Excitation and ionization in H(1s)–H(1s) collisions: II. Inclusion of electron exchange

Merle E Riley† and A Burke Ritchie‡

† Sandia National Laboratories, Albuquerque, NM 87185, USA
‡ Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

Abstract. Hydrogen atom–hydrogen atom scattering is a prototype for many of the fundamental principles of atomic collisions. In this work we present the formalism and the predictions of a time-dependent self-consistent-field description of the H + H system for scattering in the intermediate energy regime of 1–100 keV. Because of the unrestricted nature of the numerical orbital description, this method includes the effects of an unlimited basis set within each orbital. Electron exchange and a limited amount of electron correlation are included as well. We solve numerically coupled three-dimensional Schrödinger equations for the two-electron orbitals in singlet and triplet symmetries. Excitation and ionization cross sections are computed and compared with other theory and experiment. The results capture many features of the problem but illustrate a need for more quantitative experimental information concerning the H + H system in this energy range.

1. Introduction

The collision of two hydrogen atoms is a basic problem in atomic physics that deserves attention in order to quantify the dynamics. Not only is it difficult to perform experimental studies of neutral atomic collisions in the energy region of interest, the theoretical description is complicated by many features that are still being explored, not only for the H + H problem, but for atomic collisions in general. Within the framework of the impact parameter approximation, which is an adequate description of the nuclear motion is this energy range, H + H scattering is complicated by many of the more difficult aspects of quantum scattering. Among these are inelastic excitation, electron exchange symmetry, multichannel rearrangement of particles, channel-state translation factors, transitions to the continuum (ionization), electron correlation, and varying degrees of adiabatic behaviour of the electrons.

In this work we solve a self-consistent field (SCF) description of the H + H system for scattering in the intermediate energy regime of 1–100 keV where most of the inelastic processes occur. This energy range corresponds to a relative velocity range of 0.2–2 au. In our theoretical description, basis-set limitations are not an issue for the representation of the electron orbitals. By solving the Schrödinger equation in space and time our calculation allows the electrons to undergo excitation and ionization *without* the constraints of an atom-centred atomic or molecular basis set. The limitation is of course the time-dependent SCF approximation for the two electrons. In general, we will compare our study with what we regard as the most accurate of the available experimental and theoretical data. Notable among the existing theoretical studies of H + H are the recent calculations of Hansen and Dubois (1998) and Wang *et al* (2000). These studies use a large atomic basis set to obtain nearly convergent results for excitation and charge transfer.

Unfortunately, the state of the experimental data is such that some discrepancies between our SCF approximation and other accurate theory cannot be appraised. In some cases, there would appear to be the necessity of additional experiments in order to resolve excitation cross sections.

2. Theoretical approach

The time-dependent Schrödinger equation (TDSE) for the scattering of H on H in the impact parameter approximation is written in Hartree atomic units as

$$
\begin{aligned}
&\mathrm{i}\dot{\psi} \equiv \mathrm{i}\partial\psi/\partial t = \hat{H}\psi \qquad \psi = \psi(1, 2) \\
&H = \hat{H}^o(1) + \hat{H}^o(2) + V^I \\
&\hat{H}^o(i) = -\tfrac{1}{2}\nabla_i^2 - 1/\big|\vec{r}_i - \vec{R}_A(t)\big| - 1/\big|\vec{r}_i - \vec{R}_B(t)\big| \\
&V^I = 1/\big|\vec{r}_1 - \vec{r}_2\big|.
\end{aligned}
\tag{1}
$$

We use the circumflex to denote a quantity containing a differential operator. Electron coordinates are denoted by $\vec{r}_1$ or 1 for example. The nuclear coordinates are prescribed functions of time, which are assumed to be simple rectilinear motion specified by an impact parameter b and the relative velocity. The time variable is implicit in the wavefunction. The partial derivative with respect to time is taken at fixed electron coordinates in a coordinate system whose reference frame is the nuclear geometric centre. The position of this reference system is immaterial for the solution, since a change in reference frame produces only a global phase change in the total wavefunction (Riley 1973). The Pauli principle must be imposed on the solution, which requires $\psi^\pm(1, 2) = \pm\psi^\pm(2, 1)$ for the singlet or triplet symmetry. Singlet and triplet solutions must be combined to simulate collisional events.

Our approximation for the solution is to invoke a symmetrized product form for the wavefunction:

$$
\psi^\pm(1, 2) \approx \phi_1^\pm(1)\,\phi_2^\pm(2) \pm \phi_2^\pm(1)\,\phi_1^\pm(2)
\tag{2}
$$

where the individual orbitals $\phi_i^\pm$ are completely unrestricted in space and time dependence. Our justification for making this approximation is to move from a six-dimensional coordinate space for the two electrons to two three-dimensional spaces. One notes that this form allows an exact incorporation of electron exchange symmetry and electron correlation in the sense of bonding. Some obvious consequences of this approximation are that we cannot reliably predict double-excitation events or atomic correlation of electrons. This trial form could be systematically generalized by including additional product terms. An alternative approach for some systems such as H on H is to use the unsymmetrized trial substitution,

$$
\psi^\pm(1, 2) \approx \phi_1(1)\,\phi_2(2)
\tag{3}
$$

and to use linear superposition with another independent solution of the same form to generate singlet and triplet symmetry. This is permissible since the exchange operator commutes with the Hamiltonian. The equations of motion (EOM) for the latter method are significantly simpler than those derived from the first ansatz. The solutions are not identical because the EOM for the individual electron orbitals, ϕ_i, are highly nonlinear due to the self-consistent fields. The first symmetrized ansatz is of superior quality. Consider the united-atom states of ground singlet and triplet symmetry resulting from a slow adiabatic collision. These two states would be generated from the *same* orbitals if one uses the unsymmetrized trial product. This is a gross approximation at lower energies.

The notational time dependence of the wavefunctions and orbitals will be suppressed, as will be the $\pm$ label on all quantities except where necessary. The EOM for the electrons is found by requiring the TDSE solution to be stationary with respect to arbitrary variations of this trial form. This is equivalent to a one-electron projection of each of the two orbitals onto equation (1). It is convenient to introduce a 2×2 matrix representation based on the one-electron orbitals. This has the properties

$$\psi(1, 2) = \phi_1(1)\,\phi_2(2) \pm \phi_2(1)\,\phi_1(2) \equiv \phi^T(1)\boldsymbol{P}_\pm \phi(2)$$

$$\phi = \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} \qquad \boldsymbol{P}_\pm = \begin{pmatrix} 0 & 1 \\ \pm 1 & 0 \end{pmatrix} \qquad \boldsymbol{P}_\pm^T = \pm \boldsymbol{P}_\pm. \tag{4}$$

Superscript T denotes the matrix transpose, and vectors and matrices are written in boldface. This form of the product wavefunction is just as general as the form in which the matrix $\boldsymbol{P}_\pm$ is *any* time-dependent matrix with transpose symmetry. The 2×2 overlap, derivative, and Hamiltonian matrices of the orbitals are defined as follows, where the bracket notation denotes a one-electron integration:

$$\boldsymbol{S} = \langle \phi | \phi^T \rangle \qquad \boldsymbol{D} = \langle \phi | \dot{\phi}^T \rangle \qquad \hat{\boldsymbol{H}}(\vec{r}) = \langle \phi | \hat{H} | \phi^T \rangle$$

$$\hat{\boldsymbol{H}}(\vec{r}) = \boldsymbol{H}^o + \boldsymbol{S}\hat{H}^o(\vec{r}) + \boldsymbol{V}^I(\vec{r}). \tag{5}$$

These are all time dependent, of course. The resulting coupled EOM that are derived from projection with the two orbitals may be written compactly as

$$\mathrm{i}\boldsymbol{D}\boldsymbol{P}_\pm \phi + \mathrm{i}\boldsymbol{S}\boldsymbol{P}_\pm \dot{\phi} = \hat{\boldsymbol{H}}\boldsymbol{P}_\pm \phi \tag{6}$$

or, if we define the matrices with the symmetrization explicitly included within the coupling matrices:

$$\mathrm{i}\boldsymbol{D}_\pm \phi + \mathrm{i}\boldsymbol{S}_\pm \dot{\phi} = \hat{\boldsymbol{H}}_\pm \phi$$

$$\boldsymbol{M}_\pm \equiv \boldsymbol{P}_\pm^T \boldsymbol{M}\boldsymbol{P}_\pm \qquad \boldsymbol{M} = \boldsymbol{S}, \boldsymbol{D} \text{ or } \hat{\boldsymbol{H}}. \tag{7}$$

These coupled nonlinear time-dependent partial differential equations (PDE) are the EOM for solving the scattering problem. The dependent variables are the two three-dimensional orbitals. The EOM are essentially ready to use except that part of the time derivative of the orbitals is still buried under the space integration within the $\boldsymbol{D}$-matrix. This is a practical difficulty for the use of a numerical propagation scheme for integrating the PDEs. We will show how to solve for the $\boldsymbol{D}$-matrices algebraically and eliminate the problem.

The normalization of the wavefunction is

$$N = \langle \psi | \psi \rangle = 2(S_{11}S_{22} \pm S_{12}S_{21}). \tag{8}$$

From a further projection of the orbitals on the EOM in equations (6) and (7), we can deduce the algebraic relation, for both the singlet and triplet,

$$D_{11}S_{22} + S_{11}D_{22} \pm D_{12}S_{21} \pm S_{12}D_{21} = -\mathrm{i}(H_{12,21} \pm H_{12,12})$$

$$H_{ij,kl} = \int \mathrm{d}^3 r_2\, \phi_i^*(2) \int \mathrm{d}^3 r_1\, \phi_j^*(1)\, \hat{H}\, \phi_k(1)\, \phi_l(2). \tag{9}$$

The following symmetry relations hold for the $H_{ij,kl}$ elements:

$$H_{ij,kl} = H_{ji,lk}$$

$$H_{ij,kk} = H_{ji,kk} \tag{10}$$

$$H_{ii,kl} = H_{ii,lk}.$$

For the singlet, there are two additional relations to be derived by one-electron orbital projection onto the EOM as written in (6) or (7):

$$2D_{22}S_{21} + 2S_{22}D_{21} = -i(H_{22,21} + H_{22,12}) = -2iH_{22,21}$$

$$2D_{11}S_{12} + 2S_{11}D_{12} = -i(H_{11,21} + H_{11,12}) = -2iH_{11,21}$$

$$(11)$$

which will be used later to solve for the D-matrix. Note that we have an undetermined set of algebraic equations for the D_{ij} at the moment (three equations and four unknowns).

It is important to know the conditions for invariance of the EOM to linear time-dependent transformations. If we carry out a linear time-dependent transformation $L(t)$ among the orbitals,

$$\phi = L(t)\chi \tag{12}$$

then it can be shown using equation (4) that ψ and the EOM for the new orbitals χ are *identical* to ψ and the EOM for the old orbitals ϕ if

$$L^T P_{\pm} L = P_{\pm} \tag{13}$$

which will be true if and only if $\det(L) = 1$ for the singlet and triplet, *and* if L is diagonal (or off-diagonal) for the singlet. Thus the triplet EOM is invariant to *any* time-dependent unitary transformation, but the singlet is not.

We can completely eliminate D from the triplet EOM as follows: let a unitary L solve

$$\dot{L} = D_\Phi^T L \tag{14}$$

where the D_Φ notation indicates that the derivative matrix defined in equation (4) is evaluated in the old basis. This may be shown to allow us to set, in the new or transformed basis χ:

$$S_X = 1 \qquad D_X = 0. \tag{15}$$

The EOM in the new basis are written as

$$i\dot{\chi} = \hat{H}_{\pm}\chi \tag{16}$$

which is simple in form once the Hamiltonian matrix is decomposed into the kinetic and potential terms as written above. One notes that this is the same as requiring the basis orbitals to be orthogonal and having a *zero* D-matrix. We must now solve for the singlet D relations, which is done by finding a new permissible relation among the elements afforded by the freedom in the singlet linear transformation.

We need one more equation in singlet symmetry involving the elements of D in order to be able to solve for them directly. In fact, it is not difficult to show that we can introduce a diagonal phase matrix $L(t)$ for an orbital transform defined as in equation (12) that enables us to set

$$D_{dd} = D_{11} = D_{22} \tag{17}$$

which from the differential identity, $\dot{S} \equiv D + D^{\dagger}$, shows that we can set, for all time

$$S_{dd} = S_{11} = S_{22}. \tag{18}$$

The three algebraic equations for the D elements are collected from equations (9) and (11) with equations (17) and (18) incorporated:

$$2S_{dd}D_{dd} + S_{21}D_{12} + S_{12}D_{21} = -i(H_{12,21} + H_{12,12})$$

$$S_{21}D_{dd} + S_{dd}D_{21} = -iH_{22,21}$$

$$S_{12}D_{dd} + S_{dd}D_{12} = -iH_{11,21}.$$

$$(19)$$

If we eliminate D_{dd} from equation (19) we can solve for D_{12} and D_{21} from the resulting two simultaneous equations. Define

$$A = 2S_{dd}^2 - S_{12}S_{21} \qquad B = -S_{12}^2 \qquad C = -S_{21}^2 \qquad D = A$$

$$E = iS_{12}(H_{12,21} + H_{12,12}) - 2iS_{dd}H_{11,12} \tag{20}$$

$$F = iS_{21}(H_{12,21} + H_{12,12}) - 2iS_{dd}H_{22,21}$$

so that the solution is given by

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} D_{12} \\ D_{21} \end{pmatrix} = \begin{pmatrix} E \\ F \end{pmatrix}$$

$$D_{12} = (DE - BF)/\Delta \tag{21}$$

$$D_{21} = (AF - CE)/\Delta$$

$$\Delta = AD - BC = 4S_{dd}^2(S_{dd}^2 - S_{12}S_{21}).$$

D_{dd} can now be found from the first equation in the set above:

$$D_{dd} = -\left(i(H_{12,21} + H_{12,12}) + S_{21}D_{12} + S_{12}D_{21}\right)/2S_{dd}. \tag{22}$$

This completes the determination of $\boldsymbol{D}$ from the other matrices and affords the integration of the singlet coupled PDEs as an explicit set of EOM. The triplet EOM are already in convenient form once we take advantage of the invariance to an arbitrary unitary transformation.

The initial condition for the electrons is that of 1s orbitals on the two identical nuclei. In this case, we could make use of inversion symmetry in the Hamiltonian. In fact, the wavefunction must preserve the inversion symmetry of the initial state which implies for our approximation (equation (2)):

$$\psi(\vec{r}_1, \vec{r}_2, t) \equiv \psi(-\vec{r}_1, -\vec{r}_2, t)$$

$$\varphi_2(\vec{r}, t) \equiv \varphi_1(-\vec{r}, t) \tag{23}$$

if the coordinates are measured from the geometric centre of the nuclei. We will not make use of this, however, as the generality of the formalism is lost.

The cross sections are evaluated in the usual way from the probabilities as a function of impact parameter b. The probabilities are evaluated by projection onto the channel states, including translation factors as appropriate, after the time-dependent collision is completed:

$$P_f(b) = \langle \phi_f | \psi \rangle$$

$$\sigma_f = 2\pi \int_0^\infty b \, db \, P_f(b). \tag{24}$$

However, the ionization cross section is evaluated from the loss of normalization of the wavefunction during the collision:

$$\sigma_f = 2\pi \int_0^\infty b \, db \, (1 - N(b)). \tag{25}$$

This loss is due to the absorption by the optical potential, which can contain absorption from highly excited bound states of the reaction products.

The form of the channel states is that of atomic excitations including translation factors and exchange symmetrization. We do not include the H^- state as it is not bound in our approximation. In terms of the H atomic orbitals φ_i, a channel state is given by

$$\phi_{ij}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left(\phi_i^A(1)\,\phi_j^B(2) \pm \phi_i^B(1)\,\phi_j^A(2)\right) \tag{26}$$

where the ϕ_i^C contain the translation factor appropriate for centre C:

$$\phi_i^C(\vec{r}) = \exp(\mathrm{i}\vec{v}_C \cdot \vec{r}) \, \varphi_i^C(\vec{r}). \tag{27}$$

Only the space-dependent part is given above. The amplitudes and probabilities are obtained by projection of the total wavefunction onto the channel states.

3. The ISOP method for numerical propagation

The numerical method we use is based on an implicit split-operator procedure (ISOP) (Ritchie *et al* 1997) for solving the three-dimensional TDSE using fast Fourier transforms (FFT). This has been applied to alpha particle scattering on H (Riley and Ritchie 1999a) and a one-electron approximation to H on H scattering (Riley and Ritchie 1999b). The advantages of a fully numerical procedure are that *no subjective basis restrictions* are built into the solution and that translation factors are not needed except in channel state analysis. The disadvantages are that the computational zone (the 'box') must be large to contain excited Coulombic states and that absorptive boundary conditions must be imposed to allow for a proper treatment of ionization. We develop this quickly for a coupled pair of TDSE of the form developed in the previous section for the SCF problem. We rewrite the EOM in 2×2 matrix notation:

$$\mathrm{i}D_{\pm}\phi + \mathrm{i}S_{\pm}\dot{\phi} = \hat{H}_{\pm}\phi$$

$$S_{\pm}\dot{\phi} = -\mathrm{i}\left(H_{\pm}^o + S_{\pm}\hat{H}^o(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}\right)\phi. \tag{28}$$

An explicit propagation procedure could be implemented as this stands. The EOM for the triplet spin state can be written without the S- and D-matrices and the singlet will utilize the algebraic solution for the D-matrix. However, experience has taught us that an implicit method is much better to propagate the Schrödinger solution, and that is given by the ISOP. We begin by writing down the second-order-accurate, time-symmetric form of the finite difference advance of the matrix EOM for equation (7), analogous to the Crank–Nicolson procedure:

$$\left[S_{\pm} + \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\left(H_{\pm}^o + S_{\pm}\hat{H}^o(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}\right)\right]\phi_{t+\mathrm{d}t}$$

$$= \left[S_{\pm} - \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\left(H_{\pm}^o + S_{\pm}\hat{H}^o(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}\right)\right]\phi_t. \tag{29}$$

The procedure is correct through order $(\mathrm{d}t)^2$. What is desired is to split the space and momentum parts of the Hamiltonian (Feit *et al* 1982) to enable the use of the fast Fourier transform as in the scalar ISOP. We regroup the terms in the coefficients of the orbitals:

$$\left[S_{\pm}\left(1 + \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\,\hat{T}\right) + \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\left(H_{\pm}^o + S_{\pm}V(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}\right)\right]\phi_{t+\mathrm{d}t}$$

$$= \left[S_{\pm}\left(1 - \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\hat{T}\right) - \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\left(H_{\pm}^o + S_{\pm}V(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}\right)\right]\phi_t. \tag{30}$$

This is factored approximately as

$$\phi_{t+\mathrm{d}t} = \left(\frac{1 - \tfrac{1}{4}\mathrm{i}T\,\mathrm{d}t}{1 + \tfrac{1}{4}\mathrm{i}T\,\mathrm{d}t}\right) M_{\mathrm{bot}}^{-1} M_{\mathrm{top}} \left(\frac{1 - \tfrac{1}{4}\mathrm{i}T\,\mathrm{d}t}{1 + \tfrac{1}{4}\mathrm{i}T\,\mathrm{d}t}\right)\phi_t$$

$$M_{\mathrm{top}} = S_{\pm} - \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\,N \qquad M_{\mathrm{bot}} = S_{\pm} + \tfrac{1}{2}\mathrm{i}\,\mathrm{d}t\,N \tag{31}$$

$$N = H_{\pm}^o + S_{\pm}V(\vec{r}) + V_{\pm}^I(\vec{r}) - \mathrm{i}D_{\pm}.$$

The outside kinetic energy operators are diagonal in momentum space as well as in the 2×2 orbital representation. The time in the central factor, which contains all the space dependent operators, is taken to be at the midpoint of the interval rather than the present and advanced times. The 2×2 inverse must be computed at each space point in the central factor. The order of the M_{top} and M_{bot} factors can be shown to be immaterial.

The advantage of this factorization is that the operator is now a product of momentum and coordinate dependences which allows the FFT procedure to be used with only 2×2 operators applied to the very large solution vector, which typically is many millions of words in length. This is a simple process. Beginning with the wavefunction in the coordinate representation, one Fourier transforms to momentum space, multiplies by the above Cayley fraction containing the kinetic energy operator, reverse transforms, multiplies by the matrix fraction containing the potential, forward transforms to momentum space again, and applies the kinetic energy fraction again. The sequence is repeated until the end of the time evolution. This is the implicit split-operator procedure (ISOP).

The calculations presented here typically use a representation of $80 \times 80 \times 240$ grid points for ϕ_i in a box of dimension $24 \times 24 \times 72$ in Bohr atomic units for the singlet symmetry. For the triplet symmetry, we use $96 \times 96 \times 320$ grid points in a box of $30 \times 30 \times 100$ au. The reason for the difference will be explained shortly. The interior walls of the box were 'coated' with an absorptive optical potential (Kulander 1987) whose profile was a half-Gaussian 0.9 Bohr in thickness with a strength coefficient of 2.0. The box size must be large enough that significant absorption does not occur for any channel states of interest. The optical potential must be strong enough *and* smooth enough not to allow significant reflection. The time increment was typically 0.05 or 0.1 au. The collision length in z, the coordinate parallel to the relative velocity vector, must be chosen to achieve channel decoupling. In the coordinate frame located at the geometric centre, the starting and stopping points in z were typically -15 to 25 and 15 to -25 Bohr for the two nuclei. In addition, a cut-off was applied to the singular nuclear Coulomb interactions that was consistent with the spatial increments (Riley and Ritchie 1999b). All of these numerical conditions were developed from exploratory calculations. In pursuing a numerical solution of the TDSE in partial differential equation form by purely numerical means, one must realize that we are trading the numerically precise, basis-defined, accuracy of an expansion method for the more loosely defined numerical accuracy and stability of the finite-difference methods.

4. Cross sections for 2s and 2p excitation and ionization—comparison with experimental data

Excitation of the 2s and 2p atomic states has a long history of investigation beginning with the Born calculations of Bates and Griffing (1954). In figure 1 we compare our results for the excitation cross section of the projectile to the 2s state with experiment and recent theory. The two sets of experimental measurements do not agree well at less than 10 keV so we do not have a benchmark there. The recent calculations of Wang *et al* (2000) are combined with those of Hansen and Dubois (1998) at higher energies which include 'total excitation' (TE) of the other centre. The calculations of Hansen *et al* agree best with the data of Morgan *et al* (1980). We do not show the 22 state per centre calculations of Shingal *et al* (1989), which, with the Born correction at higher energy, tend to overestimate the experimental data. A comparison with that work is shown in the study of Hansen and Dubois. Our calculation agrees best with Hill *et al*'s (1979) measurements over the whole energy range, but we are slightly low on the higher-energy side.
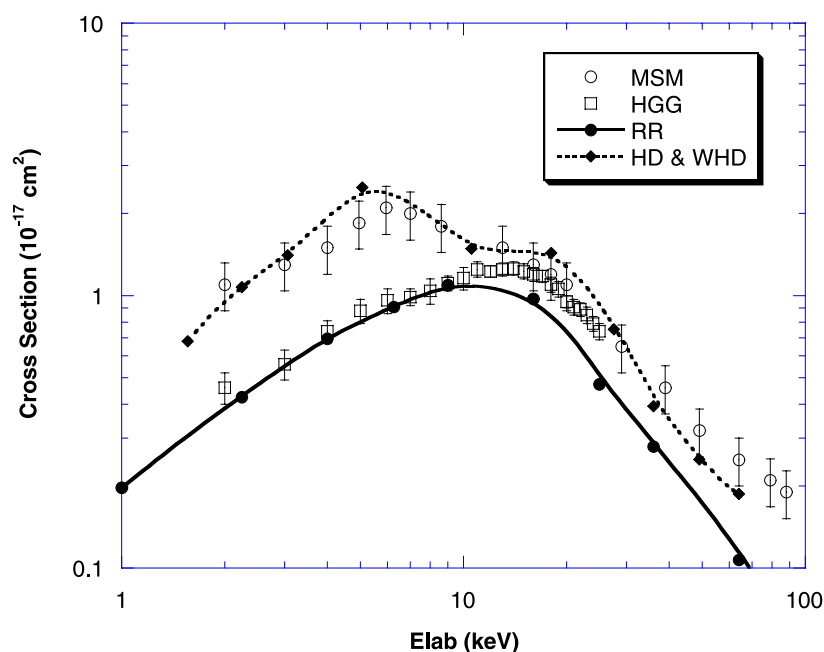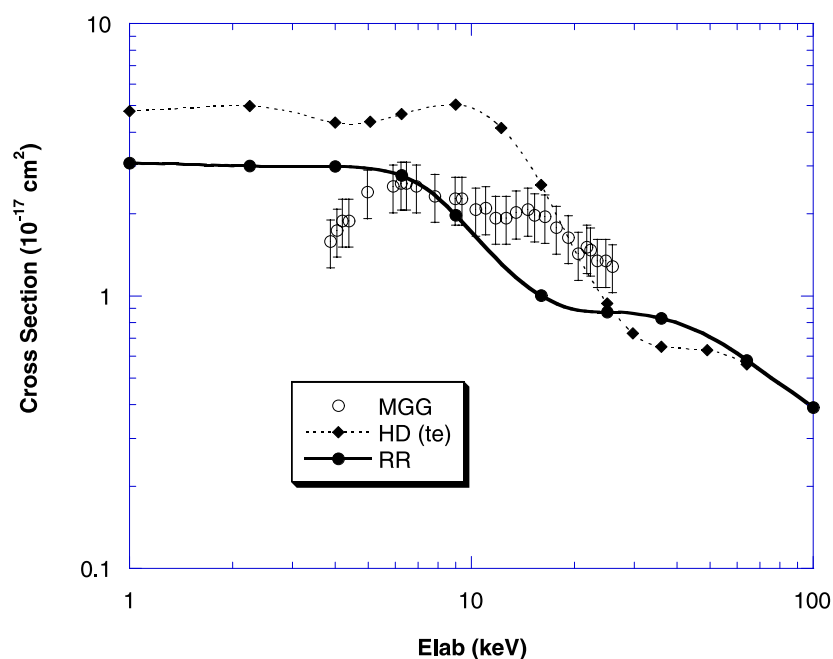
Figure 1. Excitation cross sections to the projectile 2s state for H on H. MSM denotes Morgan *et al*'s experimental data; HGG denotes Hill *et al*'s measurements; RR denotes the present results and HD & WHD denotes Wang *et al*'s predictions combined with those of Hansen and Dubois at higher energy. Elab denotes the laboratory kinetic energy of the incident H atom in keV, here and in all figures.

The experimental measurements of Morgan *et al* (1974) and the most recent of the theoretical predictions for excitation of the 2p level are shown in figure 2. The agreement is not especially good. Our results are in fair agreement with the experimental data above 4 keV, but the overall shape is not satisfactory. The results of Hansen and Dubois are high up to 15 keV. The results of Hansen and Dubois as well as ours would seem to be capable of describing the low-energy region accurately, and, if so, indicate that the experimental results may be in error there. The shape of the experimental data shows a decrease in cross section in the 4–10 keV region that is not shown by either of the theories. The study of Borondo *et al* (1970) using a molecular basis with common translation factor also predicts a large 2p cross section at 1 keV. Because of the lack of determination of a parameter in the translation factor, however, their results are indeterminate by a factor of two.

Our ionization cross sections are computed by evaluating the total loss of probability of the two-electron wavefunction during the collision. This loss is due to absorption of the electrons in the optical potential that coats the inner walls of the computational box. One should note that the cross sections are historically both measured and computed for the production of an ionized projectile H. Otherwise the cross sections would (by symmetry arguments) be doubled for the total single-ionization cross section. In figure 3 we compare our results with the experimental measurements of Gealy and Van Zyl (1987) and of McClure (1968). The lower-energy predictions (4 keV and less) of Krstic *et al* (1996) and Bent *et al* (1998) agree extremely well with the data at low energy, all the way down to 0.1 keV. The recent calculation of Shingal *et al* (1989) of the ionization cross section includes electron symmetry with a 22-state per centre atomic basis with translation factors

Figure 2. Excitation cross sections to the projectile 2p level for H on H. MGG denotes Morgan *et al*'s experimental data; RR denotes the present results, and HD (te) denotes Hansen and Dubois's predictions with excitation of the target.
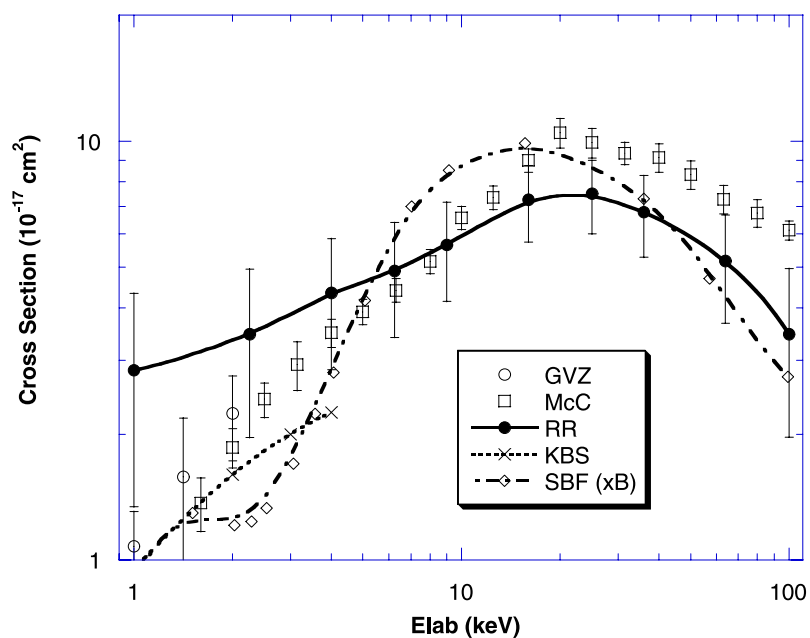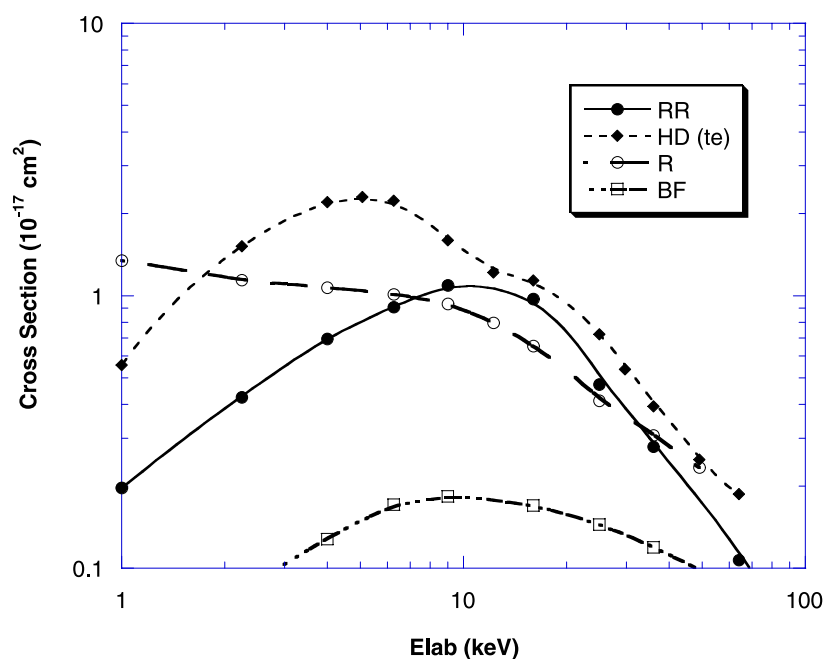

Figure 3. Ionization cross section to the projectile continuum for H on H. GVZ denotes Gealy and Van Zyl's experimental data, McC denotes McClure's measurements, RR denotes the present results, KBS denotes Krstic *et al*'s predictions, and SBF(xB) denotes Shingal *et al*'s calculations with the Born correction.

but without double excitation channels. Their results with the 'Born correction' are the best of the theories, except that their results show an oscillatory feature in the 2–3 keV region not seen in the experiments or other theories. Our predictions of ionization have error bars attached to represent the fact that we were unable to predict ionization accurately when the probability of electron loss was less than about 1%. Nevertheless, our fully numerical SCF method agrees qualitatively with the best theory and McClure's measurements at higher energy. It is interesting to note that our SCF method is not in as good agreement with ionization experiments at all energies as our earlier frozen-atom approximation. This limitation lies in the numerical accuracy with which we can compute the loss of normalization at the per cent level. It is not believed to be any argument against the SCF method for ionization.

5. Discussion of theoretical cross sections including exchange

To better interpret the results of this work, we present some of the major theoretical cross sections that have been computed which explicitly include electron exchange symmetry. It is difficult to make a precise comparison of exchange and non-exchange calculations because of other subsidiary differences in the relevant studies. For example, our previous work on H + H (Riley and Ritchie 1999b) did not include exchange, but used a 'frozen-atom' model in order to solve for the electronic excitation. This is not the same as omitting exchange from the present theory, which would lead to an unsymmetrized Hartree approximation for the electrons, a calculation that has not been done to the best of our knowledge.

Figure 4. Theoretical excitation cross sections to the projectile 2s state for H on H. RR denotes the present results; R denotes the predictions of Ritchie; BF denotes the predictions of Bottcher and Flannery and HD (te) denotes the Hansen and Dubois results including excitation of the target. The newer calculations of Wang *et al* are slightly different as seen in figure 1.

In figure 4 we show the 2s excitation by this work, by Hanson and Dubois (1998), by Ritchie (1971), and by Bottcher and Flannery (1970). Remember that Hanson and Dubois have no basic restrictions as to accuracy except the size of the two-electron basis. Our results are limited by the SCF approximation. Ritchie did a two-state atomic-basis study including exchange and translation factors, and Bottcher and Flannery did a molecular state calculation with exchange and no translation factors. Above 10 keV, the Hanson–Dubois results and ours agree to about 40%. Below 10 keV, our results are lower than theirs by almost a factor of three. The *experimental* measurements disagree among themselves by nearly the same amount. Part of the disagreement of our results with those of Hanson and Dubois at higher energy is due to the limited ability of our SCF approximation to incorporate their 'total excitation'. This latter process would require a degree of electron correlation that our SCF method cannot reproduce. The early two-state atomic calculation of Ritchie appears to be reasonable above 10 keV, but has an apparently erroneous behaviour at lower energy. In that calculation, approximations made to the exchange term containing translation factors may have caused this difference. The molecular calculation of Bottcher and Flannery is systematically lower than other theory (and all experiments) and has greatly exaggerated the effect of exchange.

Predictions of 2p excitation with exchange are shown in figure 5. These include those of Hanson and Dubois, our results including spin decomposition, and the study of Bottcher and Flannery. The latter results are small, and also disagree with experiment at all energies. The striking feature in this comparison is the large low-energy cross section, which in our case at least, is seen to be due to the triplet process. We find that our cross sections are large because of the triplet promotion effect at close encounter, where the correlation of two ground state
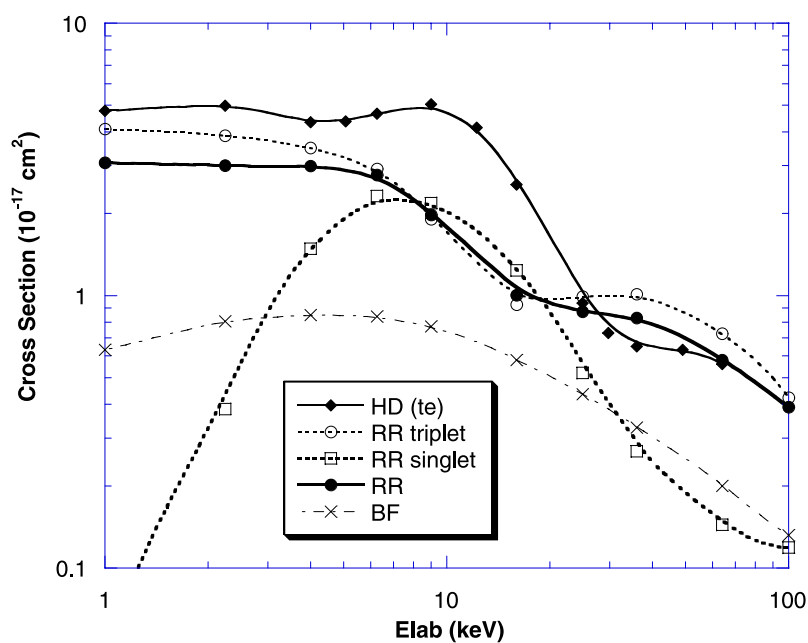

Figure 5. Theoretical excitation cross sections to the projectile 2p level for H on H. RR denotes the present results including the singlet and triplet components, BF denotes Bottcher and Flannery's predictions, and HD (te) denotes Hansen and Dubois's predictions with excitation of the target.

H atoms in triplet symmetry leads to the nearly degenerate 1s2s and 1s2p triplet manifold. Strong coupling among those nearly degenerate levels leads to excitation as well as ionization. This has been exploited by Bent *et al* (1998) and Krstic *et al* (1996) as a means of calculating ionization in H + H scattering.

The triplet united-atom limit at close encounters is difficult for us to solve by the purely numerical methods because of the great difference in size (a factor of eight) of an inner electron that sees a nuclear charge of two, and the outer excited electron that sees charge one. The size of the cross section in our computations was somewhat dependent on the box size and grid resolution with which we could solve the TDSE. The important question is how well we can resolve the coupling among the nearly degenerate molecular states that dominate the wavefunction at low energy. We found it necessary to use a larger box and grid for the triplet to help with this issue. However, in spite of the fact that we obtain a cross section some 50% smaller than Hanson and Dubois at low energy, we never saw any dramatic change in shape of the triplet cross section. Again, no experiments exist at less than 4 keV, although those around 10 keV agree somewhat better with our calculations. Above that energy, the experiments cross over the theories as seen in figure 2.

In figure 6 we show the decomposition of our 2p excitation cross section into angular and exchange components. To be noted is the large minimum in the $2p^0$ triplet at 16 keV, which is large enough to show up in the total 2p cross section. Also of interest is the marked difference in low-energy behaviour of the singlet and triplet cross sections, due to the promotion effect as discussed below.
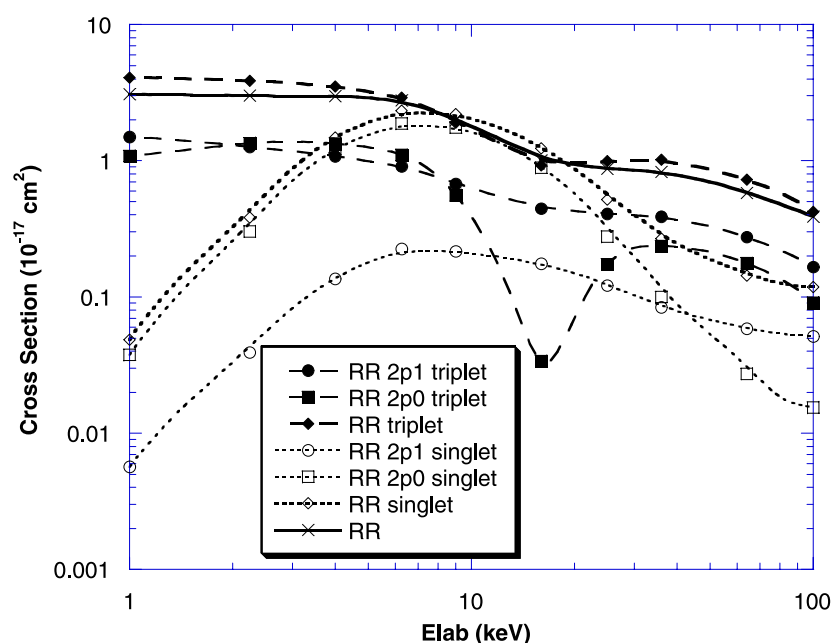
Figure 6. The decomposition of our 2p excitation cross section into singlet, triplet and angular components.

6. Discussion

In the middle of a moderately slow H + H collision event, an electron tends to delocalize from its initial atomic orbital centre to the other centre. This process is greatly different for the singlet and triplet. In the singlet symmetry, this occurs in the presence of the second electron creating a favourable binding situation near the united-atom or molecular limit. This is related to the favoured Hartree–Fock form of the molecular two-electron ground state near the united-atom limit as compared with the valence-bond form preferred at larger separation. As the nuclei separate, a part of the electron orbital on the centre with the other electron is non-adiabatically 'lifted' to the continuum as the heavy particles separate with two electrons localized on the same centre. Since our description does not allow the H⁻ bound state, all parts of a singlet or triplet electron orbital that are transiently trapped on the other centre are ionized in our theory. In triplet symmetry, the delocalization occurs, but with the most important effect being the promotion of the excited orbital towards the continuum as one moves from the molecular binding region toward the united-atom limit. There the time dependence causes a large amount of coupling to excited states. The net effect is the triplet cross sections dominating the lower-energy cross sections for excitation and ionization.

Theoretical studies of H + H collisions have advanced in several aspects, mainly due to the computing power that can now be applied to the problem. In fact, theory is now at the point where the predictions should be quantitative. It is obvious that more experimental work is needed to resolve the differences that appear in the prior work as well as the theory. The inclusion of exchange is crucial to describe the low-energy scattering because of promotional excitation and ionization within the triplet system.

This work provides two contributions to the atomic scattering area. First, it shows that a time-dependent, self-consistent field description of the fully symmetrized two-electron problem is possible, and, secondly, that the method is capable of reasonable predictions of the event without the elaboration of the large basis expansion methods.

Acknowledgments

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