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LETTER TO THE EDITOR

Electron-impact ionization of H_2^+ using a time-dependent close-coupling method

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Abstract
The first application of the time-dependent close-coupling method to electron–molecule scattering is used to calculate electron-impact ionization cross sections for H_2^+. The time-dependent Schrödinger equation for the six-dimensional wavefunction is reduced to a set of close-coupled equations on a four-dimensional numerical lattice in $(r_1, \theta_1, r_2, \theta_2)$ centre-of-mass spherical polar coordinates. When the non-perturbative close-coupling results for low lM angular momenta are combined with perturbative distorted-wave results for high lM angular momenta, the resulting *ab initio* ionization cross sections are found to be in excellent agreement with experimental measurements in the intermediate energy range.

Accurate knowledge of the strength of electron-impact ionization processes for molecules and their ions is important in many different areas of physics and chemistry, with a number of applications in laboratory and astrophysical plasma science. In particular, electron ionization of simple molecules containing one or more H atoms is important in understanding edge plasma dynamics in controlled fusion experiments [1]. In the past a number of *ab initio* theoretical methods have been developed to treat electron-impact excitation of molecules and their ions at low energies [2]. Although semi-empirical methods based on binary encounter theory have been extended from atoms [3] to molecules [4, 5], only a limited number of *ab initio* theoretical methods have been developed to treat electron-impact ionization of molecules at energies near the peak of their cross sections; the so-called intermediate energy regime. Recently, perturbative distorted-wave methods [6, 7] have been applied to the electron ionization of H_2^+, while a non-perturbative *R*-matrix with pseudo-states method [8, 9] has been applied to the electron ionization of H_2 and H_3^+.

In this letter, we present a time-dependent close-coupling method which is used to calculate the electron-impact ionization cross section for H_2^+. The time-dependent Schrödinger equation for the six-dimensional wavefunction of a two-electron molecular system is reduced to a set of close-coupled equations on a four-dimensional numerical lattice in $(r_1, \theta_1, r_2, \theta_2)$ centre-of-mass spherical polar coordinates. In our calculation for H_2^+, we employ the fixed-nuclei approximation. The molecular time-dependent close-coupling method has previously

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been used to calculate the double photoionization cross section for H_2 at a fixed internuclear distance [10]. Unless otherwise stated, all quantities are given in atomic units.

Due to the reduced symmetry of molecules, the time-dependent wavefunction for a given MS symmetry is expanded in products of rotation functions:

$$\psi(\vec{r}_1, \vec{r}_2, t) = \sum_{m_1, m_2} \frac{P^{\mathrm{MS}}_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t)}{r_1 r_2 \sqrt{\sin\theta_1}\sqrt{\sin\theta_2}} \Phi_{m_1}(\phi_1)\Phi_{m_2}(\phi_2), \tag{1}$$

where $\Phi(\phi) = \frac{\mathrm{e}^{\mathrm{i}m\phi}}{\sqrt{2\pi}}$ and $M = m_1 + m_2$. The angular reduction of the time-dependent Schrödinger equation for the two-electron wavefunction of equation (1) yields a set of time-dependent close-coupled partial differential equations for each MS symmetry:

$$\begin{aligned} \mathrm{i}\frac{\partial P^{\mathrm{MS}}_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t)}{\partial t} &= T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) P^{\mathrm{MS}}_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t) \\ &\quad + \sum_{m_1', m_2'} V^{M}_{m_1 m_2, m_1' m_2'}(r_1, \theta_1, r_2, \theta_2) P^{\mathrm{MS}}_{m_1' m_2'}(r_1, \theta_1, r_2, \theta_2, t). \end{aligned} \tag{2}$$

The single-particle operator is given by

$$T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) = \sum_{i=1}^{2} (K(r_i) + \bar{K}(r_i, \theta_i) + A_{m_i}(r_i, \theta_i) + N(r_i, \theta_i)), \tag{3}$$

where $K(r_i)$ and $\bar{K}(r_i, \theta_i)$ are the kinetic energy operators,

$$A_{m_i}(r_i, \theta_i) = \frac{m_i^2}{2 r_i^2 \sin^2\theta_i}, \tag{4}$$

$$N(r_i, \theta_i) = -\frac{Z_1}{\sqrt{r_i^2 + \frac{1}{4}R_1^2 - r_i R_1 \cos\theta_i}} - \frac{Z_2}{\sqrt{r_i^2 + \frac{1}{4}R_2^2 + r_i R_2 \cos\theta_i}}, \tag{5}$$

Z_1 and Z_2 are the nuclear atomic numbers, and $R = R_1 + R_2$ is the internuclear separation. The two-particle operator is given by

$$\begin{aligned} V^{M}_{m_1 m_2, m_1' m_2'}(r_1, \theta_1, r_2, \theta_2) &= \sum_{\lambda} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} \sum_{q} \frac{(\lambda - |q|)!}{(\lambda + |q|)!} P_{\lambda}^{|q|}(\cos\theta_1) P_{\lambda}^{|q|}(\cos\theta_2) \\ &\quad \times \langle (m_1, m_2)M | \mathrm{e}^{\mathrm{i}q(\phi_2 - \phi_1)} | (m_1', m_2')M \rangle, \end{aligned} \tag{6}$$

where $P_{\lambda}^{|q|}(\cos\theta)$ is an associated Legendre function.

The time-dependent close-coupled equations, equations (2)–(6), are solved using standard numerical methods to obtain a discrete representation of the wavefunctions, $P^{\mathrm{MS}}_{m_1 m_2}$, and the operators, $T^{M}_{m_1 m_2}$ and $V^{M}_{m_1 m_2, m_1' m_2'}$, on a four-dimensional lattice. For a low-order finite difference representation, the variational principle yields kinetic energy operators given by

$$(K(r)P(r, \theta, r', \theta', t))_{i,j,i',j'} = -\frac{1}{2}\left(\frac{c_i P_{i+1,j,i',j'}(t) + c_{i-1} P_{i-1,j,i',j'}(t) - \bar{c}_i P_{i,j,i',j'}(t)}{\Delta r^2}\right) \tag{7}$$

where

$$c_i = \frac{r^2_{i+\frac{1}{2}}}{r_i r_{i+1}}, \qquad \bar{c}_i = \frac{\left(r^2_{i+\frac{1}{2}} + r^2_{i-\frac{1}{2}}\right)}{r_i^2},$$

and

$$\begin{aligned} &(\bar{K}(r, \theta)P(r, \theta, r', \theta', t))_{i,j,i',j'} \\ &\qquad = -\frac{1}{2r_i^2}\left(\frac{d_j P_{i,j+1,i',j'}(t) + d_{j-1} P_{i,j-1,i',j'}(t) - \bar{d}_j P_{i,j,i',j'}(t)}{\Delta\theta^2}\right), \end{aligned} \tag{8}$$

where

$$d_j = \frac{\sin\theta_{j+\frac{1}{2}}}{\sqrt{\sin\theta_j \sin\theta_{j+1}}} \qquad \text{and} \qquad \bar{d}_j = \frac{\left(\sin\theta_{j+\frac{1}{2}} + \sin\theta_{j-\frac{1}{2}}\right)}{\sin\theta_j}.$$

In both equations (7) and (8), $P_{i,j,i',j'}(t) = P(r_i, \theta_j, r_{i'}, \theta_{j'}, t)$. The coefficients reflect the adoption of half-spacing in both coordinate directions so that the proper boundary conditions may easily be applied. Our implementation on massively parallel computers is to partition the radial coordinates, (r_1, r_2), over the many processors.

The initial condition for the solution of the time-dependent close-coupling equations is given by

$$\begin{aligned} P^{\mathrm{MS}}_{m_1m_2}(r_1, \theta_1, r_2, \theta_2, t = 0) &= \sqrt{\tfrac{1}{2}}(P_{1s0}(r_1, \theta_1) G_{k_0l_0M}(r_2, \theta_2)\delta_{m_1,0}\delta_{m_2,M} \\ &\quad + (-1)^S G_{k_0l_0M}(r_1, \theta_1) P_{1s0}(r_2, \theta_2)\delta_{m_1,M}\delta_{m_2,0}), \end{aligned} \tag{9}$$

where $P_{1s0}(r, \theta)$ is the ground-state wavefunction for H_2^+. The Gaussian wavepacket is given by

$$G_{k_0l_0m}(r, \theta) = \frac{\mathrm{e}^{-\frac{(r-a)^2}{2w^2}}}{(w^2\pi)^{\frac{1}{4}}} \,\mathrm{e}^{-\mathrm{i}(k_0r - \frac{l_0\pi}{2})}\sqrt{2\pi \sin\theta}\, Y_{l_0m}(\theta, \phi = 0), \tag{10}$$

where a is the localization radius, w is the packet width, l_0 is the incident angular momentum, and the incident energy equals $\frac{k_0^2}{2}$. The time-dependent close-coupling equations are propagated forward in time using an implicit algorithm:

$$\begin{aligned} P^{\mathrm{MS}}_{m_1m_2}(t + \Delta t) &= \sum_{m_1',m_2'} \mathrm{e}^{-\mathrm{i}\frac{\Delta t}{2} V^M_{m_1m_2,m_1'm_2'}} \left(1 + \mathrm{i}\frac{\Delta t}{2} U(1)\right)^{-1} \left(1 + \mathrm{i}\frac{\Delta t}{2} \bar{U}_{m_1'}(1)\right)^{-1} \\ &\quad \times \left(1 + \mathrm{i}\frac{\Delta t}{2} U(2)\right)^{-1} \left(1 + \mathrm{i}\frac{\Delta t}{2} \bar{U}_{m_2'}(2)\right)^{-1} \left(1 - \mathrm{i}\frac{\Delta t}{2} \bar{U}_{m_2'}(2)\right) \\ &\quad \times \left(1 - \mathrm{i}\frac{\Delta t}{2} U(2)\right) \left(1 - \mathrm{i}\frac{\Delta t}{2} \bar{U}_{m_1'}(1)\right) \left(1 - \mathrm{i}\frac{\Delta t}{2} U(1)\right) \\ &\quad \times \sum_{m_1'',m_2''} \mathrm{e}^{-\mathrm{i}\frac{\Delta t}{2} V^M_{m_1'm_2',m_1''m_2''}} P^{\mathrm{MS}}_{m_1''m_2''}(t), \end{aligned} \tag{11}$$

where

$$U(i) = K(r_i) + N(r_i, \theta_i) \qquad \text{and} \qquad \bar{U}_{m_i}(i) = \bar{K}(r_i, \theta_i) + A_{m_i}(r_i, \theta_i).$$

Probabilities for all the inelastic collision processes possible are obtained by $t \to \infty$ projection onto bound wavefunctions. Excitation probabilities are given by

$$\begin{aligned} \mathcal{P}^{\mathrm{MS}}_{nlm} &= 2\sum_{m'} \int_0^\infty \mathrm{d}r_1 \int_0^\pi \mathrm{d}\theta_1 \left| \int_0^\infty \mathrm{d}r_2 \int_0^\pi \mathrm{d}\theta_2 P^{\mathrm{MS}}_{m'm}(r_1, \theta_1, r_2, \theta_2, t) P_{nl|m|}(r_2, \theta_2) \right|^2 \\ &\quad - \sum_{n'l'm'} \left| \int_0^\infty \mathrm{d}r_1 \int_0^\pi \mathrm{d}\theta_1 \int_0^\infty \mathrm{d}r_2 \int_0^\pi \mathrm{d}\theta_2 P^{\mathrm{MS}}_{m'm}(r_1, \theta_1, r_2, \theta_2, t) \right. \\ &\quad \left. \times P_{n'l'|m'|}(r_1, \theta_1) P_{nl|m|}(r_2, \theta_2) \right|^2, \end{aligned} \tag{12}$$

Table 1. Electron-impact partial ionization cross sections for H_2^+. TDCC: time-dependent close-coupling results, DW: distorted-wave results (cross sections in Kb = 1.0×10^{-21} cm^2).

		TDCC			DW		
M	l_0	50 eV	75 eV	100 eV	50 eV	75 eV	100 eV
0	0	356	417	379	692	608	479
0	1	419	421	347	654	536	410
0	2	502	533	429	750	644	482
0	3	361	414	368	513	468	385
0	4	230	289	273	331	324	279
0	5	122	192	196	209	227	204
0	6				104	143	142
0	7				46	85	95
0	8				19	47	58
0	9				8	24	34
1	1	385	426	373	740	636	493
1	2	352	374	320	542	479	384
1	3	338	360	304	517	443	347
1	4	212	266	246	336	327	279
1	5	112	174	179	207	228	204
1	6				103	142	141
1	7				45	84	94
1	8				19	46	57
1	9				8	24	34
2	2	398	420	357	750	619	472
2	3	321	354	307	536	462	365
2	4	198	259	244	342	334	282
2	5	109	172	177	203	227	206
2	6				100	141	141
2	7				45	83	94
2	8				19	46	57
2	9				7	24	34

and the ionization probability is given by

$$\mathcal{P}_{\rm ion}^{\rm MS} = 1 - \sum_{nlm} \mathcal{P}_{nlm}^{\rm MS} - \sum_{nlm} \sum_{n'l'm'} \bigg| \int_0^\infty {\rm d}r_1 \int_0^\pi {\rm d}\theta_1 \int_0^\infty {\rm d}r_2 \int_0^\pi {\rm d}\theta_2 \times P_{mm'}^{\rm MS}(r_1, \theta_1, r_2, \theta_2, t) P_{nl|m|}(r_1, \theta_1) P_{n'l'|m'|}(r_2, \theta_2) \bigg|^2, \tag{13}$$

where the bound-state wavefunctions, $P_{nl|m|}(r, \theta)$, are obtained by direct diagonalization of the one-electron Hamiltonian:

$$H_m(r, \theta) = K(r) + \bar{K}(r, \theta) + A_m(r, \theta) + N(r, \theta). \tag{14}$$

The total cross section for excitation or ionization is given by

$$\sigma = \frac{\pi}{4k_0^2} \sum_{M,S,l_0} (2S+1)\mathcal{P}^{\rm MS}. \tag{15}$$

The molecular time-dependent close-coupling method, outlined above, is used to calculate the electron-impact ionization cross section for H_2^+ at an internuclear separation of $R = 2.0$. We employ a $192 \times 16 \times 192 \times 16$ point lattice with a uniform radial mesh spacing of $\Delta r = 0.2$

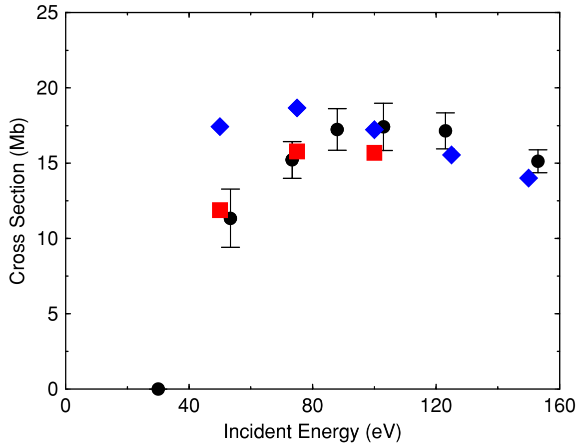

Figure 1. Electron-impact total ionization cross sections for H_2^+. Solid squares: close-coupling/distorted-wave results, solid diamonds: pure distorted-wave results, solid circles: experimental measurements [11] (cross sections in Mb = 1.0×10^{-18} cm^2).

from 0 to 38.4 in both r_1 and r_2 and a uniform mesh spacing of $\Delta\theta = 0.0625\pi$ from 0 to π in both θ_1 and θ_2. Five coupled channels are employed for the $M = 0$ and $M = 1$ symmetries, while six coupled channels are employed for the $M = 2$ symmetry. In table 1 we compare the non-perturbative close-coupling partial cross section results with perturbative distorted-wave results, obtained using an expansion in prolate spheroidal coordinates [6], at incident electron energies of 50 eV, 75 eV and 100 eV. Each partial cross section for M and l_0 is summed over the two-spin angular momentum numbers, $S = 0$ and $S = 1$. The partial cross sections for $-M$ are, of course, identical to those shown. For 100 eV incident energy, the close-coupling and distorted-wave cross sections for $l_0 = 5$ are in good agreement. For 50 eV and 75 eV incident energies, the contribution to the total M partial cross section is small for $l_0 \geqslant 6$. We also carried out perturbative distorted-wave calculations using an expansion in spherical polar coordinates [7] and found good agreement with the prolate spheroidal distorted-wave results found in table 1.

The electron-impact ionization cross section results for H_2^+ are shown in figure 1. The solid diamonds are perturbative distorted-wave results, obtained using an expansion in prolate spheroidal coordinates. Each total cross section is found by summing partial cross sections for $S = 0$ and $S = 1$, $M = 0$ to $|M| = 16$, and $l_0 = |M|$ to $l_0 = 16$. The solid squares are non-perturbative time-dependent close-coupling results for low lM angular momenta combined with perturbative distorted-wave results for high lM angular momenta. The close-coupling partial cross sections for $S = 0$ and $S = 1$, $M = 0$ to $|M| = 2$, $l_0 = |M|$ to $l_0 = 5$ are topped up using distorted-wave cross sections for $l_0 \geqslant 6$. A simple extrapolation procedure is then used to smoothly join the close-coupling partial cross sections for $|M| \leqslant 2$ with the distorted-wave partial cross sections for $|M| \geqslant 3$ to $|M| = 16$. Overall, the close-coupling/distorted-wave results at relatively low energies and the pure distorted-wave results at relatively high energies are found to be in excellent agreement with the classic experimental measurements of Peart and Dolder [11]. We note that semi-empirical cross section results [4], based on binary encounter theory, are also within the error bars of the experimental measurements over the same energy range.

In summary, we have developed a time-dependent close-coupling method to calculate electron-impact excitation and ionization cross sections for diatomic molecules and their ions. We have applied the molecular time-dependent close-coupling method to calculate the electron ionization cross section for H_2^+. The *ab initio* non-perturbative close-coupling and perturbative distorted-wave results are found to be in excellent agreement with long-standing experimental measurements in the intermediate energy regime. We look forward to applying the molecular time-dependent close-coupling method to calculate excitation and ionization cross sections for a wide variety of diatomic molecules. Our first step will be the electron ionization of H_2 in a frozen core approximation to compare with recent R-matrix pseudo-states calculations [9] and experiment. We also hope to stimulate experimental measurements of energy differential ionization cross sections for which the close-coupling and distorted-wave methods could easily be combined to produce accurate predictions.

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