\phi_n(r) = (\lambda r) e^{-\lambda r/2} L_n^1(\lambda r) , \tag{2.1}$$

and we used $N=3$ (i.e., V^n is a 3×3 matrix representation of the static-exchange potential in the set $\{\phi_n\}$). We employed the single-channel formula of Sec. II of I. Figure 1 shows the smooth nature of the resulting phase shift; each dot represents an independent calculation. The squares are the "exact" results given in the Burke and Smith review article.[3] We note that our results in Fig. 1 are not Kato-corrected; we consider this correction in Sec. II B.

B. Approximate Kato correction

In I we have shown that second-order accuracy may be obtained with the assistance of the Kato[2] correction formula

$$\tan\delta_s = \tan\delta_t + (2/k)\langle\psi_t| V^R |\psi_t\rangle , \tag{2.2}$$

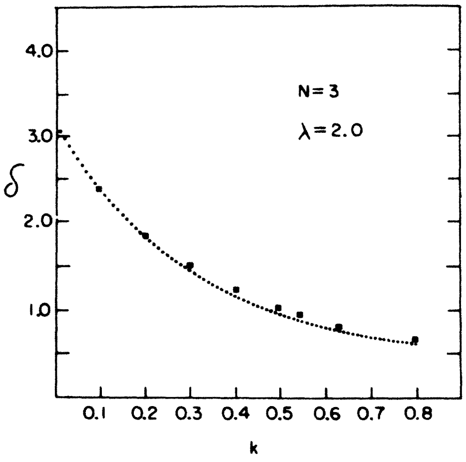

FIG. 1. Static exchange e-H scattering, with $N=3$ and $\lambda=2.0$. Each dot represents a separate calculation. The squares show the results given in Burke and Smith, Ref. 3.

where

$$\psi_t = \Phi + S + (\tan\delta_t)C\ ,$$

and where δ_s is the stationary result and (δ_t, ψ_t) are the results of the J-matrix calculation. The correction (2.2) can be carried out exactly if the bound-free and free-free matrix elements of the potential are known. However, the Kato correction can be approximated using only bound-bound integrals by utilizing the L^2 expansion of ψ_t in the basis set. We take the first M terms past N ($M \geqslant 0$); i.e.,

$$\psi_t^M = \sum_{n=0}^{N-1} a_n \phi_n + \sum_{n=N}^{M+N-1} (s_n + \tan\delta_t\, c_n)\frac{\phi_n}{n+1}\ . \tag{2.3}$$

Putting ψ_t^M into Eq. (2.2), we have

$$\begin{aligned}\langle \psi_t | V^R | \psi_t \rangle &\simeq \langle \psi^M | V^R | \phi^M \rangle \\ &= 2\sum_{m=0}^{N-1} \sum_{m'=N}^{M+N-1} \frac{a_m V_{mm'}(s_{m'} + \tan\delta_t c'_m)}{m'+1} \\ &\quad + \sum_{m,m'=N}^{M+N-1} \frac{(s_m + \tan\delta_t c_m) V_{mm'}(s_{m'} + \tan\delta_t c_{m'})}{(m+1)(m'+1)}\ .\end{aligned} \tag{2.4}$$

Since the coefficients a_m, s_m, c_m, $\tan\delta_t$ are known from the method of I, and since the $V_{mm'}$ are presumed known, it is easy to carry out the sum in Eq. (2.4). Defining $\tan\delta_M$ as our partially corrected result ($\tan\delta_M = \tan\delta_t$, for $M=0$), we have

$$\tan\delta_s \simeq \tan\delta_M = \tan\delta_t + \langle \psi^M | V^R | \psi^M \rangle\ . \tag{2.5}$$

Figure 2 shows the effect of this partial Kato correction on an $N=3$ static electron-hydrogen calculation for several values of M and k. In each of the four examples the abscissa intersects the ordinate at the exact phase shift.[3] From this figure it is seen that whenever δ_t is in substantial error, the partial Kato correction provides, for large enough M, significant improvement. In circumstances where the bound-free and free-free matrix elements of V are not known or difficult to compute, the approximate correction may be useful. In none of the following calculations have we applied an exact or approximate Kato correction.

III. SINGLET ELECTRON-HYDROGEN SCATTERING MODEL

The radial limit electron-hydrogen Hamiltonian, in atomic units, reads

$$H = -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} + H_{\text{target}}(r_2) + \left(\frac{-1}{r_1} + \frac{1}{r_>}\right)\ , \tag{3.1}$$

where $r_>$ is the greater of r_1 and r_2, and

$$H_{\text{target}} = -\frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{1}{r_2}\ . \tag{3.2}$$

The separation of H into target part and free-electron part corresponds to the initial configuration of particle 2 bound to the nucleus and particle 1 incident on particle 2. H_{target} generates the well-known hydrogenic states. We could, in the manner of the multichannel section of I, truncate the potential [in this case $(-1/r_1 + 1/r_>)$] so that a small number of hydrogenic states would be coupled. This would correspond simply to the usual close-coupling procedure without pseudostates. This approach, as a function of the number of hydrogenic states retained, would be slowly convergent below the ionization threshold and virtually impossible above it. The introduction of pseudohydrogenic states is known to significantly improve convergence,[4] and was recently shown to yield rea-

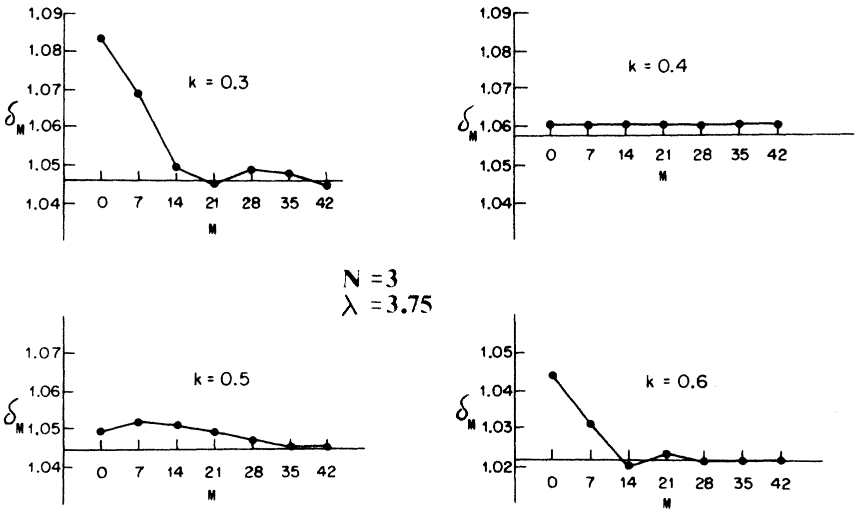

FIG. 2. Effect of approximate Kato correction to static e-H phase shifts. The uncorrected results ($M=0$) are the result of a calculation with $\lambda = 3.75$ and $N=3$. The intersection of the abscissa and ordinate gives the exact result (see Ref. 3) for each value of k. $M=\infty$ would correspond to exact Kato correction; see text for precise definition of M.

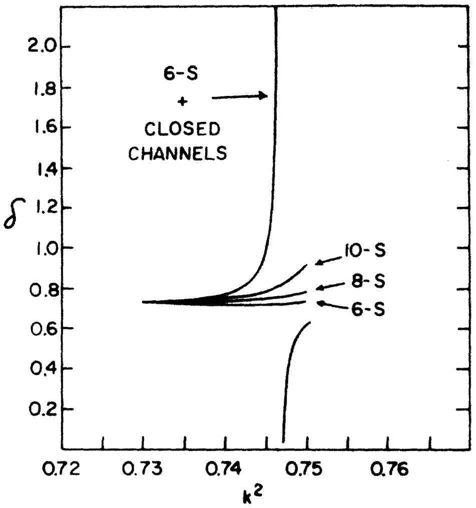

FIG. 3. Effect of the addition of asymptotic closed-channel forms on the elastic s-wave radial limit e-H resonance below the $n=2$ threshold. Shown are 6-s, 8-s, and 10-s results, which included only the open 1s channel asymptotically, and the 6-s result with all asymptotic forms included.

sonable results even above the ionization threshold.[5] One way to generate a set of pseudostates is to diagonalize the hydrogen Hamiltonian [Eq. (3.2)] in a finite set of fixed-exponent Laguerre functions of the type (2.1). Using N such functions as a basis, we obtain N pseudostate wave functions χ_α with eigenvalues E_α, some of which may be in the continuum for hydrogen. The set $\{\chi_\alpha\}$, $\alpha = 0, \ldots, N-1$ defines the finite model space for the target. The uncoupled Hamiltonian for the free electron $-\frac{1}{2}(\partial^2/\partial r_1^2)$ is to be treated exactly in the J-matrix sense. Finally, the potential $V = (-1/r_1 + 1/r_>)$ must be truncated in the Laguerre basis for the free electron, and in the target space spanned by $\{\chi_\alpha\}$. This procedure is the same as first evaluating the close-coupling pseudostate matrix of V in the target space consisting of the χ_α's followed by a truncation of the resulting potential matrix, each element of which is a function of r_1, in the free-electron space consisting of the ϕ_n's. Since the target space is finite, we have the option of retaining up to N of the χ_α's as channels coupled by V.

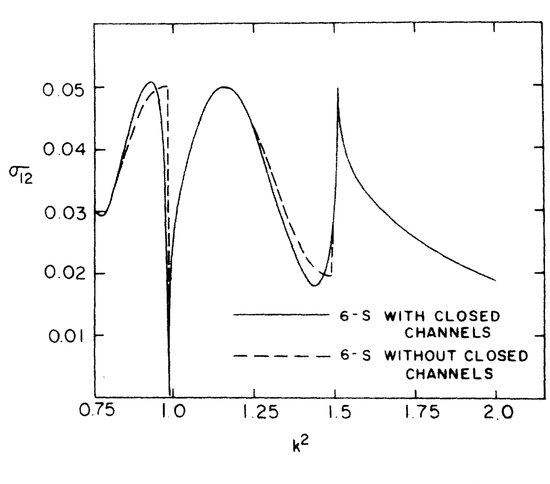

FIG. 4. Effect of closed-channel asymptotic forms on σ_{1s-2s} (6-s radial-limit calculation, $\lambda = 2.0$).

The basic approach of the J-matrix method is to solve a well-defined model scattering Hamiltonian exactly. The Hamiltonian we are dealing with here is

$$\mathcal{H} = H^T_{\text{target}} - \frac{1}{2}\frac{\partial^2}{\partial r_1^2} + \left(\frac{-1}{r_1} + \frac{1}{r_>}\right)^T , \tag{3.3}$$

where T signifies the truncations referred to above.

One may well ask what has happened to the symmetry of the original Hamiltonian. If the same basis set is employed for both the target and free electron, we notice that within the subspace of Laguerre functions below the truncation limit, the Hamiltonian $\mathcal{H}$ is symmetric, while above the truncation limit the Hamiltonian is no longer symmetric. These symmetries of $\mathcal{H}$ dictate the symmetry of the Hilbert space in which the wave function Θ is to be expanded. The complete space of functions corresponding to $\mathcal{H}$ consists firstly of the symmetric two-electron functions (for singlet scattering)

$$\chi_n(1)\chi_m(2) + \chi_n(2)\chi_m(1), \quad m \le n, \quad n < N, \tag{3.4}$$

where the χ's are expanded in the first N Laguerres, and by $\chi_n(i)$ we mean $\chi_n(r_i)$, and secondly of the unsymmetric configurations

$$\chi_n(2)\phi_l(1), \quad l \ge N, \quad n < N. \tag{3.5}$$

In this Hilbert space we expand the wave function as

TABLE I. s-wave radial limit phase shifts for singlet e-H scattering.

k (a.u.)	10 s[a]	Adelman and Reinhardt[b]
0.2	1.8987	1.8973
0.202 499[c]	1.887 64	...
0.386 936[c]	1.302 51	...
0.4	1.2700	1.2696
0.584 173[c]	0.934 96	...
0.6	0.9115	0.9105
0.8	0.7319	0.7261
0.810 305[c]	0.726 12	...

[a] Exponent $\lambda = 2.0$, present method.

[b] S. A. Adelman and W. P. Reinhardt, Ref. 7.

[c] Phase shift computed at eigenvalues of full 10-s ($\lambda = 2.0$) CI matrix, using Eq. (2.21a) of I.

$$\Theta=\Phi_\alpha+\frac{\chi_\alpha(2)S_\alpha(1)}{\sqrt{k_\alpha}}+\sum_{\alpha'=0}^{N_c-1}\frac{R_{\alpha\alpha'}\chi_{\alpha'}(2)C_{\alpha'}(1)}{\sqrt{k_{\alpha'}}}\,,\tag{3.6}$$

where

$$\Phi_\alpha=\sum_{\substack{n,m\\ m\leq n}}^{N_c}a_{nm}^\alpha[\chi_n(1)\chi_m(2)+\chi_m(1)\chi_n(2)]\,,\tag{3.7}$$

and $N_c \leqslant N$. Note that Φ_α fully accounts for exchange in the correlation region and that, since $S_\alpha(1)$ and $C_\alpha(1)$ begin their expansions with ϕ_N, the remaining terms in Eq. (3.6) are truly asymptotic and thus need not include exchange.

If we wish to retain all the pseudochannels in the calculation, we project from the left on

$$\left[H^T_{\text{target}}-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}+\left(-\frac{1}{r_1}+\frac{1}{r_>}\right)^T\right]|\Theta\rangle=0\tag{3.8}$$

by the basis functions given in (3.4) and (3.5). We then arrive at a finite set of equations very similar to the multichannel equations discussed in I. Since we are using the same Laguerre exponent for both electrons, the inner configuration-interaction matrix is of dimension $N\times(N+1)/2$.

Since in the applications to follow we have used a single basis set to describe both electrons, only the 1*s* target state is exact with the exponential parameter used ($\lambda=2.0$); all other *ns* states are pseudostates. However, with six or more basis functions the 2*s* state is so accurately described that we consider it to be essentially exact.

Having defined the model, we can now turn to the applications which are presented in the next section.

IV. APPLICATIONS OF THE MODEL

A. Effect of asymptotic closed channels

In I, we pointed out that adding the closed-channel asymptotic forms to the expansion of Θ has the effect, near thresholds, of including diffuse functions in the basis set. These diffuse functions are expected to improve threshold behavior, and may be especially helpful in describing Feshbach closed-channel resonances. This expectation is borne out in Figs. 3 and 4. In Fig. 3, we have shown the phase shift just below the 2*s* threshold using 6, 8, and 10 *s*-type Laguerre functions including the asymptotic form for only the open 1*s* channel. Shown also in the same figure the result for 6-*s* Laguerres including all asymptotic channels. While the 6-, 8-, and 10-*s* calculations are attempting unsuccessfully to describe the resonance[6] at $k^2=0.747$, the addition of the closed-channel asymptotic forms to a 6-*s* calculation gives proper resonance behavior. Similarly, in Fig. 4 we have plotted $\sigma(1s\text{-}2s)$ with and without closed channels. The behavior below the pseudostate threshold is altered by the addition of the closed-channel forms, and yields more realistic threshold effects. In Sec. III B, our results will include the closed-channel asymptotic forms.

B. Elastic and inelastic results

Table I shows elastic *s*-wave phase shifts for our 10-*s* model comparing with the work of Adelman and Reinhardt,[7] who used the Fredholm method with an optical potential. We have also given the phase shifts at the Harris eigenvalues E_m using the formula

$$\tan\delta(E_m)=\tan(N+1)\theta(E_m)\,,$$

where in this case $N=10$. [This is Eq. (2.21a) of I].

In Fig. 5, we show the $\sigma(1s\text{-}1s)$ results for 6-*s* and 10-*s* calculations, along with the 1*s*-2*s*-3$\bar{s}$-4$\bar{s}$ results of Burke and Mitchell[5] both above and below the ionization threshold. Note that the 10-*s*

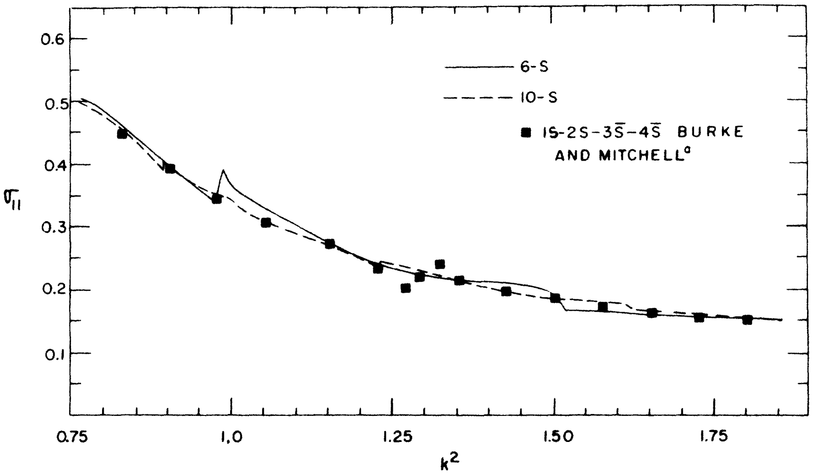

FIG. 5. Elastic *s*-wave radial limit *e*-H cross sections (σ_{1s-1s}), above and below the ionization threshold. Results of 6-*s* and 10-*s* calculations, and comparison with Burke and Mitchell (Ref. 5).

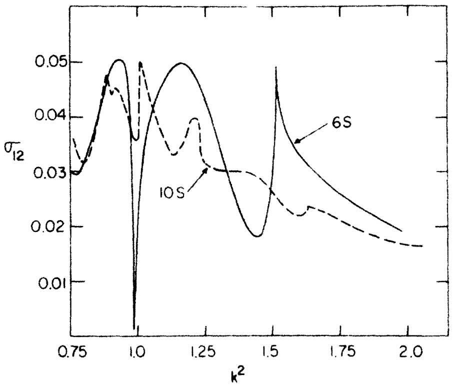

FIG. 6. Inelastic-scattering σ_{1s-2s} cross sections for 6-*s* and 10-*s* functions. Note that the 2*s* state is really a pseudostate in our model, since our choice of $\lambda = 2.0$ makes 1*s* the only exact hydrogenic state.

model agrees well with the 6-*s* model, except that it possesses suppressed pseudostate threshold anomalies. The agreement with the results of Burke and Mitchell is quite satisfactory.

Figure 6 shows the inelastic-scattering $\sigma(1s\text{-}2s)$ results for 6-*s* and 10-*s* models. One interesting feature of the figure is the apparent reduction in the maximum error, with the increasing number of basis functions used, compared with the exact $\sigma(1s\text{-}2s)$, which is expected to be smooth above the ionization threshold. This kind of convergence may be a result of the nature of our pseudostates which, above ionization threshold, are quite diffuse; e.g., the 10-*s* case contains pseudostates which are as diffuse as $(\lambda r)^{10}e^{-\lambda r}$.

TABLE II. Various radial limit cross sections, comparing with the work of Burke and Mitchell.[a]

		$1s\text{-}2s\text{-}3\bar{s}\text{-}4\bar{s}^{a}$	Present work, 10-*s*, $\lambda = 2.0$
$k_1^2 = 1.0$			
	$\sigma(1s, 1s)$	0.3281	0.3458
	$\sigma(1s, 2s)$	0.0373	0.0362
	$\sigma_{\text{tot}}(1s, ns)$, $n \neq 1, 2$	0.0089	0.0134
	$\sigma_{\text{tot}}(1s\text{-}ns)$	0.3743	0.3953
$k_1^2 = 1.21$	$\sigma(1s, 1s)$	0.2290	0.2450
	$\sigma(1s, 2s)$	0.0499	0.0400
	$\sigma_{\text{tot}}(1s, ns)$, $n \neq 1, 2$	0.0179	0.0162
	$\sigma_{\text{tot}}(1s\text{-}ns)$	0.2968	0.3013
$k_1^2 = 1.7$			
	$\sigma(1s, 1s)$	0.1542	0.1610
	$\sigma(1s, 2s)$	0.0240	0.0222
	$\sigma_{\text{tot}}(1s, ns)$, $n \neq 1, 2$	0.0269	0.0302
	$\sigma_{\text{tot}}(1s\text{-}ns)$	0.2051	0.2134
$k_1^2 = 2.0$			
	$\sigma(1s, 1s)$	0.1323	0.1355
	$\sigma(1s, 2s)$	0.0168	0.0165
	$\sigma_{\text{tot}}(1s, ns)$, $n \neq 1, 2$	0.0270	0.0311
	$\sigma_{\text{tot}}(1s, ns)$	0.1761	0.1831

[a] Burke and Mitchell, Ref. 5.

In Table II we have compared our results for $\sigma(1s\text{-}1s)$, $\sigma(1s\text{-}2s)$, $\sigma_{\text{tot}}(1s\text{-}ns)$, $n \neq 1, 2$, and $\sigma_{\text{tot}}(1s\text{-}ns)$ with those of Ref. 5. Considering the presence of pseudostates in both methods (and of course the fact that the number and position of the thresholds are different in the two methods), the agreement is quite good.

C. Elastic *s*-wave scattering with *p* and *d* coupling

So far we have exclusively considered *s*-type configurations for both target and incident electrons. Within the context of our *s*-wave asymptotic forms, it is possible to include one electron *p*, *d*, ..., etc. configurations with total $L = 0$, as long as one stays below the $n = 2$ threshold where the corresponding *p*, *d*, ..., etc., target channels are closed. In this way, we need only the *s*-wave asymptotic forms. Of course, threshold behavior below $n = 2$ would be improved by the addition of the 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, ... asymptotic forms. However, these additions fall outside the domain of this paper.

So, restricting the correlation terms in Θ to *s*, *p*, and *d* states, while keeping only the 1*s* asymptotic open channel term, we have calculated phase shifts which are compared with the results of Schwartz[8] in Table III. The results shown are not Kato-corrected. Figure 2 would seem to indicate that significant increase in precision would result by the addition of Kato correction.

V. DISCUSSION

We wish to emphasize the simplicity of the calculations. Basically, an atomic configuration inter-

TABLE III. Electron-hydrogen singlet correlated phase shifts, using 8-*s*, 5-*p*, and 5-*d* type Laguerre functions, $\lambda = 2.0$ for each symmetry.

k^2	Schwartz[a]	Present
0.01	2.553	2.605
0.04	2.0673	2.0803
0.09	1.6964	1.6962
0.16	1.4146	1.4337
0.25	1.202	1.197
0.36	1.041	1.0425
0.49	0.930	0.937
0.64	0.886	0.881

[a] C. Schwartz, Ref. 8.

action (CI) matrix is augmented with an easily constructed extra row and column for each asymptotically important channel. If the prediagonalization, discussed in I, which is performed only once, is applied, the method is very efficient. In fact, the computation of the cross sections at each new energy requires the same effort as in the Wigner R-matrix method. This can easily be shown along similar lines as the single channel comparison made in I.

In this paper, we have used the same basis set for both target and free electron for our e-H model. This is not a necessary procedure in order to apply the method, nor is it a desirable one in applications to more complex systems. One way to apply our method to collision with many-electron atoms is to first find the close-coupling direct and exchange potential matrix using any desired atomic wave functions, and then to truncate the multichannel matrix in the Laguerre representation for the free-electron coordinate.

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