**Excitation and Ionization
in H(1s)-H(1s) Collisions**

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Abstract

Hydrogen atom - hydrogen atom scattering is a prototype for many of the fundamental principles of atomic collisions. In this work we present an approximation to the H+H system for scattering in the intermediate energy regime of 1 to 100 keV. The approximation ignores electron exchange and two-electron excitation by assuming that one of the atoms is frozen in the 1s state. We allow for the evolution of the active electron by numerically solving the 3D Schroedinger equation. The results capture many features of the problem and are in harmony with recent theoretical studies. Excitation and ionization cross sections are computed and compared to other theory and experiment. New insight into the mechanism of excitation and ionization is inferred from the solutions.

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I. Introduction

The collision of two hydrogen atoms is a basic problem in atomic physics that is still under active investigation. Not only is it difficult to do 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. Even restricted to the framework of the impact parameter description, the problem is rife with 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 behavior of the electrons. Several theoretical studies on H+H exist and we will discuss a subset of them in due course. In general we will compare our approximation with what we regard as the most accurate of the available data.

In this work we solve a one electron description of the H+H system (H + "frozen" H) for scattering in the intermediate energy regime of 1 to 100 keV where most of the inelastic processes occur. This energy range corresponds to a relative velocity range of 0.2 to 2 atomic units. In our theoretical description, basis limitations are not an issue for the representation of the electron orbital. By solving the Schrodinger equation in space and time our calculation allows the electron to undergo excitation and ionization without the constraints of an atom-centered atomic basis set. The issue is, of course, the approximation of the two-electron problem as an effective one-electron system. Cross sections are compared to other theory and experiment with results that give information about the importance of electron delocalization during the collision.

II. Theoretical Approach

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

$$\begin{aligned} i\dot{\Psi} &\equiv i\partial\Psi/\partial t = H\Psi \quad , \quad \Psi = \Psi(1,2) \quad , \\ H &= H(1) + H(2) + V_{12} \quad , \\ H(i) &= -\frac{1}{2}\nabla_i^2 - Z_A/|\vec{r}_i - \vec{R}_A(t)| - Z_B/|\vec{r}_i - \vec{R}_B(t)| \quad , \\ V_{12} &= 1/|\vec{r}_1 - \vec{r}_2| \quad . \end{aligned}$$

The nuclear coordinates are prescribed functions of time, which are assumed to be simple rectilinear motion prescribed by an impact parameter b and the relative

velocity. The time variable is implicit in the wave function. The nuclear charges Z_N are set to unity for the H atoms. The partial derivative with respect to time is taken at fixed electron coordinates in a coordinate system whose reference frame is the nuclear geometric center. 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 wave function. 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 restrict the form of the wave function by the ansatz:

$$\Psi(1,2) \approx \chi(\vec{r}_1) \Phi_{1s}(|\vec{r}_2 - \vec{R}_B|)$$

where χ is completely unrestricted in functional form. The Pauli principle is not enforced in this approximation. Φ_{1s} is a product of the initial hydrogenic wave function ϕ_{1s} and a translation factor appropriate for the chosen reference frame. This approximation is a generalization of the studies begun with Bates and Griffing (1954) and quantitatively extended by Flannery (1969) to close coupling, and continuing through the later work of McLaughlin and Bell (1983). It is to be noted that this one-electron picture by nature does not include exchange (Bottcher and Flannery (1970), Ritchie (1971), and the more recent papers to be cited) or double excitation of the two electrons. The TDSE for the active electron is found by variational optimization, equivalent to substitution and projection, to be:

$$\begin{aligned} i\dot{\chi} &= H^{eff} \chi \quad , \quad \chi = \chi(1) \quad , \\ H^{eff} &= H(1) + V^{eff}(1) \quad , \\ H(1) &= -\frac{1}{2}\nabla_1^2 - Z_A / |\vec{r}_1 - \vec{R}_A(t)| - Z_B / |\vec{r}_1 - \vec{R}_B(t)|, \\ V^{eff}(1) &= \int d^3r_2 \phi_{1s}^*(2) 1/|\vec{r}_1 - \vec{r}_2| \phi_{1s}(2) \\ &= 1/r_{1B} - (1 + 1/r_{1B}) \exp(-2r_{1B}). \end{aligned}$$

The initial condition for the active electron is that of a 1s orbital on nucleus A. We note that a concise description of this approximation representing H on H is that we are solving a one electron Hamiltonian with two centers in relative motion where center A is an unscreened and center B is a screened Coulomb potential. The origin of

the electron can be taken to be the geometric center of the nuclei for simplicity. Any other origin simply changes the wave function by an overall phase factor as pointed out by Riley (1973).

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 final channel states, including translation factors as appropriate, after the time-dependent collision is completed:

$$P_f(b) = \int d^3r_1 \Phi_f^*(\vec{r}_1 - \vec{R}_A) \chi(\vec{r}_1),$$

$$\sigma_f = 2\pi \int_0^\infty b db P_f(b) .$$

However the ionization cross section is evaluated from the loss of normalization of the one electron orbital during the collision:

$$\sigma_f = 2\pi \int_0^\infty b db (1 - N(b)) .$$

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

III. The ISOP Method for Numerical Propagation

The numerical method we use is based on an implicit split operator procedure (ISOP) for solving the three-dimensional TDSE using fast Fourier transforms (FFT) as implemented by Ritchie *et al* (1997). This method has been applied to alpha particle-hydrogen atom scattering by Riley and Ritchie (1999). The advantages of the fully numerical ISOP 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. Reviewing this quickly for a general one electron TDSE whose special case is as written above:

$$\dot{\chi} = -iH\chi,$$

$$H = T + V, T = -\frac{1}{2}\nabla^2.$$

The potential V is a function of position and time. The usual exponential split operator procedure (ESOP) of Feit *et al* (1982) formulates the numerical integration as the repeated application of the factored (split) incremental propagator to advance the solution in time:

$$\chi_{t+dt} = \exp(-\frac{1}{2}iT dt) \exp(-iV dt) \exp(-\frac{1}{2}iT dt) \chi_t.$$

This numerical procedure uses the speed of the FFT to convert from the space to momentum representation and back, and in so doing, always applies *diagonal* operators to the wave function. We should add that the ESOP conserves norm but not energy due to the lack of commutation of the incremental propagator with the Hamiltonian. The procedure is correct through order $(dt)^2$ and the truncation error is proportional to commutators of T and V operating on the wave function. In atomic physics applications we found that the truncation error in the ESOP grew faster than we liked with time steps that would have appeared to be adequate for a second-order-accurate method. A large variation in the energy $\langle \chi | H | \chi \rangle / \langle \chi | \chi \rangle$ was an immediate symptom of the error. In order to improve upon the solution, we recalled that the implicit Crank-Nicolson method would be an ideal stable algorithm for a one-space-dimensional problem. Generalization to two space dimensions in the form of the alternating direction implicit method is practical, but three space dimensional solutions are tentative at best (Press *et al*, 1989). We begin by writing down the second-order-accurate, time-symmetric form of the finite difference advance in the TDSE, exactly analogous to the CN procedure:

$$\chi_{t+dt} + \frac{1}{2}iH dt \chi_{t+dt} = \chi_t - \frac{1}{2}iH dt \chi_t.$$

A direct numerical solution appears impractical due to the difficulties in resolving the implicit part of the operator. The truncation error is $O(dt)^3$, which is the same as in the ESOP. What is desired is to split the space and momentum parts of the Hamiltonian to enable the use of the fast Fourier transform (FFT) as in the ESOP. One way to do this is to rewrite:

$$\chi_{t+dt} = \frac{1 - \frac{1}{2}iHdt}{1 + \frac{1}{2}iHdt} \chi_t$$

and to factor the propagator quotient approximately, all the while preserving accuracy through $O(dt)^2$:

$$\chi_{t+dt} = \left(\frac{1 - \frac{1}{4}iTdt}{1 + \frac{1}{4}iTdt} \right) \left(\frac{1 - \frac{1}{2}iVdt}{1 + \frac{1}{2}iVdt} \right) \left(\frac{1 - \frac{1}{4}iTdt}{1 + \frac{1}{4}iTdt} \right) \chi_t.$$

The time in the central factor is taken to be at the midpoint of the interval rather than the present and advanced times. This was found to make a slight improvement in the accuracy of the method.

The advantage of this factorization is that the operator is now a product of momentum and coordinate dependencies which allows the FFT procedure to be used as in the ESOP with only diagonal 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 wave function 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 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). Other factorizations of the incremental propagator may be better - we do not have any unique prescription for factoring the propagator.

An item that needs to be resolved is the use of a Cartesian grid with the singular coulomb potential. There can be an arbitrarily large error introduced in the potential operator if a grid point lies too near the singularity of a moving potential. The following argument is used for the modification of the Coulomb field when used in conjunction with the FFT grids. Consider the integral of the potential over a spherical volume dV of radius $R = (3dV / 4\pi)^{1/3}$ centered about the origin of the potential:

$$\int d^3r \, 1/r = 4\pi \int_0^R r^2 dr \, 1/r = 2\pi R^2.$$

Let $dV = dx dy dz$ be chosen to be the volume of a Cartesian volume element in the grids used for the FFT procedures. If we now *equate* the integral of the potential in the spherical coordinates to the integral of the potential over the Cartesian volume element with a cutoff of r_x imposed in the Coulomb potential, we have

$$2\pi R^2 = (1/r_x) dV = (1/r_x) dx dy dz.$$

We can now solve for r_x using the value of R above:

$$r_x = (2 dV / 9\pi)^{1/3} \approx 0.414 (dx dy dz)^{1/3}.$$

The Coulomb potential $1/r$ is evaluated with the distance r chosen to be $r = \max[r, r_x]$. This bounds the operator and has been successful in practice in our scattering studies. A slight oscillation is sometimes observed in the energy during a collision, but this is small compared to the energy error introduced by the finite grid.

The calculations presented here typically use a representation of 80x80x256 grid points for $\chi(\vec{r})$ in a box of dimension 24x24x80 in Bohr atomic units (a.u.). The interior walls of the box were "coated" with an absorptive optical potential (Kulander 1987) whose profile was a half-Gaussian a few grid points 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 smooth enough and strong enough not to allow reflection. The time increment was typically 0.05 or 0.1 a.u. and the space increment approximately 0.3 a.u. The collision length in z , the coordinate parallel to the relative velocity vector, must be chosen to achieve channel decoupling. All these numerical conditions were developed from exploratory calculations. An example of such convergence studies is given in Figure 1 where we plot the probability of excitation of the level 2 orbitals and the ionization probability at an impact parameter of 0.5 a.u. for varying transverse box dimension and grid size with other parameters held fixed. It is seen that a *reasonable* convergence is obtained for transverse dimension of 24 a.u., with the ionization probability being the most sensitive to box size.

In the calculations of the 2s excitation probabilities, especially at velocities greater than 1 a.u. where the probabilities are 0.01 and smaller, we noticed that the probabilities did not always become and remain small at the larger impact parameters.

This was associated with a lack of stabilization of the 2s amplitudes with final state separation in the post-collision region. We isolated this problem to be a lack of Fourier grid resolution as the nuclei move through the grid. Two remedies were found for this problem. The first was to initialize the travelling orbital prior to the collision by diagonalizing the numerical Hamiltonian in a space consisting of the 1s, 2s, and 3s analytic orbitals. The numerical orbital for the initial state was used to start the integration and analogous numerical orbitals used for the final state projections. The second remedy was to carry a non-interacting 2s orbital "along for the ride" through the collision. The final state projection was then done with this numerical orbital rather than the analytic hydrogenic state with translation factor. Presumably this would not be necessary if we used a finer space grid for the problem.

III. Cross Sections for 2s and 2p Excitation and Ionization

Excitation of the 2s and 2p states has a long history of investigation beginning with the Born calculations of Bates and Griffing (1954). In Figure 2 we compare our results for the excitation cross section of the projectile to the 2s state with experiments of Hill *et al* (1979) and Morgan *et al* (1980), and the recent theory of Hansen and Dubois (1998). The two sets of measurements do not agree well at less than 10 keV so we do not have an experimental benchmark there. The four-atomic-state close coupling calculation of Flannery (1969) is included to show how much the additional freedom in our description of the active orbital changes the cross section. Flannery's calculations, like ours, represent a H plus "frozen" H model of the system. The difference in cross sections is almost a factor of three around the maximum, but the values are converging at high energy as they should. The recent calculations of Hansen and Dubois are those which include "total excitation" (te) of the other center. The agreement of the Hansen and Dubois calculations with the Morgan, Stone, and Mayo data is remarkable. The calculations of Hansen and Dubois which do not include target excitation are in closer agreement with our frozen target results as seen in Figure 2. We do not show the 22 state per center calculations of Shingal *et al* (1989), which, with the Born correction at higher energy, tend to overestimate the experimental data. A comparison with this work is shown in Hansen and Dubois study.

The experimental measurements of Morgan *et al* (1974) and some of the theoretical predictions for excitation of the 2p level are shown in Figure 3. Our results are in qualitative agreement with the Hansen and Dubois (1998) results above 4 keV. In this energy range, the Hansen and Dubois results present a structure that is not

present in the simpler calculations. The 4-state close coupling of Flannery (1969) is shown to see the effect of basis restrictions. This effect is more than a factor of three at less than 10 keV, but his results and ours again tend to converge in the high-energy limit. The Hansen and Dubois results 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. Our one-active-electron results are in error at low energy due to the lack of an adequate description of the “inert” electron and the mechanism of promotional excitation through the united atom triplet symmetry. In other words, although we have delocalization, we cannot generate the proper correlation of singlet and triplet solutions. The study of Borondo *et al* (1987) 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 about a factor of two.

The ionization cross sections are computed by evaluating the total loss of probability of the one electron orbital χ during the collision. This loss is due to absorption of the electron 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 ionization cross section. In Figure 4 we compare our results with the experimental measurements of Gealy and Van Zyl (1987) and 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* of the ionization cross section includes electron symmetry with a 22 state per center atomic basis with translation factors but without double excitation channels. Their results with the “Born correction” are very close to ours, except that our results are missing an oscillatory feature in the 2 to 3 keV region. However neither the experiments or the calculations of Krstic *et al* show this feature. Our calculations cannot predict the ionization cross section reliably when it is less than 10^{-17} cm^2 as the absolute error becomes too large (Riley and Ritchie (1999)) due to numerical resolution.

Overall the ionization cross sections of our one electron approximation are very good in the sense that they agree semi-quantitatively with the best theory. All theoretical studies appear low by a factor of two at 100 keV compared to experiment, though, and we suspect that will not be easily resolved. The fact that the one electron approximation appears semi-quantitative suggests the following mechanism for

ionization. In the middle of a collision event, an electron tends to delocalize from its initial atomic orbital center to the other center. This occurs in the presence of the second electron due to the favorable binding situation near the united atom or molecular limit. This is related to the favored Hartree-Fock form of the molecular two-electron state near the united atom limit as compared to the valence-bond form preferred at larger separation. As the nuclei separate, the part of the active electron orbital residing on the center with the other electron is "lifted" to the continuum as the heavy particles separate. Since our description does not allow the H^- bound state, all parts of the electron orbital that are transiently trapped on the other center are ionized in our theory. In the two-electron description this mechanism is also effective because the H^- state is weakly bound. The detailed time-dependent graphics of our solution indeed show this transient probability density that is localized on the frozen-H center as the nuclei separate.

IV. Discussion

The previous calculations on H+H collisions have progressed in several aspects. The early Born calculations probably should only be considered in the $v > 1$ ($E_{lab} > 25$ keV) regime. The atomic-centered close coupling solutions extended this but only marginally because of the lack of electron configuration rearrangement. The inclusion of exchange is crucial to describe the low energy scattering because of promotional excitation and ionization. Our one-electron study contains aspects of this mechanism and shows the importance of delocalization. In future work we will apply the ISOP procedure to the solution of time-dependent self-consistent field equations for the hydrogen atom – hydrogen atom scattering problem. In so doing we will address many of the effects of electron exchange symmetry that are not included in the present treatment.

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Figure 1. Example of a convergence study. Here the transverse box dimensions are varied with other parameters fixed. The transverse grid for the FFT increased from 64 points to 96 points as the box sides L_x and L_y increased from 20 to 30 a.u. The impact parameter is 0.5 a.u. and the relative collision velocity is 0.5 a.u. The computational box is 80 a.u. in length with a grid of 256 and the active atom is moving on the longitudinal box centerline from -15 to 25 a.u. The various curves denote the probabilities of excitation of atomic states and ionization as labeled.

Figure 2. Excitation cross sections to the projectile 2s state for H on H. MSM denotes the Morgan, Stone, and Mayo experimental data, HGG denotes the Hill, Geddes, and Gilbody measurements, RR denotes the present results, HD denotes the Hansen and Dubois predictions, HD(te) denotes the Hansen and Dubois results including excitation of the target, and F(4S) denotes the four state solution of Flannery. In this and following figures, the smooth curves are chosen to guide the eye across the theoretical data points.

Figure 3. Excitation cross sections to the projectile 2p level for H on H. MGG denotes the Morgan, Geddes, and Gilbody experimental data, RR denotes the present results, HD denotes the Hansen and Dubois predictions with unexcited target, HD (te) denotes their results with excitation of the target, and F(4S) denotes the four state solution of Flannery.

Figure 4. Ionization cross section to the projectile continuum for H on H. GVZ denotes the Gealy and Van Zyl experimental data, McC denotes the McClure measurements, RR denotes the present results, KBS denotes the Krstic, Bent, and Schultz predictions, and SBF(xB) denotes the Shingal, Bransden, and Flower calculations with the Born correction.