Lattice, Time-Dependent Schrödinger Equation Solution for Ion-Atom Collisions

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Utilizing a lattice representation of the wave function and operators, we have solved the time-dependent Schrödinger equation over a wide range of collision energies and impact parameters to study excitation to low-lying states in collisions of protons with atomic hydrogen. The technique circumvents many of the shortcomings of commonly applied close coupling and perturbation theory approaches that are valid only in restricted regimes. Thus, the investigation represents a step towards precise knowledge of the dynamical quantities characterizing this and other fundamental collisions. [S0031-9007(99)09204-2]

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In atomic physics it has been possible to measure and calculate certain quantities with exquisite precision. Witnesses to this fact are the accomplishments of experimental spectroscopy and atomic structure calculations which together are precise enough to test the very fine scale effects of quantum electrodynamics [1]. Such work has been made possible by advances in technique and by the invention and evolution of new technologies such as magneto-optical traps and high-performance computers. From a theoretical point of view, these advances have hinged on several simplifying characteristics. That is, for many situations, the atomic system is described completely by a differential equation of rather simple mathematical structure (the Schrödinger equation), the interaction is simple in form (the Coulomb potential), and the well-developed techniques of eigensolution via basis function expansion and perturbation theory are generally applicable. In contrast, research in nuclear structure or solid state physics, for example, must contend with not knowing the precise form of the many-body interaction of the nuclear or condensed matter constituents.

However, for dynamic problems such as atomic collisions or interactions of atoms with strong time-varying electromagnetic fields, even for systems with only one or a few electrons, such a high precision description of observables has not often been achieved in calculations. The necessity to thoroughly describe the possibly multielectron, multicenter [2] continuum, the need to represent processes driven through channels involving states on more than one center, or involving the interaction among electrons, are examples of inherent complexities that limit their accuracy. Therefore, to treat ion-atom collisions, a wide range of theoretical approaches has been devised which are applicable in various regimes.

At high energies, perturbation theories such as the Born approximation or its improvements through use of distorted waves have been successful. When the interaction is longer with stronger coupling, such as at intermediate energies, other approaches are generally required. These include atomic orbital close coupling, with one- (ion or atom), two- (ion and atom), or even three- (ion, atom, and saddle point) center bases, with or without inclusion of pseudocontinuum states, or even classical or semiclassical methods. At low collision energies, the dynamic electronic wave function is reasonably characterized by molecular orbital close coupling, although somewhat arbitrary electron translation factors must be utilized and the continuum is very difficult to include. So-called adiabatic approaches, such as the method of hidden crossings, are also useful at low energies. All of these approaches have significant merits and particular limitations.

Our goal has been to develop an approach which can overcome many of the difficulties associated with these methods by solving the time-dependent Schrödinger equation (TDSE) as directly as possible on a numerical lattice, taking advantage of modern techniques of computational science. Many methods satisfy these general criteria, such as discrete variable representations and finite-difference, finite-element, and basis-spline approaches. However, the implementations and properties of these methods can be quite different. For example, the computational speed of the fast Fourier transform (FFT) and the highly accurate representation of the derivative operations Fourier expansions provide has led us to adopt the method of Fourier collocation in which the wave function and operators are represented implicitly in terms of Fourier functions.

Early applications of this method treating $\bar{p} + \mathrm{H}$ [3] and $\bar{p} + \mathrm{He}^+$ [4] collisions provided encouraging results. They demonstrated the utility of directly solving the TDSE by helping to elucidate the novel underlying dynamics of these collision systems and by providing results with essentially the same level of precision as the best standard methods. They also served to bridge the energy ranges in which different methods are applicable. Those studies were performed only for a limited number of impact energies and considered systems in which

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the impacting ion was an antiproton and thus did not have the same range of channels and mechanisms present for positive particle impact. Thus, a more strenuous test of the lattice approach is the study of p + H collisions in which the projectile-center channels are, in fact, crucial.

We have used the lattice method [5] to solve the TDSE for the electronic wave function on a three-dimensional grid for p + H collisions over a wide range of impact energies and impact parameters. To facilitate comparison with the best available theories and experiments, we have concentrated on target excitation to low-lying states. Specifically, employing straightline projectile trajectories, we have considered 30 laboratory frame impact energies between 1 and 1000 keV, roughly evenly spaced logarithmically. For the higher energies, as few as ten or twelve impact parameters were considered due to the smoothness of the behavior of the excitation probabilities as a function of impact parameter. For the lower energies, the probabilities often display several local maxima and thus as many as 20 or 25 impact parameters were needed to obtain convergence. At the high impact energies, the projectile may be started as close as, say, 15 a.u. from the target, and the time propagation carried out for as little as 200 to 300 a.u. since within that period the excitation probabilities as a function of time converge. At low collision energy, the projectile must start much farther from the target and the final state takes longer to converge due to the strong Stark oscillations (beating between states) induced by the slowly receding projectile. The numerical grid extended over a range of 52 a.u. in each of the three Cartesian directions, with 135 points uniformly spaced along each direction. A 225^3 lattice was used, extending over a range of 60 a.u. along each direction, for the lowest collision energies where a slightly smaller mesh spacing and larger overall box size were needed. In total, the number of floating point operations used in the present calculations was on the order of 10^{15}. All of the calculations were performed on midlevel computing systems such as a SGI Power Challenge or Cray J90.

At the end of each time propagation, the excitation probabilities were determined by projection of the wave function onto each of the lowest lattice eigenstates. Flux to the continuum or carried by the projectile as a result of charge transfer was removed through the use of a complex potential localized at the edge of the box [5]. This potential was empirically determined to reduce reflections. Also, in the absence of the projectile interaction, it was verified that the complex potential did not significantly reduce the probability density of initial test excited states.

Figure 1 compares the present lattice TDSE (LTDSE) results for excitation with the best available low- and high-energy theories for $2s$ and $2p$ excitation. It is expected that the molecular orbital close coupling (MOCC) approach would be accurate at low energies. The principal drawbacks of this approach are its reliance on relatively arbitrary electron-translation factors at energies above about 1 keV and the lack of a convenient way to include effects due to loss to the continuum. The figure shows good agreement between the LTDSE and MOCC results of Kimura and Thorson [6], deviating by, at most, 15% (at 1 keV), but also shows the failure of the MOCC calculation to predict the downturn of the cross section above about 4 keV. Similarly, for $2p$ excitation, we compare in this figure the LTDSE results with those of Janev and Krstić [7] computed using the method of hidden crossings (HC). This method is expected to be valid in the limit of low velocities. It, too, fails to predict the downturn of the cross section above 4 keV.

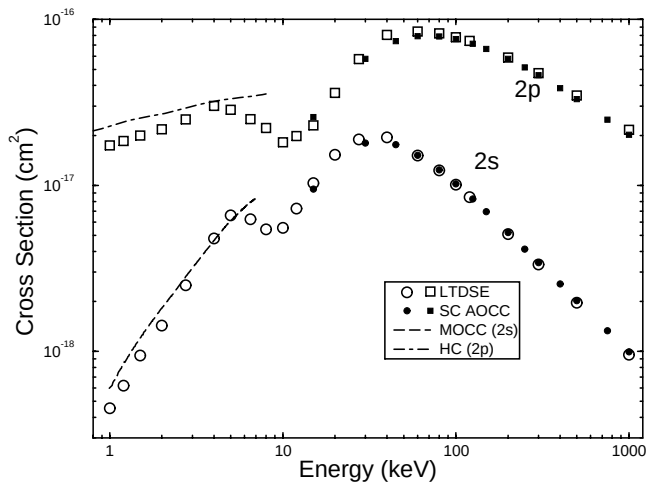

FIG. 1. Comparison of the LTDSE results for $2s$ (circles) and $2p$ (squares) excitation in H^+ + H collisions with other approaches applicable at low- (MOCC [6], HC [7]) and intermediate- to high- (SC AOCC [8]) collision energy.

At high energies, excellent agreement is found between the single-center atomic orbital close coupling (SC AOCC) treatment of Ford *et al.* [8] and the LTDSE results for both $2s$ and $2p$ excitation, differing by between 2.5% and 6% at high energies, but by as much as 9% at intermediate energies. Significantly, neither the low-energy nor high-energy theories reproduce the oscillation of the cross sections between about 5 to 15 keV. Fritsch and Lin [9] have previously attributed the oscillation of the $2p$ cross section to the superposition of two mechanisms for excitation—rotational coupling dominant at low energies and radial coupling dominant at high energies.

The rotational coupling channel is particularly strong in this system and leads to a dominance of $2p_{\pm 1}$ excitation at low energies. Fritsch and Lin's calculations also showed two oscillations, or plateaus, in the $2s$ and $2p_0$ excitation cross sections at low energies that suggest a connection with our recent analysis [10] of the origins of the predominantly radial coupling driven oscillations in other systems. We expect this kind of oscillation to be ubiquitous for ion-hydrogen and possibly other ion-atom

inelastic collisions. In brief, during the time in which the saddle point of the potential is below the initial binding energy, the electronic density swaps between the target and projectile through the resonant or nearly resonant projectile state. Promotion to either a higher state of the target, the projectile, or of the continuum occurs at small distances, terminating the swapping. This leads to a kind of orbital timing which accounts for the oscillation's position along the energy axis. A quantum mechanical analysis formalizes this classical picture in terms of the relevant interfering pathways along the dominant molecular routes describing these processes.

In Figs. 2 and 3 we provide a comparison of LTDSE results for $2s$ and $2p$ excitation, respectively, with those of a wide range of theories and experiments. Kimura and Lane [15] have presented a similar comparison of the $2s$ excitation data available before 1970. Those results consisted of close coupling using a few states and perturbation theory, and display a very wide spread of results that we do not repeat here. Figure 2 shows that the measurements of Morgan *et al.* [16] and Higgins *et al.* [17] fit well the LTDSE results between 5 and 10 keV, but that between 10 and 100 keV the experiments are systematically lower. For $2p$ excitation, good agreement through the entire energy range is found between the LTDSE results and the experimental results, except at the lowest energies where the LTDSE results are systematically below the early experiments of Stebbings *et al.* [18] and Kondow *et al.* [19].

Also notable are the two-center (TC) AOCC calculations of Slim and Ermolaev [20] which display unphysical oscillations, pointed out by others [21] as being due to over-completeness of the two-center AO expansions. The triple-center AOCC results of McLaughlin *et al.* [22] reproduce the low-energy part of the LTDSE results, but then display exaggerated or unphysical oscillations at higher energies. Surprisingly, the recent eikonal time-dependent Hartree-Fock (TDHF) approach of Runge and Micha [23] differs greatly in magnitude and shape from the LTDSE results. Earlier theories such as the two-center Sturmian (TC Sturmian) results of Shakeshaft [24] or AO^+ results of Fritsch and Lin [25] agree well with the LTDSE results in limited ranges of energy, but differ significantly in others. In summary, the LTDSE results provide a bridge between the best available theoretical results at low, intermediate, and high energy and, in fact, display a level of precision comparable to the best theories. Other approaches either vary significantly from this behavior or agree reasonably with it in only very limited energy ranges.

Figure 4 compares the LTDSE results for $3s$, $3p$, and $3d$ excitation with the best available low- and high-energy results. Again, very good agreement with the SC AOCC

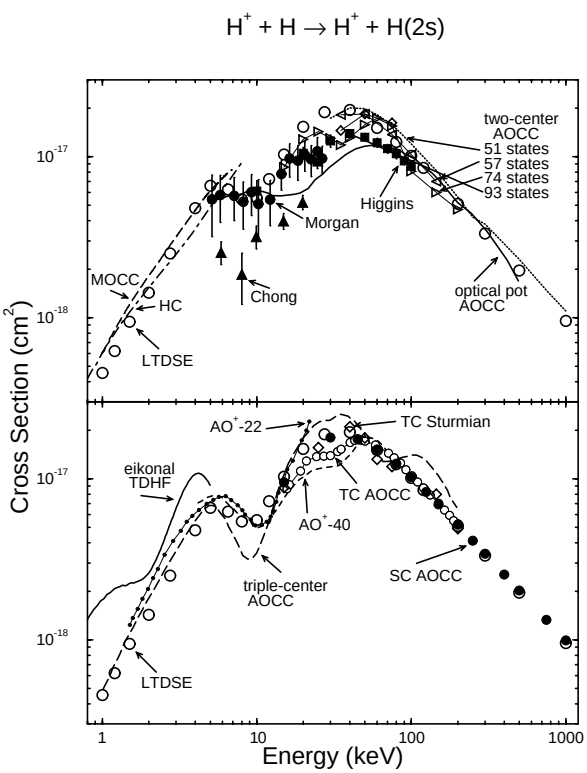

FIG. 2. Comparison of the LTDSE results for $2s$ (circles) excitation with various other theories and experiments as described in the text. Not mentioned in the text are the experimental results of Chong and Fite [11], the optical potential results of Lüdde and Dreizler [12], and the two-center (TC) AOCC calculations of Kuang and Lin [13].

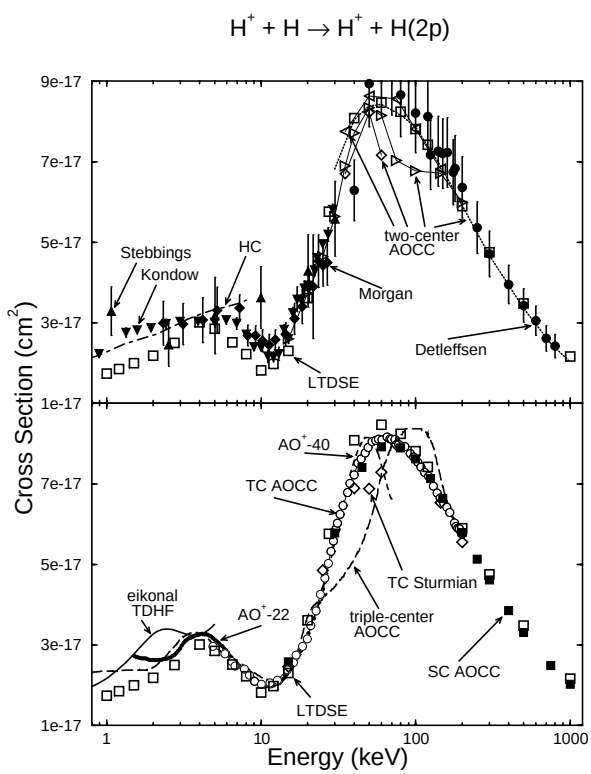

FIG. 3. Same as Fig. 2 except for $2p$ (squares) excitation. Not mentioned in the text are the experimental measurements of Detleffsen *et al.* [14].

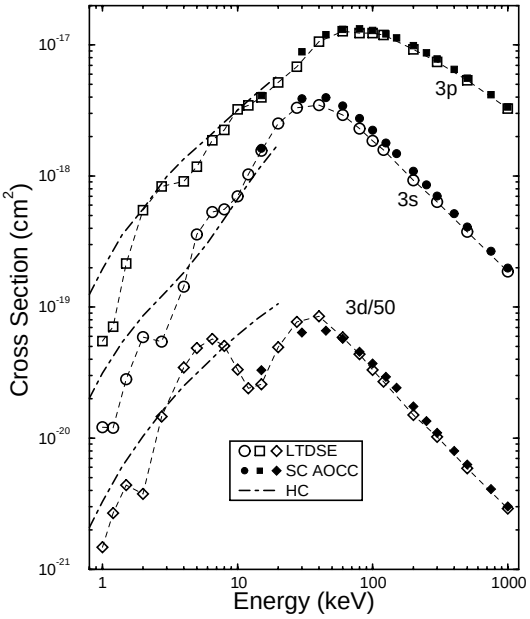

FIG. 4. The same as Fig. 1 except for excitation to the $3s$ (circles), $3p$ (squares), and $3d$ (diamonds) states. Note that the 3d results have been divided by a factor of 50 for clarity of the displayed curves.

calculations [8] is found at high energy, and at low energy the HC results [7] approximate well the LTDSE results in the sense of an average over the oscillatory behavior of the cross sections since they lack a full treatment of the phase. It will be of significant interest to explore the origins of these oscillations and seek what we expect will be a correspondence with the previous explanation [10].

Extension of these excitation calculations to larger values of principal quantum numbers or for projectile-centered states (i.e., charge transfer [26]) is possible, either through increased box size or use of alternate methods such as nonuniform mesh spacing or other coordinate systems. Similarly, lower impact energies could be considered by coupling a nuclear Schrödinger equation solution to the electronic motion to account for the effects of nonstraightline projectile trajectories important for very slow collisions.

For the present case, our comparisons with the best available theories and our analysis of the convergence of our results with respect to time of propagation, number, and range of impact parameters, box size, and mesh spacing lead us to believe that the LTDSE results are uncertain by about 5% at the highest energies, 7% at intermediate energies, and about 10% at the lowest energies. Owing to the general flexibility of this approach, application to other atomic problems such as collisions in strong electromagnetic fields and treatment of the continuum electron production, hold significant promise for further investigations.

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