Complete Collision Data Set for Electrons Scattering on Molecular Hydrogen and its Isotopologues

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MCCC method

The Molecular Convergent Close-Coupling **(MCCC)** method is an ***ab-initio*** method for calculations of electron- and positron-scattering on molecules. At present the method has been applied to the H_2^+ and H_2 molecules, with the generalisation to arbitrary quasi one- and two-electron diatomics planned for the near future.

The defining feature of the MCCC method is the capacity for large-scale **convergence studies** to verify the accuracy of the calculated cross sections.

At a fixed internuclear distance, the total scattering wave function is expanded in terms of the asymptotic channels of the scattering Hamiltonian:

$$\Psi_i^N(\boldsymbol{r}_0,\boldsymbol{r}_1,\boldsymbol{r}_2) = \mathcal{A}\sum_{n=1}^{N} f_n^N(\boldsymbol{r}_0)\Phi_n^N(\boldsymbol{r}_1,\boldsymbol{r}_2) \qquad \langle\Phi_{n'}^N|H_{\rm T}|\Phi_n^N\rangle = \epsilon_n\delta_{n'n},$$

where $\{\Phi_n^N\}_{n=1}^N$ is a set of target (pseudo)states. The projectile wave function is expanded in partial waves up to a maximum angular momentum $L_{\rm max}$, and the scattering-system Schrödinger equation is transformed into a set of coupled Lippmann-Schwinger equations for the partial-wave T matrix:

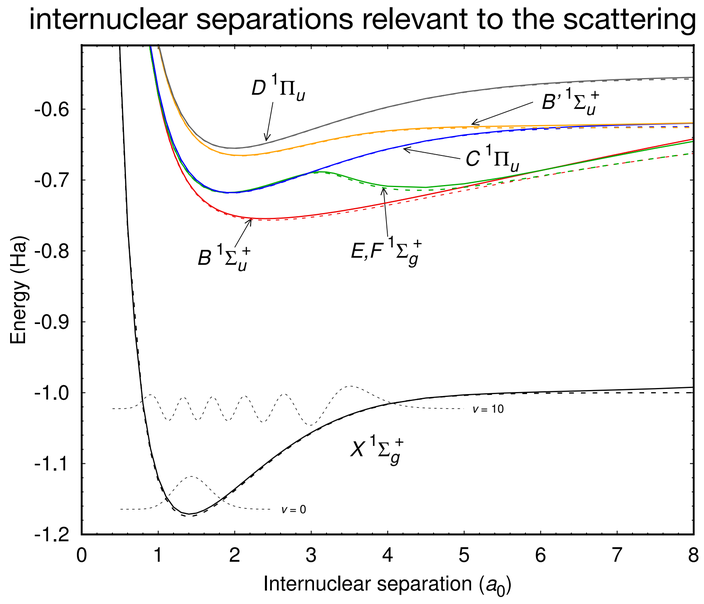
$$\langle q_f L_f M_f\, f\,|T|\,i\,q_i L_i M_i\rangle = \langle q_f L_f M_f\, f\,|V|\,i\,q_i L_i M_i\rangle + \sum_{n=1}^{N}\sum_{L=0}^{L_{\rm max}}\sum_{M=-L}^{L}\int \frac{\langle q_f L_f M_f\, f\,|V|\,n\,qLM\rangle\,\langle qLM\,n\,|T|\,i\,q_i L_i M_i\rangle}{E-\epsilon_n-\epsilon_q+i0}{\rm d}q.$$

Once partial-wave scattering amplitudes are obtained from the T matrix over a range of internuclear distances R, and vibrational wave functions ν_{nv_n} are calculated, **vibrationally-resolved cross sections** are obtained using the **adiabatic-nuclei** approximation:

$$\sigma_{fv_f,iv_i} = \frac{q_{fv_f}}{4\pi q_i}\sum_{L_fM_f,L_iM_i}\left|\langle\nu_{fv_f}|F_{fL_fM_f,iL_iM_i}|\nu_{iv_i}\rangle\right|^2.$$

In all MCCC calculations, **convergence is verified** with respect to the number of target states N and size of the partial-wave expansion $L_{\rm max}$. The partial-wave convergence is accelerated with the use of the **Analytical Born Completion (ABC)** method, which is important for dipole-allowed transitions, particularly those will small excitation thresholds.

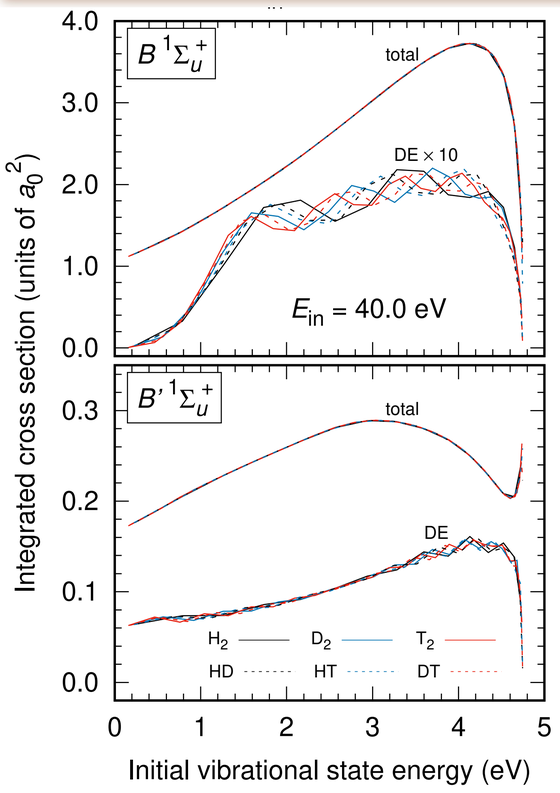
The MCCC method has been developed in **prolate spheroidal coordinates** which allows accurate structure calculations to be performed at all internuclear separations relevant to the scattering calculations.

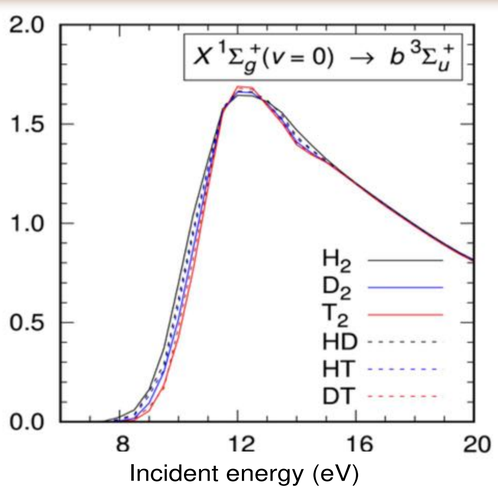


Left: Potential-energy curves for a selection of singlet states from the MCCC structure calculations (solid lines) compared with accurate calculations (dashed lines) from Refs. [1—5].

Also shown are the v = 0 and v = 10 vibrational wave functions in the ground electronic state.

Isotopic effects



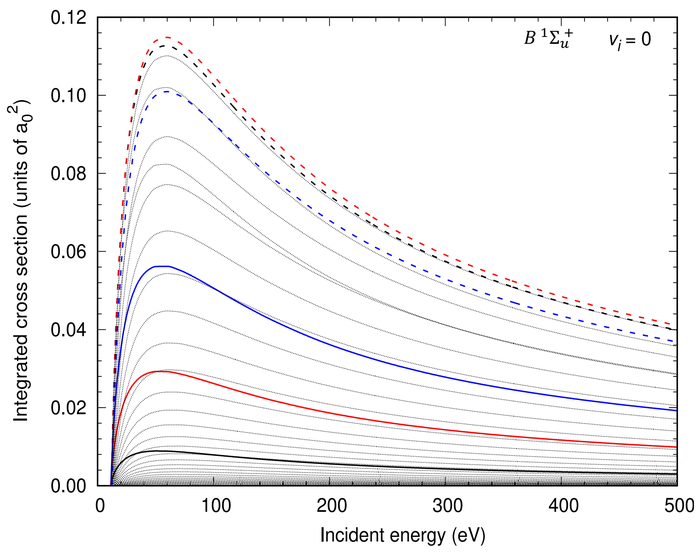


Above: Small isotopic effects for scattering on the ground (electronic and vibrational) state to the dissociative $b\,^3\Sigma_u^+$ state are seen only at near-threshold energies.

Left: Cross sections for total excitation (summed over final vibrational levels) and dissociative excitation of the $B\,^1\Sigma_u^+$ and $B'\,^1\Sigma_u^+$ states of each isotopologues as a function of the initial vibrational state energy (relative to the ground-state equilibrium energy) at 40 eV.

Scattering on the ground electronic state

MCCC calculations have been performed for scattering on all bound vibrational levels of the $X\,^1\Sigma_g^+$ state of H_2, D_2, T_2, HD, HT, and DT. We have considered excitation of all bound vibrational levels and dissociative excitation of the $B\,^1\Sigma_u^+$, $EF\,^1\Sigma_g^+$, $C\,^1\Pi_u$, $B'\,^1\Sigma_u^+$, $GK\,^1\Sigma_g^+$, $I\,^1\Pi_g$, $J\,^1\Delta_g$, $H\,^1\Sigma_g^+$, $b\,^3\Sigma_u^+$, $a\,^3\Sigma_g^+$, $c\,^3\Pi_u$, $e\,^3\Sigma_u^+$, $h\,^3\Sigma_g^+$, $d\,^3\Pi_u$, $g\,^3\Sigma_g^+$, $g\,^3\Sigma_g^+$, $i\,^3\Pi_g$, and $j\,^3\Delta_g$ states, representing all states with $n = 2$—3 in the atomic limit. The number of transitions is in excess of 58,000. Convergence was obtained with N = 210 target electronic states and $L_{\rm max}$ = 10.

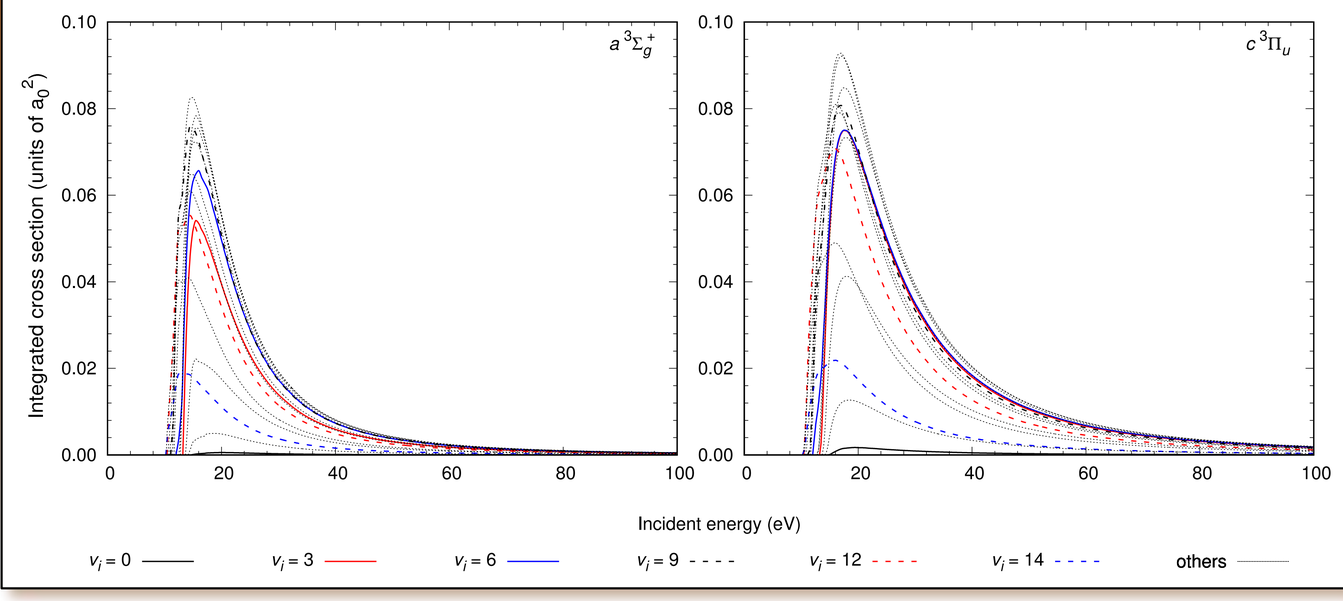


Cross sections are available as numerical values or analytic fits from:

- *Atom. Data Nucl. Data Tables* [6-7]
- *MCCC database:* mccc-db.org
- *HCDB* database: db-amdis.org/hcdb

Left: Cross sections for excitation of the bound vibrational levels in the $B\,^1\Sigma_u^+$ state from the $X\,^1\Sigma_g^+(v_i = 0)$ state of H_2

Below: Dissociative excitation cross sections of the $a\,^3\Sigma_g^+$ and $c\,^3\Pi_u$ states of H_2 for electrons scattering on the bound levels of the $X\,^1\Sigma_g^+$ state.



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Scattering on excited electronic states

Convergence studies for scattering on the n = 2 states ($c\,^3\Pi_u$, $a\,^3\Sigma_g^+$, $B\,^1\Sigma_u^+$, $C\,^1\Pi_u$, and $EF\,^1\Sigma_g^+$) have been performed at the fixed internuclear separation R = 2.0 a_0. Adiabatic-nuclei calculations have been performed for scattering on the v_i = 0 level of each state, including elastic, superelastic, excitation, ionisation, and grand-total cross sections [8].

Convergence was established for all transitions with N = 210 target states, however the partial-wave convergence was found to be much slower than for scattering on the ground electronic state. Even with Analytic Born Completion many dipole-allowed transitions required $L_{\rm max}$ = 20.

Below and Right: Cross sections for scattering on the $c\,^3\Pi_u(v_i = 0)$ state of H_2. Comparison is made with the recent UKRMol+ calculations [8], Schwinger Multichannel (SMC) calculations [9], and Impact-Parameter (IP) calculations [10]. In addition to the adiabatic-nuclei results, fixed-nuclei (R = 2.0) MCCC cross sections are presented using a smaller partial-wave expansion ($L_{\rm max}$ = 6) and without the Analytic Born Completion method for comparison with the UKRMol+ calculations.