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# Adiabatic-nuclei calculations of positron scattering from molecular hydrogen

Mark C. Zammit[1,2],* Dmitry V. Fursa[2], Jeremy S. Savage[2], Igor
Bray[2], Luca Chiari[3], Antonio Zecca[4], and Michael J. Brunger[5]
[1] *Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States*
[2] *Curtin Institute for Computation and Department of Physics,*
*Astronomy and Medical Radiation Sciences, Curtin University, Perth, Western Australia 6102, Australia*
[3] *Department of Physics, Tokyo University of Science,*
*1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan*
[4] *Department of Physics, University of Trento, Via Sommarive 14, Povo, Trento 38123, Italy and*
[5] *School of Chemical and Physical Sciences, Flinders University,*
*GPO Box 2100, Adelaide, South Australia 5001, Australia*
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The single centre adiabatic-nuclei convergent close-coupling method has been used to investigate positron collisions with molecular hydrogen ($H_2$) in the ground and first vibrationally excited state. Cross sections are presented over the energy range from 1 to 1000 eV for elastic scattering, vibrational excitation, total ionisation and the grand total cross section. The present adiabatic-nuclei positron-$H_2$ scattering length was calculated as $A = -2.70\ a_0$ for the ground state and $A = -3.16\ a_0$ for the first vibrationally excited state. The present elastic differential cross sections are also used to "correct" the low-energy grand total cross section measurements of the Trento group [Zecca *et al.* Phys. Rev. A 80, 032702 (2009)] for the forward angle scattering effect. In general the comparison with experiment is good. By performing convergence studies we estimate that our $R_m = 1.448\ a_0$ fixed-nuclei results are converged to within ±5% for the major scattering integrated cross sections.

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## I. INTRODUCTION

Positron scattering from molecular hydrogen ($H_2$) is a natural testing ground for both theoretical and experimental studies of collision physics and transport modelling [1, 2], which underpins several areas of technological and scientific research. Of particular interest is to quantify the radiation damage associated with positron thermalization [1–3] and the subsequent secondary species [4, 5] in positron emission tomography scans. Our focus on $H_2$ is the foundation for molecules of biological relevance.

Another area of active research is to determine the source of positrons in the Milky Way galaxy, where over the last 40 years positron-annihilation radiation has been detected from various directions of the galaxy. In particular, in the central region of our galaxy $\approx 10^{43}$ positrons are produced per second [6]. Given that $H_2$ is the most abundant molecule in interstellar space, studies of positron collisions with $H_2$ are particularly important in modelling positron propagation through the interstellar medium [6].

Positron-$H_2$ scattering experiments have measured the grand total cross section (GTCS) [7–13], direct ionisation cross section (DICS) [14–16], positronium (Ps) formation cross section [10, 13, 14], total ionisation cross section (TICS) [14, 17], electronic $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ excitation cross section [18, 19], vibrational $0 \rightarrow 1$ excitation cross section [19], elastic integrated cross section and low-energy elastic differential cross sections (DCS) [13]. Measurements of the GTCS vary greatly in the low-energy region. These variations are primarily due to different experimental resolution of scattering to forward angles [12, 13, 20]. Theoretical results have been used to "correct" the low-energy measurements of the integrated cross sections for this forward scattering effect [13, 20–22].

Theoretical studies of the positron-molecule scattering problem presents a range of complexities. These include the multi-centre nature of the problem, the difficulty of accounting for the Ps-formation channel and the molecular electronic, vibrational and rotational degrees of freedom. In addition the positron-electron interaction is strongly correlated [23] and needs to be treated accurately at relatively large distances. The two-centre close-coupling method (that includes the positronium formation channels explicitly) is the most consistent way to account for long-range positron-electron correlations. This method, however, is computationally demanding and relatively complicated to implement. Pioneering work was conducted by Hewitt *et al.* [24, 25], Higgins and Burke [26], Mitroy [27], and Walters *et al.* [28], who demonstrated the success of using two-centre expansions consisting of Ps and atomic states. The two-centre approach has also been utilised within the convergent close-coupling (CCC) method formalism for positron-atom scattering [29–31] and recently for positron-$H_2$ scattering [32]. For a recent review see Ref. [33]. To date the only other two-centre coupled-channel positron-molecule ($H_2$) calculations were conducted by Biswas *et al.* [34],

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*electronic address: `mzammit@lanl.gov`

which only included the ground states of $H_2$ and Ps.

Alternatively, the single-centre approach (close-coupling expansion over the target space) can be applied to positron scattering. This method is significantly simpler to implement than the two-centre approach and is found to be computationally very stable. In the single-centre expansion method the long-ranged correlations of the positron-electron potential can be described by a relatively large partial-wave expansion of the potential. These large partial waves are constructed from one-electron orbitals that have large orbital angular momentum. In addition, coupling positive-energy target pseudostates collectively takes into account electron loss, which includes both the direct ionisation and Ps-formation channels. This method is capable of obtaining reliable results for energies outside the small energy region between the Ps-formation and ionisation thresholds [35]. For positron-$H_2$ scattering this method has been used extensively by coupled-channel methods, which include the $R$-matrix with pseudostates (RMPS) [36], Schwinger multichannel (SMC) [37, 38], and Complex Kohn Variational [39] methods. These multichannel calculations have traditionally focused on the low-energy region. In general these methods are in good agreement with old experiments in the energy-range from 0 to 10 eV for the GTCS [8, 40], however they considerably underestimate the most recent measurements of Karwasz *et al.* [11], Zecca *et al.* [12] and Machacek *et al.* [13].

Following Zammit *et al.* [41], which presented the single-centre CCC method and fixed-nuclei results for positron-$H_2$ scattering, we provide details of the method and explicitly demonstrate convergence of the fixed-nuclei results. Calculations are performed within the fixed-nuclei and adiabatic-nuclei approximations. The latter is used to verify the accuracy of the fixed-nuclei calculations and to model scattering from the $v_i = 0$ ground state and $v_i = 1$ first excited vibrational state. Results are presented for the scattering length, GTCS, TICS, vibrational excitation integrated cross section, elastic integrated cross section and elastic DCS.

## II. METHOD

The CCC method is formulated in a spherical coordinate system where the origin is set at the midpoint between the two nuclei and the $z$ axis is chosen to align along the internuclear axis $\boldsymbol{R}$ (body frame). Atomic units are used throughout the paper unless specifically indicated.

### A. Target states

The $H_2$ target electronic Hamiltonian $H_{\mathrm{T}}^{\mathrm{Elec}}$ in the Born-Oppenheimer approximation describes two electrons in the Coulomb potential of two protons that are fixed at a distance $R$ and is defined as

$$H_{\mathrm{T}}^{\mathrm{Elec}} = H_1^{\mathrm{Elec}} + H_2^{\mathrm{Elec}} + V_{12} + 1/R, \tag{1}$$

where $1/R$ is the internuclear Coulomb repulsion term. The one-electron (or positron) electronic Hamiltonian $H_i^{\mathrm{Elec}}$ is

$$H_i^{\mathrm{Elec}} = K_i(r_i) + V_i(\boldsymbol{r}_i;\boldsymbol{R}), \tag{2}$$

where

$$K_i(r_i) = -\frac{1}{2}\frac{d^2}{dr_i^2} + \frac{l(l+1)}{2r_i^2}, \tag{3}$$

$$V_i(\boldsymbol{r}_i;\boldsymbol{R}) = \left(\frac{z_{\mathrm{e}}}{\left|\boldsymbol{r}_i + \frac{\boldsymbol{R}}{2}\right|} + \frac{z_{\mathrm{e}}}{\left|\boldsymbol{r}_i - \frac{\boldsymbol{R}}{2}\right|}\right), \tag{4}$$

$z_{\mathrm{e}} = -1$ for the charge of an electron or $z_{\mathrm{e}} = 1$ for the charge of a positron. The fixed-nuclei electron-nuclei (or positron-nuclei) potential (4) is expanded in partial waves

$$V_i(\boldsymbol{r}_i;\boldsymbol{R}) = 2z_{\mathrm{e}} \sum_{\lambda=0,2,4,..}^{\infty} \sqrt{\frac{4\pi}{(2\lambda+1)}}\, v_\lambda(r_i, R/2) Y_{\lambda 0}(\hat{\boldsymbol{r}}_i), \tag{5}$$

where $v_\lambda(r_i, r_j) = r_<^{\lambda}/r_>^{\lambda+1}$, $r_< = \min(r_i, r_j)$ and $r_> = \max(r_i, r_j)$. $V_{12}$ is the electron-electron (or positron-electron) potential and is expanded in partial waves

$$\begin{aligned} V_{i,j} &= -\frac{z_{\mathrm{e}}}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \\ &= -z_{\mathrm{e}} \sum_{\lambda\mu}^{\infty} (-1)^{\mu} \frac{4\pi}{(2\lambda+1)} \\ &\quad \times v_\lambda(r_i, r_j) Y_{\lambda -\mu}(\hat{\boldsymbol{r}}_i) Y_{\lambda\mu}(\hat{\boldsymbol{r}}_j). \end{aligned} \tag{6}$$

$H_2$ electronic target states are characterised by their orbital angular momentum projection $m$, parity $\pi$ and spin $s$. The target Hamiltonian (1) is diagonalised for each ($m$,$\pi$,$s$) term in a set of antisymmetrised two-electron configurations $\bar{\phi}^{m\pi s}(\mathbf{x}_1, \mathbf{x}_2)$

$$\begin{aligned} \bar{\phi}_{\gamma,\delta}^{m\pi s}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2(1+\delta_{\gamma,\delta})}} \mathcal{A} \\ &\quad \times |\phi_\gamma(\mathbf{x}_1)\phi_\delta(\mathbf{x}_2) : m\pi s m_s\rangle, \end{aligned} \tag{7}$$

where $\mathbf{x}$ is used to denote both the spin and spatial coordinates and the antisymmetrisation operator $\mathcal{A} = 1 - P_{12}$. The one-electron orbitals $\phi(\mathbf{x})$

$$\phi_j^{m'\pi'}(\mathbf{x}) = \frac{1}{r}\varphi_{k_j l_j}(r) Y_{l_j m_j}(\hat{\boldsymbol{r}}) \chi_{m_{s_j}}(\sigma), \tag{8}$$

are represented by Laguerre basis functions with $m_j = m'$, $(-1)^{l_j} = \pi'$ and $\chi_{m_{s_j}}(\sigma)$ is the spin-$\frac{1}{2}$ eigenfunction with angular projection $m_{s_j}$. These Laguerre basis functions have the form

$$\begin{aligned} \varphi_{kl}(r) &= \sqrt{\frac{\alpha_l (k-1)!}{(k+l)(k+2l)!}} (2\alpha_l r)^{l+1} \\ &\quad \times \exp\left(-\alpha_l r\right) L_{k-1}^{2l+1}(2\alpha_l r), \end{aligned} \tag{9}$$

where $\alpha_l$ is the exponential fall-off parameter, $L_{k-1}^{2l+1}$ are the associated Laguerre polynomials of order $2l+1$ and $k$ ranges from 1 to $N_l$. We designate $N_l$ as the number of Laguerre basis functions per orbital angular momentum $l$ up to $l_{\max}$. Matrix elements of the target Hamiltonian are evaluated analytically utilising properties of the Laguerre basis functions [42].

Upon diagonalisation of the $H_2$ target Hamiltonian (1), configuration interaction (CI) coefficients $C_{\gamma,\delta}^{(n)}$ and eigenvalues are obtained. For brevity of notation, the $H_2$ two-electron target states are represented by ordered configurations

$$\begin{aligned}\Phi_n^{m\pi s}(\mathbf{x}_1,\mathbf{x}_2) &= \sum_{\gamma\delta} C_{\gamma,\delta}^{(n)} |\phi_\gamma(\mathbf{x}_1)\phi_\delta(\mathbf{x}_2) : m\pi s m_s\rangle \\ &= \frac{1}{r_1 r_2}\sum_{\gamma\delta} C_{\gamma,\delta}^{(n)} \varphi_\gamma(r_1)\varphi_\delta(r_2) \\ &\quad \times Y_{l_\gamma m_\gamma}(\hat{\boldsymbol{r}}_1) Y_{l_\delta m_\delta}(\hat{\boldsymbol{r}}_2) X_{m_s}^{s}, \end{aligned} \tag{10}$$

where, to account for the antisymmetry of the two-electron wave functions (10), the CI coefficients satisfy $C_{\gamma\delta}^{(n)} = (-1)^s C_{\delta\gamma}^{(n)}$ and

$$X_{m_s}^s = \sum_{m_{s_\gamma} m_{s_\delta}} C^{s m_s}_{\frac{1}{2}m_{s_\gamma},\frac{1}{2}m_{s_\delta}} \chi_{m_{s_\gamma}}(\sigma_1)\chi_{m_{s_\delta}}(\sigma_2). \tag{11}$$

It is important to note that as in the case of $H_2^+$ [43, 44] the single-centre Laguerre basis expansion of $H_2$ leads to slow convergence with respect to the orbital angular momentum $l$ of the basis, in particular, for the $X^1\Sigma_g^+$ ground state. To improve accuracy and save on computational resources, structure calculations are performed in two steps. First, a large Laguerre basis is used to diagonalize the $H_2^+$ target Hamiltonian and generate an accurate $1s\sigma_g$ state of $H_2^+$. Second, a new (smaller) Laguerre basis is produced. The $1s\sigma_g$ orbital of this new basis is replaced by the accurate $1s\sigma_g$ state calculated at the first step. This new basis is then used to construct the antisymmetrised two-electron configurations and diagonalise the $H_2$ target Hamiltonian (1).

### B. Single-centre CCC method

This work utilises the molecular CCC formalism [44] to model positron-$H_2$ scattering within the single-centre close-coupling expansion technique. Here the dependence on $R$ is omitted from the notation unless it is explicitly indicated. In the positron single-centre expansion method the total scattering wave function is expanded in terms of the target ($H_2$) pseudostates

$$\begin{aligned}\Psi_i^{SN(+)}(\mathbf{x}_0,\mathbf{x}_1,\mathbf{x}_2) &= \sum_{n=1}^{N} f_{ni}^{SN(+)}(\mathbf{x}_0)\Phi_n^N(\mathbf{x}_1,\mathbf{x}_2) \\ &\equiv |\psi_i^{SN(+)}\rangle, \end{aligned} \tag{12}$$

where $S$ is the total electron and positron spin of the system, $N$ is the total number of pseudostates included in the close-coupling expansion, (+) denotes outgoing spherical-wave boundary conditions and $i$ denotes the initial state of the system. For positron scattering from the electronic ground state of $H_2$, the close-coupling expansion (12) contains only singlet states of $H_2$ and leads to total spin $S = 1/2$. The expansion in Eq. (12) includes Ps-formation implicitly by including configurations that have an electron and positron in the continuum, which corresponds to both the direct ionisation and Ps-formation channels. Hence the single-centre expansion includes these channels indirectly and as a result the total ionisation cross section (sum of the direct ionisation and Ps-formation cross sections) can be calculated by summing over individual excitation cross sections to positive energy pseudostates.

In the molecular CCC method we start with the body-frame scattering system Schrödinger equation for a fixed internuclear distance $R$

$$(E^{(+)} - H)|\Psi_i^{SN(+)}\rangle = 0, \tag{13}$$

where $E$ is the total energy of the scattering system. Ignoring the kinetic energy of the nuclei (fixed-nuclei approximation), the scattering system Hamiltonian $H$ is defined as

$$H = H_{\mathrm{T}}^{\mathrm{Elec}} + H_0^{\mathrm{Elec}} + V_{01} + V_{02}, \tag{14}$$

where the index 0 denotes the projectile coordinate space and $H_0^{\mathrm{Elec}}$ refers to the positron Hamiltonian given by Eq. (2).

The scattering system asymptotic Hamiltonian $H_{\mathrm{asy}}$ is chosen as

$$H_{\mathrm{asy}} = H_{\mathrm{T}}^{\mathrm{Elec}} + K_0 + U_0, \tag{15}$$

where $U_0$ is an optional short-ranged distorting potential. Details of the short-ranged distorting potential $U_0$ will be given later. For this choice of $H_{\mathrm{asy}}$ the interaction potential (known as the direct term) is

$$\begin{aligned} V_U^{\mathrm{D}} &= V_0 + V_{01} + V_{02} - U_0 \\ &= V_0 + 2V_{01} - U_0, \end{aligned} \tag{16}$$

where the form in Eq. (16) is obtained by using the antisymmetrisation property of the target states.

The CCC method utilises the Green's function approach to transform the Schrödinger equation (13) to the momentum-space Lippmann-Schwinger equation

$$\begin{aligned} |\psi_i^{SN(+)}\rangle &= |\Phi_i^N \boldsymbol{k}_i^{(+)}\rangle \\ &\quad + \sum_{n=1}^{N} \sum\!\!\!\!\!\!\int_{k} d^3k \frac{|\Phi_n^N \boldsymbol{k}^{(-)}\rangle\langle \boldsymbol{k}^{(-)}\Phi_n^N|V_U^{\mathrm{D}}|\psi_i^{SN(+)}\rangle}{E^{(+)} - \varepsilon_k - \varepsilon_n^N + i0}. \end{aligned} \tag{17}$$

Premultiplying Eq. (17) by $\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|V_U^{\mathrm{D}}$, the coupled Lippmann-Schwinger equation for the distorted-wave $T$-

matrix is obtained

$$\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|T_U^{SN}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle = \langle \boldsymbol{k}_f^{(-)}\Phi_f^N|V_U^{\mathrm{D}}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle + \sum_{n=1}^{N}\mathop{\sum\!\!\!\!\!\!\!\int}_{k} d^3k\frac{\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|V_U^{\mathrm{D}}|\Phi_n^N\boldsymbol{k}^{(-)}\rangle\langle \boldsymbol{k}^{(-)}\Phi_n^N|T_U^{SN}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle}{E^{(+)}-\varepsilon_k-\varepsilon_n^N+i0}, \quad (18)$$

where $\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|T_U^{SN}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle \equiv \langle \boldsymbol{k}_f^{(-)}\Phi_f^N|V_U^{\mathrm{D}}|\psi_i^{SN(+)}\rangle$. To solve Eq. (18), projectile distorted-wave functions $|\boldsymbol{k}^{(\pm)}\rangle$ are expanded in partial waves. The partial-wave expansion of the $V$- (or $T$-) matrix for an incident positron with linear momentum $k_i$, orbital angular momentum $L_i$ and orbital angular projection $M_i$ has the form

$$\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|V_U^{\mathrm{D}}|\Phi_i^N\boldsymbol{k}_i^{(\pm)}\rangle = (k_fk_i)^{-1}\sum_{\substack{L_f,L_i\\M_f,M_i}} i^{L_i-L_f}e^{i(\delta_{L_f}\pm\delta_{L_i})} \times V^{\bar{M}\Pi S}_{fL_fM_f,iL_iM_i}(k_f,k_i)Y_{L_fM_f}(\hat{\boldsymbol{k}}_f^{(\mathrm{b})})Y^*_{L_iM_i}(\hat{\boldsymbol{k}}_i^{(\mathrm{b})}). \quad (19)$$

For homonuclear diatomic molecules such as $H_2$ the projectile partial-wave expansion allows one to solve the Lippmann-Schwinger equations per partial-wave of total orbital angular momentum projection $\bar{M} = M_i + m_i = M_f + m_f$, total parity $\Pi = (-1)^{L_i}\pi_i = (-1)^{L_f}\pi_f$ and total spin $S$.

The distorted-wave $T$-matrix $\langle \boldsymbol{k}_f^{(-)}\Phi_f^N|T_U^{SN}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle$ in Eq. (18) is solved via a $K$-matrix formulation, which enforces unitarity. After obtaining $K$-matrix elements and subsequently distorted-wave $T$-matrix elements, the physical $T$-matrix elements ($U_0 = 0$) are extracted from the distorted-wave $T$-matrix elements via

$$\begin{aligned}&\langle \boldsymbol{q}_f\Phi_f^N|T^{SN}|\Phi_i^N\boldsymbol{q}_i\rangle \\ &\quad = \langle \boldsymbol{k}_f^{(-)}\Phi_f^N|T_U^{SN}|\Phi_i^N\boldsymbol{k}_i^{(+)}\rangle + \delta_{f,i}\langle \boldsymbol{k}_f^{(-)}|U_0|\boldsymbol{q}_i\rangle, \quad (20)\end{aligned}$$

where $\boldsymbol{q}$ refers to a plane-wave and results of physical $T$-matrix elements $\langle \boldsymbol{q}_f\Phi_f^N|T^{SN}|\Phi_i^N\boldsymbol{q}_i\rangle$ must be independent of the choice of $U_0$. Body-frame physical $T$-matrix elements are transformed to the lab-frame using standard techniques and cross sections are calculated [45]. For details of the molecular CCC method see Ref. [44].

To solve Eq. (18), $\langle \boldsymbol{k}'^{(-)}\Phi_{n'}^N|V_U^{\mathrm{D}}|\Phi_n^N\boldsymbol{k}^{(\pm)}\rangle$ need to be calculated. For positron/electron-$H_2$ scattering the partial-wave direct $V$-matrix elements are given by

$$\begin{aligned}V^{\bar{M}\Pi S}_{fL_fM_f,iL_iM_i}(k_f,k_i) &= \frac{2}{\pi}\delta_{\bar{M}',\bar{M}}\delta_{\Pi',\Pi}\delta_{S',S}\delta_{s',s} \\ &\times \sum_{\alpha\beta\gamma\delta} C^{(n')}_{\alpha,\beta}C^{(n)}_{\gamma,\delta}\delta_{l_\beta,l_\delta}\delta_{m_\beta,m_\delta}\int_0^\infty dr_2\varphi_\beta(r_2)\varphi_\delta(r_2) \\ &\times \sum_{\lambda\mu}(-1)^{\lambda+\mu}C^{L0}_{L'0,\lambda0}C^{L'M'}_{LM,\lambda-\mu}\left(\delta_{\mu,0}\delta_{l_\alpha,l_\gamma}\delta_{m_\alpha,m_\gamma}\right. \\ &\times \int_0^\infty dr_1\varphi_\alpha(r_1)\varphi_\gamma(r_1)\int_0^\infty dr_0\left[u_{L'}(r_0;k')u_L(r_0;k)\right. \\ &\times \left.(z_{\mathrm{e}}(1+(-1)^\lambda)v_\lambda(r_0,R/2)-\delta_{\lambda,0}U(r_0))\right] \\ &- 2z_{\mathrm{e}}(-1)^\lambda C^{l_\gamma0}_{l_\alpha0,\lambda0}C^{l_\alpha m_\alpha}_{l_\gamma m_\gamma,\lambda\mu}\int dr_0dr_1\left[u_{L'}(r_0;k')\right. \\ &\times \left.\left.\varphi_\alpha(r_1)v_\lambda(r_0,r_1)u_L(r_0;k)\varphi_\gamma(r_1)\right]\right). \quad (21)\end{aligned}$$

Here the target states of $H_2$ are represented by the form of Eq. (10).

The optional short-ranged distorting potential for $H_2$ is chosen as

$$U_0 = 2z_{\mathrm{e}}v_0(r_0,R/2) - 2z_{\mathrm{e}}\int d\boldsymbol{r}|\Phi_n(\boldsymbol{r})|^2v_0(r_0,r_1), \quad (22)$$

where $\boldsymbol{r}$ is collectively all target electronic spatial coordinates, $n$ is typically the electronic ground state and $v_0(r_0,r_1)$ is defined as part of Eq. (5). Equation (22) utilises the antisymmetrisation property of the target states. This form of $U_0$ is spherically symmetric, short-ranged and ensures that the $V$-matrix elements are short-ranged by removing the projectile-nuclei term $V_0$ for the $\lambda = 0$ partial-wave [referring to Eq. (5)]. The use of a distorting potential is a purely numerical technique which saves on computational resources when solving the Lippmann-Schwinger Eq. (18) [44].

## III. RESULTS

### A. Scattering calculation details

The $H_2$ structure model needs to allow for an expansion over the two electrons $(nlm, n'l'm')$. One-electron orbitals are constructed from a Laguerre basis that has $l_{\max} = 8$, $N_l = 17 - l$ functions for $l \leq 7$ and $N_{l=8} = 10$ with exponential fall-offs $\alpha_l = 1.2$ for $l \leq 4$ and $\alpha_l = 1.0$ for $l \geq 5$. In the frozen-core model, the "inner" electron of $H_2$ is restricted to the $1s\sigma_g$ orbital of $H_2^+$ and the two-electron configurations have the form $(1s\sigma, n'l'm')$. This model is not sufficiently accurate to obtain the ground state energy. Instead a more accurate model is chosen with the "inner" and "outer" electrons expanded by all $n \leq 3$ one-electron orbitals that are constructed from short-ranged Laguerre basis functions with exponential-fall offs of $\alpha_l = 1.9$. In addition, the $1s\sigma_g$ orbital $(n = n' = 1)$ is represented by a converged (at an internuclear distance of $R = 1.4$) molecular-orbital of $H_2^+$ that was constructed from a Laguerre basis that had $N_l = 60 - l$, $\alpha_l = 1.7$ functions up to $l_{\max} = 8$. Two-electron configurations with $|m_{\mathrm{T}}| \geq 2$ are restricted to the frozen-core model $(1s\sigma, n'l'm')$, where $m_{\mathrm{T}} = m + m'$. Hence the largest angular momentum projection of the states is $m_{\max} = l_{\max} = 8$.

Diagonalising the target Hamiltonian with two-electron configurations built from the above model generated $N = 1013$ target states. This 1013-state model is used in the scattering calculations of positron collisions with $H_2$ in the $v_i = 0$ and $v_i = 1$ vibrational states. The $v = 1$ vibrational wave function approximately spans the range $0.8 \leq R \leq 2.2$. In Tables I and II the $H_2$ electronic states two-electron energy and ground state static dipole polarisability are presented as a function of $R$. At the equilibrium distance of $R_0 = 1.4$, the static dipole polarisability of this model is $\alpha_\parallel = 6.375$ and $\alpha_\perp = 4.635$ for the ground state, which are both in good agreement with the accurate calculations of Kolos and Wolniewicz [46] ($\alpha_{\parallel} = 6.380$ and $\alpha_{\perp} = 4.578$). As $R$ increases beyond the equilibrium distance of $R_0 = 1.4$, the ground and low-lying excited states of $H_2$ start to become more diffuse and the present structure model becomes less accurate. For the purpose of scattering calculations the current structure model is sufficiently accurate to describe $H_2$ in the $v_i = 0$ and $v_i = 1$ states. Two-electron energies of the electronic excited states, vertical excitation energies and oscillator strengths are presented for $H_2$ at the equilibrium internuclear distance of $R_0 = 1.4$ in Tables III and IV. These excited states are hydrogenic and are well represented in the single-centre (spherical coordinate system) expansion. The present low-lying electronic excited states energies are within 1.5% of the accurate values [47–53]. The dominant oscillator strengths are also well represented in the present model.

TABLE I: Two-electron energy of the $H_2$ electronic target states $X^1\Sigma_g^+$, $B^1\Sigma_u^+$, and $C^1\Pi_u$ as a function of the internuclear distances $R$. Comparisons are made with the accurate calculations of Kolos *et al.* [47] and Wolniewicz and Dressler [49]. All values are in atomic units.

| | $X^1\Sigma_g^+$ | | $B^1\Sigma_u^+$ | | $C^1\Pi_u$ | |
|---|---|---|---|---|---|---|
| $R$ | Present | [47] | Present | [49] | Present | [49] |
| $0^*$ | -2.899 | -2.903 | -2.123 | -2.133 | -2.123 | -2.133 |
| 0.8 | -1.015 | -1.020 | -0.430 | | -0.425 | |
| 1.0 | -1.120 | -1.125 | -0.579 | -0.581 | -0.571 | -0.573 |
| 1.2 | -1.160 | -1.165 | -0.658 | -0.661 | -0.646 | -0.649 |
| 1.4 | -1.169 | -1.174 | -0.702 | -0.706 | -0.686 | -0.689 |
| 1.6 | -1.163 | -1.169 | -0.725 | -0.731 | -0.705 | -0.709 |
| 1.8 | -1.147 | -1.155 | -0.738 | -0.745 | -0.713 | -0.717 |
| 2.0 | -1.129 | -1.138 | -0.743 | -0.752 | -0.714 | -0.718 |
| 2.2 | -1.108 | -1.120 | -0.744 | -0.756 | -0.711 | -0.716 |

$^*$This entry is the combined nuclear limit of $H_2$, which omits the internuclear Coulomb repulsion term $1/R$ and is equivalent to atomic He. $R = 0$ energies are compared to the measurements of Moore [54] for He.

The present fixed-nuclei and adiabatic-nuclei results were calculated using a projectile partial-wave expansion with maximum orbital angular momentum $L_{\max} = 8$. Calculations included all possible channels (i.e. total spin $S = 1/2$, odd and even parity $\Pi$) up to the maximum total orbital angular momentum projection $\bar{M}_{\max} = 8$, where $-\bar{M}_{\max} \leq \bar{M} \leq \bar{M}_{\max}$. An orientationally averaged analytic Born subtraction (ABS) method was used to top-up the partial-wave expansion for inelastic scattering, see Ref. [44] for details. In Sect. III C, the convergence of the present partial-wave expansion is demonstrated.

In the fixed-nuclei calculation the internuclear distance was chosen as the mean internuclear distance of the $H_2$ vibrational ground state ($R_m = 1.448$), which approximates scattering from the vibrational ground state more accurately than the equilibrium distance ($R_0 = 1.4$) [58]. This is explicitly demonstrated in Fig. 7, which we will describe later. The dotted vertical lines at 8.6 and 15.4 eV in the figures, respectively indicate the Ps-formation and ionisation thresholds of $H_2$ in the ground state. Note that with the present $R_m = 1.448$ fixed-nuclei structure model, the Ps-formation and ionisation thresholds are at

TABLE II: Parallel $\alpha_{\parallel}$, perpendicular $\alpha_{\perp}$ and total $\alpha$ static dipole polarisability of the $H_2$ ground state presented as a function of the internuclear distance $R$. Comparing with the accurate calculations of Kolos and Wolniewicz [46]. All values are in atomic units.

| | $\alpha_{\parallel}$ | | $\alpha_{\perp}$ | | $\alpha$ | |
|---|---|---|---|---|---|---|
| $R$ | Present | [46] | Present | [46] | Present | [46] |
| $0^*$ | 1.397 | | 1.397 | | 1.397 | 1.383 |
| 0.8 | 3.225 | 3.204 | 2.808 | 2.783 | 2.947 | 2.923 |
| 1.0 | 4.101 | 4.088 | 3.371 | 3.341 | 3.614 | 3.590 |
| 1.2 | 5.150 | 5.147 | 3.983 | 3.944 | 4.372 | 4.345 |
| 1.4 | 6.375 | 6.380 | 4.635 | 4.578 | 5.215 | 5.179 |
| 1.6 | 7.708 | 7.781 | 5.280 | 5.228 | 6.089 | 6.079 |
| 1.8 | 9.370 | 9.320 | 6.009 | 5.878 | 7.129 | 7.025 |
| 2.0 | 11.117 | 10.964 | 6.699 | 6.511 | 8.172 | 7.995 |
| 2.2 | 13.169 | 12.638 | 7.425 | 7.110 | 9.340 | 8.952 |

$^*$This entry is the combined nuclear limit of $H_2$, which omits the internuclear Coulomb repulsion term $1/R$ and is equivalent to atomic He. The $R = 0$ polarisability is compared with the calculations of Kar and Ho [55] for He.

TABLE III: Two-electron energy $E$ of the singlet ($s = 0$) electronic target states of $H_2$ and the vertical electronic excitation energy from the ground state $\Delta E$ at the internuclear distance of $R_0 = 1.4\ a_0$. Comparisons are made with accurate calculations [47–52].

| | $E$ (a.u.) | | $\Delta E$ (eV) | |
|---|---|---|---|---|
| State | Present | Ref. | Present | Ref. |
| $X^1\Sigma_g^+$ | -1.169 | -1.174 [47] | | |
| $B^1\Sigma_u^+$ | -0.702 | -0.706 [49] | 12.71 | 12.75 [49] |
| $EF^1\Sigma_g^+$ | -0.689 | -0.692 [48] | 13.05 | 13.13 [48] |
| $C^1\Pi_u$ | -0.686 | -0.689 [49] | 13.14 | 13.22 [49] |
| $B'^1\Sigma_u^+$ | -0.627 | -0.629 [49] | 14.75 | 14.85 [49] |
| $GK^1\Sigma_g^+$ | -0.625 | -0.626 [48] | 14.80 | 14.91 [48] |
| $I^1\Pi_g$ | -0.625 | -0.626 [52] | 14.81 | 14.92 [52] |
| $J^1\Delta_g$ | -0.624 | -0.625 [51] | 14.83 | 14.94 [51] |
| $H^1\Sigma_g$ | -0.623 | -0.624 [50] | 14.86 | 14.97 [50] |
| $D^1\Pi_u$ | -0.622 | -0.624 [49] | 14.88 | 14.99 [49] |

TABLE IV: Oscillator strengths for transitions from the ground state to the lowest lying ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states of $H_2$ at the internuclear distance $R_0 = 1.4$. Comparisons are made with the calculations of Wolniewicz and Staszewska [53, 56, 57].

| Transition | Length | Velocity | Refs. [53, 56, 57] |
|---|---|---|---|
| $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ | 0.293 | 0.288 | 0.301 |
| $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ | 0.354 | 0.351 | 0.358 |
| $X^1\Sigma_g^+ \rightarrow B'^1\Sigma_u^+$ | 0.058 | 0.057 | 0.058 |
| $X^1\Sigma_g^+ \rightarrow D^1\Pi_u$ | 0.087 | 0.086 | 0.085 |

9.34 and 16.14 eV respectively.

In Ref. [59] we gave a detailed discussion of convergence studies within the (atomic and molecular) CCC method and demonstrate convergence (accurate to within numerical accuracy approximately less than 5%) of the present $R_m = 1.448$ fixed-nuclei results. Note that fixed-nuclei approximation has its own associated uncertainty which we do not account for. Here we provide a brief discussion of our convergence studies and refer the reader to Ref. [59] for the full details.

### B. Convergence with the number of states

To investigate convergence with respect to the number of states, the 1013-state model is compared with 694- and 884-state fixed-nuclei calculations. The basis used to construct the 694-state calculation was the same as 1013-state model, however the "outer" electron orbitals were constructed from Laguerre basis functions that had maximum orbital angular momentum $l_{\max} = 6$. The 884-state model was produced with the same basis as the 1013-state model, except the "outer" electron orbitals were constructed with $N_l = 15 - l$, $l_{\max} = 8$ Laguerre basis functions. The 694-, 884- and 1013-state GTCS and TICS are presented in Figs. 1 and 2 respectively. These results are practically the same and hence the 1013-state calculations are converged in the close-coupling expansion for both the number of Laguerre basis functions $N_l$ and maximum orbital angular momentum $l_{\max}$ of the basis. The convergence of the 694- and 1013-state calculations indicate that the $l_{\max} = 6$ basis functions are sufficiently accurate enough to describe the long-range correlations and (virtual) Ps-formation (in the low-energy region and) above the ionisation threshold. Note that the sharp rise in the TICS just above the ionisation threshold is from the Ps-formation and direct ionisation flux captured by the newly open positive-energy pseudostates. Hence a larger close-coupling calculation is expected to have a sharper TICS rise just above the ionisation threshold.

To further justify that we have indeed achieved convergence with respect to the number of target states, we compare in Fig. 3 the present 1013-state calculations at the internuclear distance of $R_0 = 1.4$ with our preliminary 556-, 396- and 276-states calculations [41]. These preliminary calculations had a completely different structure model in both $N_l$ and the exponential fall-offs $\alpha_l$ of the Laguerre basis functions. Hence in the two largest models, the excited states of the discrete spectrum and the discretisation of the continuum are very different. For example in the present 1013-state model 57 states are in the discrete spectrum, while for the 556-state model ten states are in the discrete spectrum. Both $l_{\max} = 8$ results are practically the same and are within 2% of the $l_{\max} = 6$ results. The $l_{\max} = 8$ and $l_{\max} = 6$ calculations are 10% larger than the $l_{\max} = 4$ results. If the $l_{\max} = 8$ and $l_{\max} = 6$ calculations were not converged we would expect a similar difference in magnitude between them like the case for the $l_{\max} = 4$ results. Hence the 1013-, 556- and 396-state results are converged, even though the preliminary calculations (396- and 556-state) are half the size of the 1013-state close-coupling expansion. CCC results presented from here onwards are calculated with the 1013-state model.

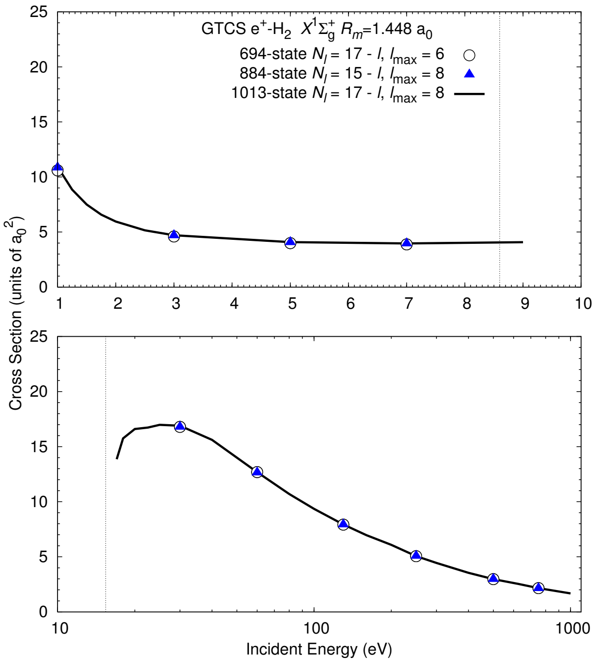

FIG. 1: Convergence studies of positron scattering from $H_2$ at the mean vibrational ground state fixed-nuclear distance of $R_m = 1.448\ a_0$. 694-, 884- and 1013-state convergent close-coupling (CCC) calculations are presented for the grand total cross section (GTCS). A Laguerre basis with $N_l$ functions for each orbital angular momentum $l$ up to $l_{\max}$ is used to construct the "outer" electron orbitals. The dotted vertical lines at 8.6 and 15.4 eV indicate the positronium-formation and ionisation thresholds of $H_2$ in the ground state.

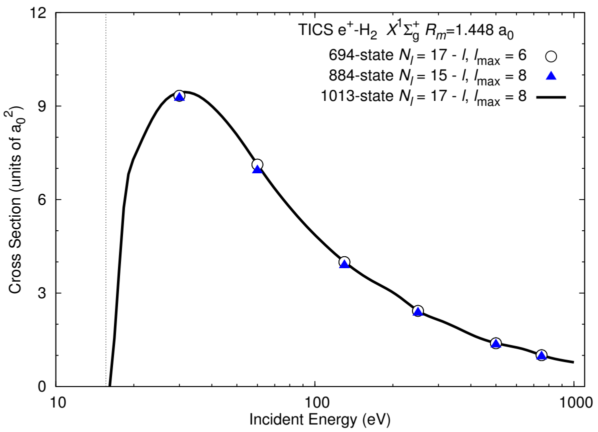

FIG. 2: Convergence studies of positron scattering from $H_2$ at the mean vibrational ground state fixed-nuclear distance of $R_m = 1.448\ a_0$. 694-, 884- and 1013-state convergent close-coupling (CCC) calculations are presented for the total ionisation cross section (TICS). A Laguerre basis with $N_l$ functions for each orbital angular momentum $l$ up to $l_{\max}$ is used to construct the "outer" electron orbitals. The dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

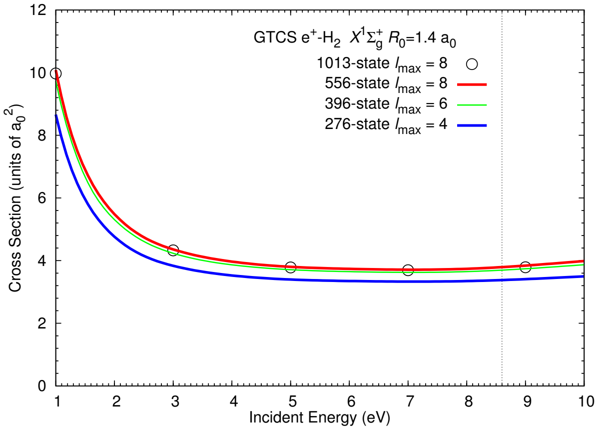

FIG. 3: Convergence studies of positron scattering from $H_2$ for the grand total cross section (GTCS) at the equilibrium fixed-nuclear distance of $R_0 = 1.4\ a_0$. The present 1013-state convergent close-coupling (CCC) calculations are compared with the preliminary CCC calculations [41]. A Laguerre basis with orbital angular momentum $l$ up to $l_{\max}$ is used to construct the "outer" electron orbitals. The dotted vertical line at 8.6 eV indicates the positronium-formation threshold of $H_2$ in the ground state.

### C. Convergence of the partial-wave expansion

Convergence of the GTCS and TICS is investigated in Figs. 4 and 5 with respect to the size of the projectile partial-wave expansion. 1013-state calculations were performed for partial-wave expansions with $L_{\max} = \bar{M}_{\max} = 7$, $L_{\max} = \bar{M}_{\max} = 8$ and $L_{\max} = \bar{M}_{\max} = 9$, which were then topped-up using the ABS method. The largest difference between the $L_{\max} = \bar{M}_{\max} = 7$ and $L_{\max} = \bar{M}_{\max} = 9$ results is less than 4% at the TICS cross section peak. The $L_{\max} = \bar{M}_{\max} = 8$ and $L_{\max} = \bar{M}_{\max} = 9$ TICS and GTCS are practically the same across the entire energy-range and are therefore converged.

Hence the 1013-state CCC results presented here are converged in both the projectile partial-wave and close-coupling expansions. From here onwards the presented results have been calculated using the 1013-state model and a partial-wave expansion with maximum orbital angular momentum and maximum total orbital angular projection $L_{\max} = \bar{M}_{\max} = 8$. Convergence studies suggest that the present fixed-nuclei $R_m = 1.448$ 1013-state CCC results are estimated to be accurate to within 5% for the GTCS and TICS. This accuracy estimate does not include the uncertainty associated with the fixed-nuclei approximation.

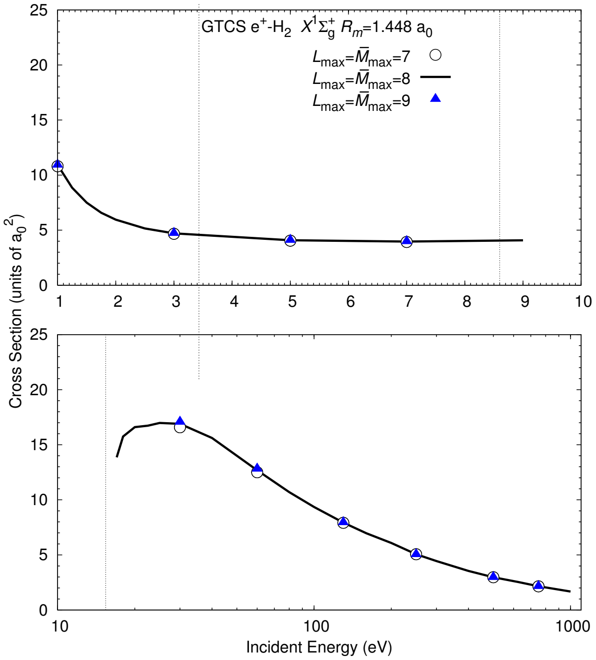

FIG. 4: Convergence studies of the grand total cross section (GTCS) for positron scattering from $H_2$ at the mean vibrational ground state fixed-nuclear distance of $R_m = 1.448\ a_0$. 1013-state convergent close-coupling (CCC) results are calculated using a partial-wave expansion with maximum orbital angular momentum $L_{\max}$ and maximum total orbital angular projection $\bar{M}_{\max}$. An orientationally averaged analytic Born subtraction method is used to top-up results. The dotted vertical lines at 8.6 and 15.4 eV indicate the positronium-formation and ionisation thresholds of $H_2$ in the ground state.

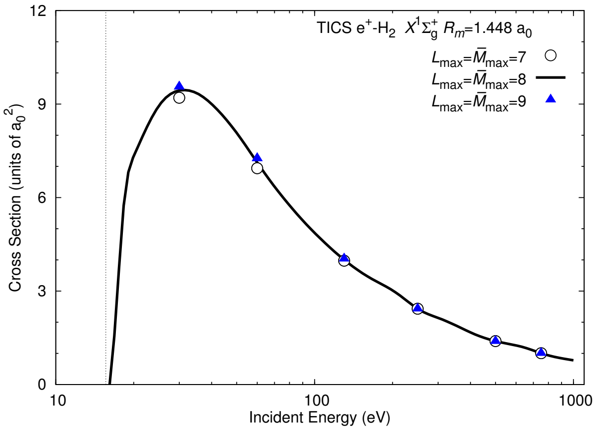

FIG. 5: Convergence studies of the total ionisation cross section (TICS) for positron scattering from $H_2$ at the mean vibrational ground state fixed-nuclear distance of $R_m = 1.448\ a_0$. 1013-state convergent close-coupling (CCC) results are calculated using a partial-wave expansion with maximum orbital angular momentum $L_{\rm max}$ and maximum total orbital angular projection $\bar{M}_{\rm max}$. An orientationally averaged analytic Born subtraction method is used to top-up results. The dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

### D. Scattering length of the ground and first vibrationally excited state

The adiabatic-nuclei integrated cross section for a transition $i, v_i \to f, v_f$ is defined as [45]

$$\sigma^S_{fv_f,iv_i} = \frac{q_f}{q_i}\frac{1}{4\pi}\sum_{\substack{L_f,L_i\\M_f,M_i}} |\langle \nu_{fv_f}|A^{S(\mathrm{b})}_{fL_fM_f,iL_iM_i}|\nu_{iv_i}\rangle_R|^2, \quad (23)$$

where the transition is from an initial electronic state $i$ and vibrational state $v_i$ to a final electronic state $f$ and vibrational state $v_f$, $\nu_{iv_i}(R)$ is the vibrational wave function,

$$\begin{aligned} A^{S(\mathrm{b})}_{fL_fM_f,iL_iM_i}(R) = {} & -(2\pi)^2(q_fq_i)^{-1}i^{L_i-L_f} \quad (24)\\ & \times T^{S(\mathrm{b})}_{fL_fM_f,iL_iM_i}(q_f,q_i;R), \end{aligned}$$

the superscript (b) indicates the body-frame and the physical $T$-matrix elements $T^{S(\mathrm{b})}_{fL_fM_f,iL_iM_i}(q_f,q_i;R)$ are from the physical $T$-matrix with the form given in Eq. (19). The vibrational wave functions only have a minor dependence on the rotational quantum number $J$ and hence it can be assumed they are independent of $J$. Here we chose $J = 0$ and the vibrational wave functions were calculated with the same method described in Ref. [44], however here we utilised the accurate $H_2$ ground state Born-Oppenheimer potential energy curve calculated by Kolos *et al.* [47].

The 1013-state CCC calculations described above in Sect. III A were conducted at eight internuclear points within the interval $0.8 \leq R \leq 2.2$. The real and imaginary parts of the $T$-matrix elements were found to be smooth as a function of $R$ and were interpolated separately over this interval.

To investigate the accuracy of the adiabatic-nuclei CCC results, calculations were performed at sufficiently low-energies to calculate the scattering length $A$, where

$$\sigma(0) = 4\pi A^2, \quad (25)$$

and $\sigma(0)$ is the GTCS at 0 eV [60]. The CCC scattering lengths are compared with the accurate calculations of Zhang *et al.* [58, 61] as a function of $R$ in Fig. 6. At $R_m = 1.448$ the CCC calculations obtain a scattering length of $A = -2.65$, which compares very well with the accurate result of $A = -2.71$ [58]. CCC results are also in excellent agreement with the calculations of Zhang *et al.* [58, 61] in the interval $0.8 \leq R \leq 2.0$. This excellent agreement indicates that the current CCC calculations model virtual Ps-formation sufficiently accurately. At $R = 2.2$ there is a difference of approximately 5% between the CCC results and the calculations of Zhang *et al.* [58, 61]. This difference comes from the choice of the structure (1013-state) model, where the low-lying excited states of $H_2$ start to become more diffuse and the present structure model becomes less accurate. As shown in Fig. 6, this interval approximately spans the range of the $H_2$ $v = 0$ and $v = 1$ vibrational state probability density functions. Adiabatic-nuclei results for scattering from the electronic ground, $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$ only have a minor contribution from $T$-matrix elements [Eq. (23)] or cross sections $\sigma_{f,i}(R)$ [Eq. (26)] for $R \geq 2.2$. Referring to Fig. 6, this is because the respective vibrational wave functions are very small at these values of $R$.

Calculating the adiabatic-nuclei GTCS at (near) zero incident energy with Eq. (23) for the the ground $v_i = 0$ and first vibrationally excited $v_i = 1$ states, we can obtain the scattering length of $H_2$ in the $v_i = 0$ and $v_i = 1$ states with Eq. (25). This calculation gives the $v_i = 1$ scattering length as $A = -3.16$, which is 17% larger than the $v_i = 0$ scattering length of $A = -2.70$.

### E. Scattering from the ground and first vibrationally excited state

Summing over all final vibrational state transitions in Eq. (23) by utilising the closure property of the complete vibrational basis, the integrated cross section for transition the $i, v_i \to f$ is calculated with

$$\sigma^S_{f,iv_i} = \int R^2 dR\ \sigma^S_{f,i}(R)|\nu_{iv_i}(R)|^2, \quad (26)$$

where $\sigma^S_{f,i}(R)$ is the fixed-nuclei integrated cross section at the internuclear distance $R$ [44, 45].

The 1013-state CCC calculations described above were conducted at eight internuclear points within the interval $0.8 \leq R \leq 2.2$. Cross sections were found to be smooth as a function of $R$ and were interpolated in this interval

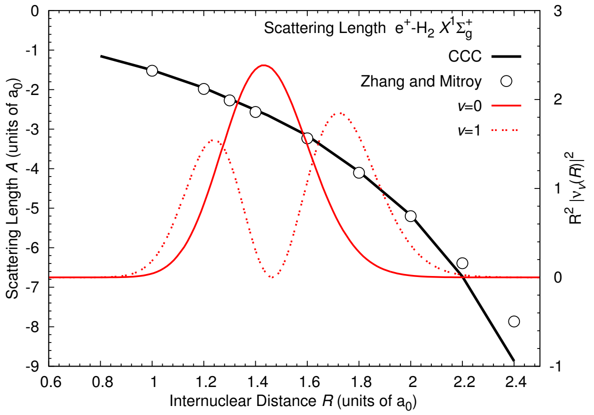

FIG. 6: The scattering length $A$ of positron scattering from the electronic ground state of $H_2$ presented as function of the internuclear distance $R$. Convergent close-coupling (CCC) results are compared with the results of Zhang *et al.* [58, 61]. The red lines are the vibrational probability density functions $R^2|\nu_v(R)|^2$ of the $H_2$ electronic ground $v = 0$ and $v = 1$ vibrational states.

of $R$. Using Eq. (26) adiabatic-nuclei results are presented for positron scattering from the electronic ground, $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$. It is important to note that in the fixed-nuclei and adiabatic-nuclei Eq. (26) approximations, the closure-method is used to analytically sum over all final vibrational and rotational excitations.

The 1013-state adiabatic-nuclei and fixed-nuclei GTCS are presented in Fig. 7 for positron scattering from the $v_i = 0$ and $v_i = 1$ states of $H_2$. Firstly in the low-energy region (1-10 eV) the adiabatic-nuclei $v_i = 1$ results are between 20-30% larger than the $v_i = 0$ results. This significant difference between the $v_i = 0$ and $v_i = 1$ cross sections likely to be important in transport models [1, 2]. Above the ionisation threshold the $v_i = 1$ results are at most 10% larger than the $v_i = 0$ results. As the incident projectile energy increases the $v_i = 0$ and $v_i = 1$ cross sections converge and by 250 eV results are practically the same.

Comparing the adiabatic-nuclei $v_i = 0$ results and the the fixed-nuclei mean internuclear distance $R_m = 1.448$ results, we find that the cross sections are practically the same. In the energy-range presented here the largest difference is approximately 3% (in the low-energy region). Note that in the low-energy region the adiabatic-nuclei $v_i = 0$ results are 5-15% larger than the equilibrium $R_0 = 1.4$ fixed-nuclei results. This confirms that for fixed-nuclei calculations the mean internuclear distance is a better approximation of $v_i = 0$ than the equilibrium distance. The fixed-nuclei cross sections taken (from interpolated values) at the mean internuclear distance of the first vibrational state $R_m = 1.545$ are compared with the $v_i = 1$ adiabatic-nuclei results. Above the ionisation threshold the mean fixed-nuclei results look to be a good approximation of the adiabatic-nuclei results, where cross sections at high energies have less of a dependence on $R$ than low-energy cross sections. At low energies there is a significant difference, where the $v_i = 1$ adiabatic-nuclei results are about 10% larger than the $R_m = 1.545$ results. We expect that using the mean internuclear distance to approximate scattering from vibrational levels will be a worse approximation for higher excited vibrational levels.

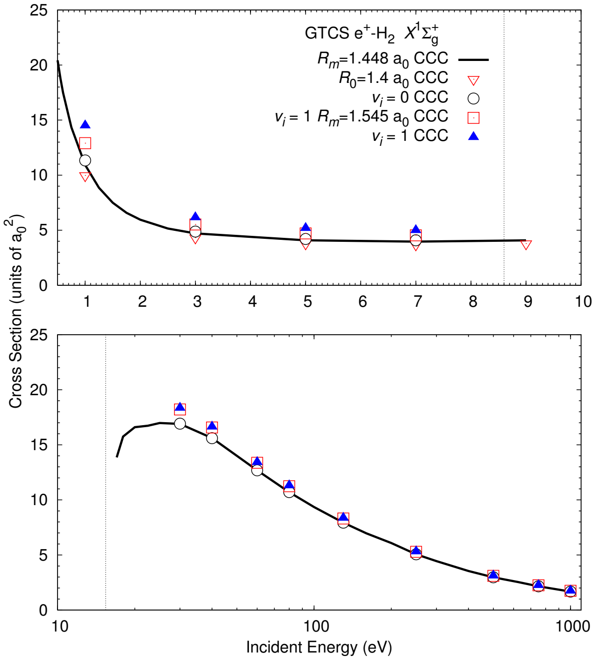

FIG. 7: The grand total cross section (GTCS) for positron scattering from the $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$. Adiabatic-nuclei convergent close-coupling (CCC) results are compared with the fixed-nuclei CCC calculations at the mean internuclear distances of the $v_i = 0$ state ($R_m = 1.448$ $a_0$), $v_i = 1$ state ($R_m = 1.545$ $a_0$) and the equilibrium ($R_0 = 1.4$ $a_0$) distance. The dash-dotted vertical lines at 8.6 and 15.4 eV indicate the positronium-formation and ionisation thresholds of $H_2$ in the ground state.

The low-energy GTCS is presented in Fig. 8 for positron scattering from the ground state of $H_2$. Fixed-nuclei $R_m = 1.448$ CCC results are compared with equilibrium distance $R_0 = 1.4$ fixed-nuclei theoretical results calculated with the continued fractions method of Tenfen *et al.* [62], the molecular $R$-matrix with pseudostates (MRMPS) method of Zhang *et al.* [36], Schwinger multichannel (SMC) method of Sanchez and Lima [38] and the first-order (ad hoc) method of Reid *et al.* [63]. It is important to note that the fixed-nuclei $R_m = 1.448$ CCC results are 5-15% larger than the $R_0 = 1.4$ CCC results. There is still, however, a large variation between fixed-nuclei single-centre close-coupling methods (CCC, MRMPS and SMC) results, where CCC results are 20-30% larger than the MRMPS and SMC results. The variation in these results comes primarily from the different size close-coupling expansions utilised in the respective calculations. The SMC and MRMPS calculations utilise basis expansions that have $l_{\max} = 3$ and $l_{\max} = 5$, respectively. Noting that the CCC calculations utilise a basis expansion with $l_{\max} = 8$ suggests that the SMC and MRMPS calculations have not modelled virtual Ps-formation to convergence. As an additional check $R_0 = 1.4$ CCC calculations were performed with the same sized basis as the MRMPS calculations [36], these CCC and MRMPS results were almost identical. The present CCC results are also in good agreement with the body-frame vibrational close-coupling (BFVCC) calculations of Gianturco and Mukherjee [64] above 4 eV. It is interesting to note that all theoretical results have the same qualitative behaviour except for the results of Reid *et al.* [63] near the Ps-formation threshold.

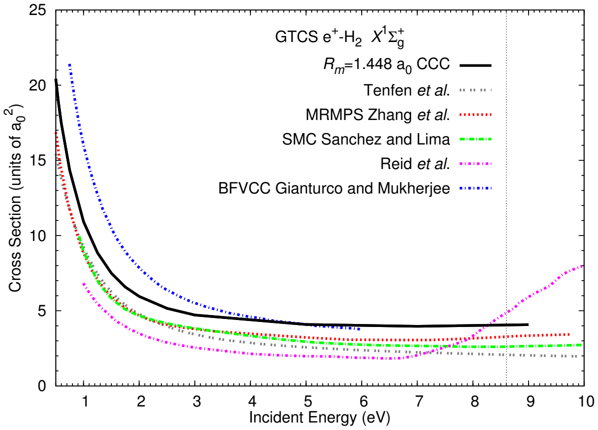

FIG. 8: The grand total cross section (GTCS) for positron scattering from the ground state of $H_2$. The mean internuclear distance $R_m = 1.448\ a_0$ fixed-nuclei convergent close-coupling (CCC) results are compared with equilibrium $R_0 = 1.4\ a_0$ fixed-nuclei results from the method of continued fractions calculation of Tenfen *et al.* [62], the molecular $R$-matrix with pseudostates (MRMPS) calculations of Zhang *et al.* [36], Schwinger multichannel (SMC) calculations of Sanchez and Lima [38] and first-order method of Reid *et al.* [63]. Results are also compared with the body-frame vibrational close-coupling (BFVCC) calculations of Gianturco and Mukherjee [64]. The dash-dotted vertical line at 8.6 eV indicates the positronium-formation threshold of $H_2$ in the ground state.

In Fig. 9 the GTCS is compared with experiments for positron scattering from the ground state of $H_2$. Fixed-nuclei $R_m = 1.448$ CCC results are compared with the measurements of Machacek *et al.* [13], Karwasz *et al.* [11], Zecca *et al.* [12], Hoffman *et al.* [8], Charlton *et al.* [7], Zhou *et al.* [10] and Deuring *et al.* [9]. Machacek *et al.* [13] have also "corrected" their low-energy measurements to account for scattering to forward angles. In the low-energy region experimental results show large variations. These variations are primarily due to different experimental resolution of scattering to forward angles [12, 13]. The angular resolutions of the Zecca *et al.* [12], Karwasz *et al.* [11] and Machacek *et al.* [13] experiments are the most superior [12, 65]. The experiments of Hoffman *et al.* [8], Charlton *et al.* [7], Zhou *et al.* [10] and Deuring *et al.* [9] may have missed a significant fraction of scattering to forward angles and, therefore, measured lower cross sections [12]. For example at 5 eV the measurements of Machacek *et al.* [13] had angular resolution of ~10 degrees, while the experiment of Hoffman *et al.* [8] had angular resolution of ~25 degrees. Note that the angular resolution of a measurement is dependent on the projectile, target and incident energy [8]. CCC results are in the best agreement with the measurements of Zecca *et al.* [12] and Karwasz *et al.* [11].

The present low-energy measurements of Zecca *et al.* [12] "corrected" to account for scattering to forward angles are also shown in Fig. 9 (upper panel) and listed in numerical form in Table V. That correction has been calculated following the method described by Hamada and Sueoka [66] and using the present CCC elastic differential cross sections (analytically summed over all vibrational and rotational excitations) in conjunction with the energy-dependent angular discrimination $\theta_c$ of the Trento spectrometer [67]. Briefly, the forward angle scattering correction was calculated as follows:

$$\sigma_T^{\text{corr}} = \sigma_T^{\text{uncorr}}/(1 - C) \tag{27}$$

where $\sigma_T^{\text{corr}}$ and $\sigma_T^{\text{uncorr}}$ are the corrected and uncorrected GTCS, respectively and the correction factor $C$ is given by

$$C = \frac{\int_0^{\theta_c} \frac{d\sigma}{d\Omega} \sin(\theta) d\theta}{\int_0^{\pi} \frac{d\sigma}{d\Omega} \sin(\theta) d\theta}. \tag{28}$$

After the correction for forward scattering, the experimental GTCS of Zecca *et al.* [12] increase between ~20% at the lowest energies and ~3% at 9 eV. Above 10 eV that correction has not been applied as it is expected to be smaller than 3% and, therefore, lies well within the experimental uncertainties. Even though the measurements of Zecca *et al.* [12] have been "corrected" with the present CCC results, there is still a considerable discrepancy between theory and experiment below 1 eV. This might be explained, at least in part, by the convolution of the measured GTCS over the finite energy distribution of the incident positron beam. The overall uncertainty on the experimental energy scale of the positron beam (±0.2 eV) might also play a role. We recall here that this stems from both the uncertainty on the calibration of the energy scale (±0.05 eV) and the energy spread of the positron beam (~0.12 eV FWHM). On the theoretical side, we also mention that at these low-energies coupling to nuclear motion may be important.

Above the ionisation threshold (lower panel of Fig. 9) all experiments [7–10, 12, 13] are in good agreement with each other and the single-centre CCC results. The good agreement with experiment at the cross section maximum (25 eV) suggests that the 1013-state CCC calculations are sufficiently converged to model Ps-formation. The two-centre CCC method [32] utilized an approximation in the rearrangement matrix elements, approximating the positron-nuclei potential as isotropic. Unfortunately testing internal consistency between the single-

TABLE V: The grand total cross section (GTCS) for positron scattering from the ground state of $H_2$. The present low-energy measurements of Zecca *et al.* [12] "corrected" to account for scattering to forward angles are compared with the present convergent close-coupling (CCC) results.

| Energy (eV) | "Corrected" GTCS ($10^{-16}$ cm$^2$) | CCC GTCS ($10^{-16}$ cm$^2$) |
|---|---|---|
| 0.10 | 12.52 ± 1.50 | 14.44 |
| 0.20 | 7.74 ± 0.87 | 10.58 |
| 0.35 | 4.92 ± 0.51 | 7.49 |
| 0.55 | 4.00 ± 0.38 | 5.27 |
| 0.75 | 3.28 ± 0.29 | 4.02 |
| 1.00 | 2.60 ± 0.21 | 3.06 |
| 1.25 | 2.25 ± 0.17 | 2.48 |
| 1.50 | 2.12 ± 0.16 | 2.10 |
| 2.00 | 1.88 ± 0.14 | 1.67 |
| 2.50 | 1.65 ± 0.11 | 1.44 |
| 3.00 | 1.52 ± 0.10 | 1.32 |
| 5.00 | 1.45 ± 0.09 | 1.14 |
| 7.00 | 1.31 ± 0.08 | 1.11 |
| 9.00 | 1.48 ± 0.08 | 1.14 |

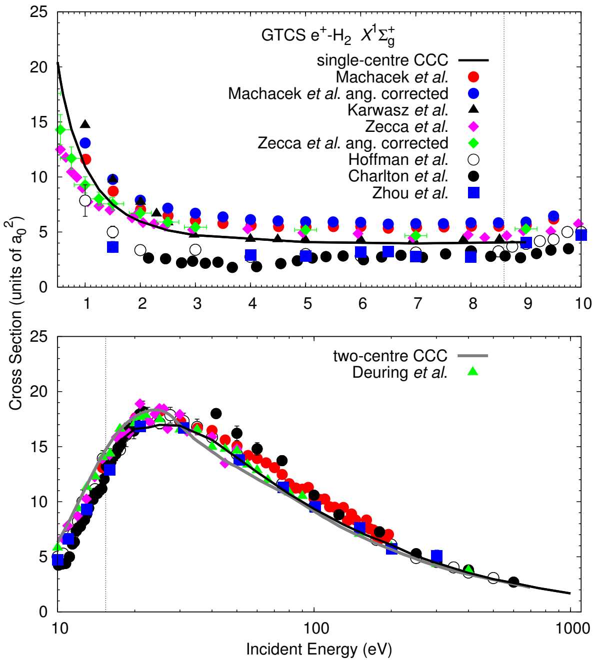

FIG. 9: Convergent close-coupling (CCC) results of the grand total cross section (GTCS) for positron scattering from the ground state of $H_2$. The mean internuclear distance $R_m = 1.448\ a_0$ fixed-nuclei single-centre CCC results (present) are compared with the two-centre CCC calculations [32] and the measurements of Machacek *et al.* [13], Karwasz *et al.* [11], Zecca *et al.* [12], Hoffman *et al.* [8], Charlton *et al.* [7], Zhou *et al.* [10] and Deuring *et al.* [9]. The dash-dotted vertical lines at 8.6 and 15.4 eV indicate the positronium-formation and ionisation thresholds of $H_2$ in the ground state.

and two-centre CCC calculations is not feasible in the low- and intermediate-energy range, where this approximation is expected to break down. However we find that the two calculations are within reasonable agreement with each other in the intermediate-energy region and converge at higher energies as expected.

It is interesting to note that the GTCS measurements of Machacek *et al.* [13] are consistently higher than other experiments [8–10] and the single- and two-centre CCC results at low and high energies. At these high energies Ps-formation is negligible and the experimental forward angle scattering effect should not be an issue.

Low-energy elastic DCS are presented in Fig. 10. The experiment of Machacek *et al.* [13] measured the electronic elastic cross section summed over all final vibrational and rotational transitions. Note that fixed-nuclei DCS and integrated cross sections are analytically summed over all vibrational and rotational excitations [45] and hence describe the same process as measured in the experiment [13]. The experiment of Machacek *et al.* [13] also sums measurements of the DCS at $\theta$ and $180° - \theta$. Here the CCC results are combined in the same way to compare with the experiment. CCC results are in good qualitative agreement with the 3.0, 7.0 and 10 eV measured DCS but underestimate experimental measurements in the forward (and backward) scattering angles. For the 1.0 eV DCS, CCC results do not agree with the shape or magnitude of the measurements. The rapid rise of the GTCS around 1 eV (see Fig. 8) is possibly a contributing factor. However even taking into account the uncertainty estimates of the present fixed-nuclei CCC results, there is still a significant difference between theory and experiment at the forward scattering angles. As shown in Sections III B and III C the fixed-nuclei CCC results are converged in both the close-coupling and partial-wave expansion and are also in excellent agreement with the scattering length results of Zhang *et al.* [58, 61]. Hence these calculations can only be improved by coupling to vibrational and rotational degrees of freedom.

The adiabatic-nuclei CCC elastic (summed over all vibrational and rotational excitations) integrated cross section is presented in Fig. 11 for positron scattering from the $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$. Firstly comparing the fixed-nuclei $R_m = 1.448$ and adiabatic-nuclei $v_i = 0$ results, we find that the cross sections are practically the same. The difference between the $v_i = 0$ and $v_i = 1$ results is relatively minor, where the $v_i = 1$ cross section is at most 10% larger than the $v_i = 0$ results.

The $R_m = 1.448$ fixed-nuclei CCC elastic (summed over all vibrational and rotational excitations) integrated cross section is compared with the corresponding measurements of Machacek *et al.* [13] in Fig. 12 for $H_2$ in the $v_i = 0$ state. As a consequence of distinguishing between the elastic and inelastic scattering processes, the elastic measurements of Machacek *et al.* [13] missed a

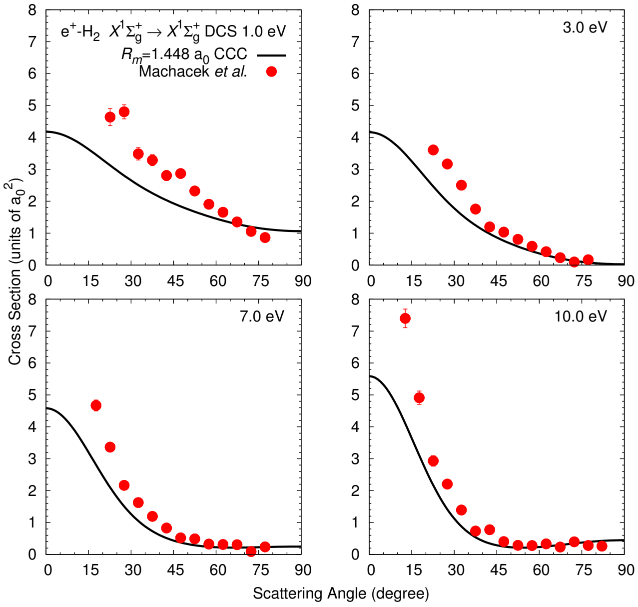

FIG. 10: 1.0, 3.0, 7.0 and 10 eV elastic (summed over all vibrational and rotational excitations) differential cross sections (DCS) for positron scattering from the ground state of $H_2$. The mean internuclear distance $R_m = 1.448$ $a_0$ fixed-nuclei convergent close-coupling (CCC) results and the measurements of Machacek *et al.* [13] have summed the DCS at $\theta$ and $180^\circ - \theta$.

larger portion of forward angle scattering compared to the measurements of the GTCS. These measurements are expected to rise when scattering to forward angles is accounted for. Given the large variation and uncertainty in the measurements it is difficult to draw any solid conclusions regarding the comparison with theory. CCC results are however within the uncertainties of almost all experimental points.

The adiabatic-nuclei TICS of positron scattering from the $v_i = 0$ and $v_i = 1$ vibrational states are presented in Fig. 13. The $v_i = 1$ state TICS is noticeably larger than the $v_i = 0$ results in the intermediate-energy region. The largest difference is at the peak of the cross section (at 30 eV), where the $v_i = 1$ TICS is approximately 7% larger than the $v_i = 0$ TICS. Again the $v_i = 1$ results converge to the $v_i = 0$ results at larger energies, about 130 eV. Comparing the $v_i = 0$ and the fixed-nuclei $R_m = 1.448$ $a_0$ calculations, results are practically the same over the entire energy range.

The $R_m = 1.448$ single-centre CCC TICS is compared with the measurements of Fromme *et al.* [14] and Moxom *et al.* [17] and the $R_0 = 1.4$ two-centre CCC TICS [32] in Fig. 14. The TICS maximum at approximately 30 eV has the largest contribution from the Ps-formation cross section compared to the DICS, which is measured by Jacobsen *et al.* [16] and Knudsen *et al.* [15]. Comparing the single- and two-centre CCC results, in the intermediate energy-range the results vary significantly, while at higher energies there is good agreement between the two calculations. This difference could be due to the two-centre CCC calculations approximating the positron-molecule potential as spherical, which is a good approximation at high impact energies. The good agreement at the cross section maximum between the single-centre CCC TICS and the TICS measurements of Fromme *et al.* [14] and Moxom *et al.* [17] suggests that the 1013-state CCC calculations have a sufficiently large close-coupling expansion to indirectly model Ps-formation. As the projectile energy increases the Ps-formation cross section diminishes and becomes negligi-

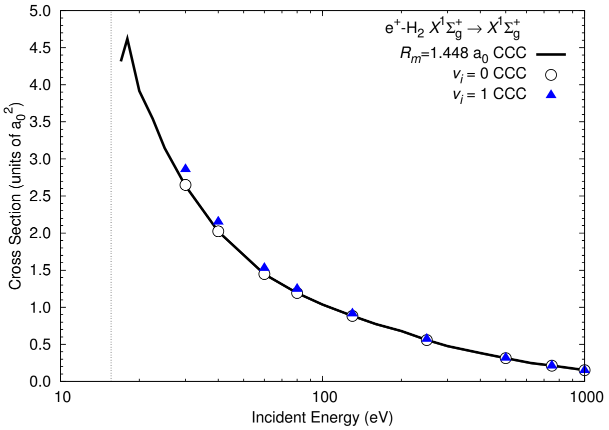

FIG. 11: Convergent close-coupling (CCC) results of the elastic (summed over all vibrational and rotational excitations) integrated cross section for positron scattering from the $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$. The mean internuclear distance $R_m = 1.448$ $a_0$ fixed-nuclei results are compared with the adiabatic-nuclei results. The dash-dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

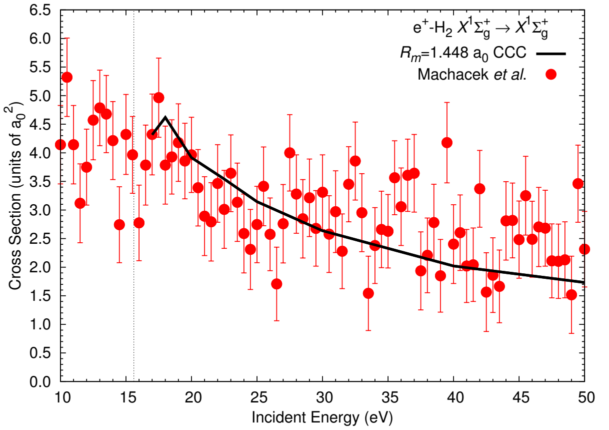

FIG. 12: Convergent close-coupling (CCC) results of the elastic (summed over all vibrational and rotational excitations) integrated cross section for positron scattering from the ground state of $H_2$. The mean internuclear distance $R_m = 1.448$ $a_0$ fixed-nuclei results are compared with the measurements of Machacek *et al.* [13]. The dash-dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

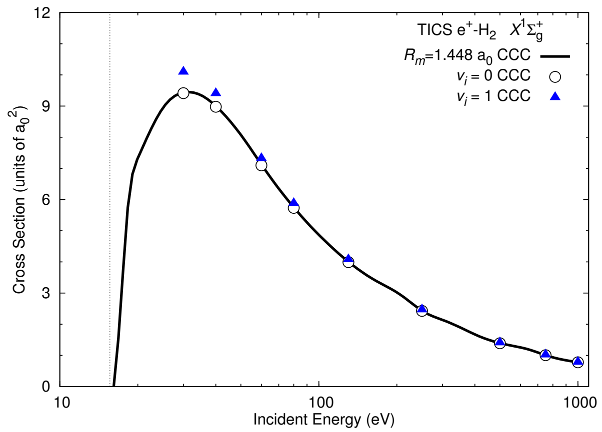

FIG. 13: The total ionisation cross section (TICS) for positron scattering from the $v_i = 0$ and $v_i = 1$ vibrational states of $H_2$. Adiabatic-nuclei convergent close-coupling (CCC) results are compared with the mean internuclear distance $R_m = 1.448$ $a_0$ fixed-nuclei calculations. The dash-dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

ble at approximately 130 eV [13]. Above 130 eV the CCC TICS can be compared with the DICS measurements of Jacobsen *et al.* [16] and Knudsen *et al.* [15]. Here the single-centre CCC results are in good agreement with both experiments but favour the measurements of Knudsen *et al.* [15].

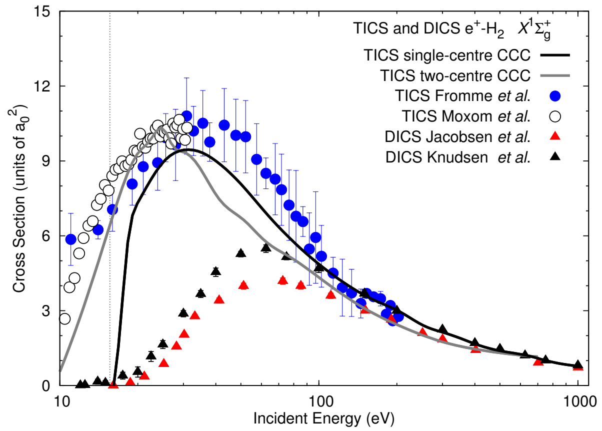

FIG. 14: Convergent close-coupling (CCC) results of the total ionisation cross section (TICS) for positron scattering from the ground state of $H_2$. The mean internuclear distance $R_m = 1.448$ $a_0$ single-centre CCC (present) TICS are compared with the $R_0 = 1.4$ two-centre CCC TICS [32], the measurements of Fromme *et al.* [14] and Moxom *et al.* [17] and the direct ionisation cross sections (DICS) measured by Jacobsen *et al.* [16] and Knudsen *et al.* [15]. The dash-dotted vertical line at 15.4 eV indicates the ionisation threshold of $H_2$ in the ground state.

## F. Vibrational excitation cross section

The vibrational excitation cross section calculated within the adiabatic-nuclei approximation [refer Eq. (23)] violates the conservation of energy law (due to a vibrational transition). Mazevet *et al.* [68] have investigated several adiabatic-nuclei energy correction methods by comparing vibrational close-coupling cross sections with adiabatic-nuclei energy corrected cross sections in e-$H_2$ scattering. They concluded that the relatively simple energy-modified adiabatic phase matrix (EMAP) method produces reasonably accurate vibrational excitation cross sections at energies away from threshold and non-adiabatic resonances. For very accurate excitation cross sections near threshold the first-order non-degenerate adiabatic approximation (FONDA) method is better suited, it retains energy conservation and produces results with the correct threshold behaviour. The energy corrected adiabatic nuclear vibration method (referred to as ANVf in their paper) is calculated simply with the adiabatic-nuclei cross section Eq. (23) but with a corrected flux factor $q_f/q_i$, so as to force the cross section to zero at threshold by having $q_f = \sqrt{2(E_i - (\varepsilon_{f,v_f} - \varepsilon_{i,v_i}))}$, where $E_i = q_i^2/2$, $\varepsilon_{n,v_n}$ is the energy of the $n$ electronic and $v_n$ vibrational state. We assume here that $J = 0$ for all states.

In Fig. 15 we compare several adiabatic-nuclei correction methods for the $0 \to 1$ vibrational excitation cross section in positron-$H_2$ scattering. The first method is the adiabatic-nuclei (AN) cross section [Eq. (23)] without the corrected flux factor i.e. $q_f/q_i = 1$, which is indicated in the figures by $T(E_i)$ AN. For electronically elastic transitions it is unclear whether to use the fixed-nuclei $T$-matrix at the incident energy $T(E_i)$ or the fixed-nuclei $T$-matrix at the (corrected) outgoing energy $T(E_f)$ [69], where $E_f = q_f^2/2$. Here we also investigate having $T(E_f)$, indicated in the figures by $T(E_f)$ AN. The third method we have used is the energy-modified adiabatic (EMA) approximation first proposed by Nesbet [70]. Here the electronically elastic fixed-nuclei $T$-matrix is set as $T(E_{\rm EMA})$, where $E_{\rm EMA} = \sqrt{E_i E_f}$ is the geometric mean of the incident $E_i$ and outgoing energy $E_f$. This approximation is appropriate to account for vibrational excitations that obey the short-range interactions threshold law, but loses its validity for long-range potentials and under conditions where vibronic interactions are strong [68]. Similar to the EMAP method, EMA applies the energy shift to the ($S$- or) $T$-matrix, while the EMAP method applies the energy shift to the $K$-matrix in order to enforce unitarity to the $T$-matrix. The EMAf method indicates that the adiabatic-nuclei cross section in Eq. (23) is calculated with $T(E_{\rm EMA})$ and the corrected flux factor. Other calculations that include the corrected flux factor are indicated by $q_f/q_i$.

Turning to Fig. 15 we compare the $T(E_i)$ AN and $T(E_f)$ AN cross sections. The qualitative behaviour between the two results is identical, however the $T(E_f)$ AN results are shifted towards the higher energies relative to the $T(E_i)$ AN results. The EMA method is between these two results. These cross sections however do not go to zero at threshold [as we are using electronic elastic $T$-matrix elements in Eq. (23)] unless they include the corrected flux factor. Surprisingly the EMAf method is practically identical to the (uncorrected) $T(E_i)$ AN results just after threshold. All these adiabatic-nuclei correction methods obtain the same results at higher energies.

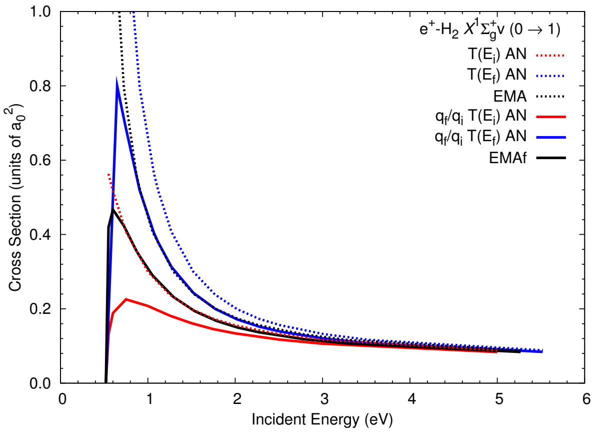

FIG. 15: Positron scattering from the ground state of $H_2$ vibrational 0 → 1 excitation cross section. Refer to the text for details of the present models.

A series of experiments on electron-molecular ion scattering [71] utilize an approximation of the adiabatic-nuclei cross section to analyse their results such that

$$\sigma_{f v_f, i v_i} \approx |\langle \nu_{f v_f}| \sqrt{\sigma_{f,i}(R)} |\nu_{i v_i}\rangle_R|^2. \quad (29)$$

We note that utilising Eq. (29) is significantly simpler and computationally more efficient than using Eq. (23). In Fig. 16 we present the approximation of Eq. (29) (indicated by $\sigma(E_i)$ in the figure), as well as the correction methods mentioned above. Comparing the $T(E_i)$ AN results and those calculated with the approximation of Eq. (29), the results are surprisingly practically identical.

The CCC EMAf results are compared with the adiabatic-nuclei SMC projection-operator calculations of Varella and Lima [72], BFVCC calculations of Gianturco and Mukherjee [64] and the measurements of Sullivan *et al.* [19] in Fig. 17. The present CCC EMAf results are in excellent agreement with experiment both in the shape and magnitude of the cross section. The CCC EMAf results shape is in good agreement with the adiabatic-nuclei SMC projection-operator results [72] and BFVCC results [64], but are systematically higher with a difference at 3 eV of about 80%. This is not due to the present correction method chosen here, as all the correction methods results are practically identical above 3.5 eV (as seen from Figs. 15 and 16). It is also important to note that the adiabatic-nuclei SMC projection-operator results [72] are based on fixed-nuclei calculations that use a much smaller basis ($l_{\max} = 1$) than the present calculations ($l_{\max} = 8$). Such a basis size [72] will produce fixed-nuclei results that are significantly unconverged, as indicated in Fig. 3.

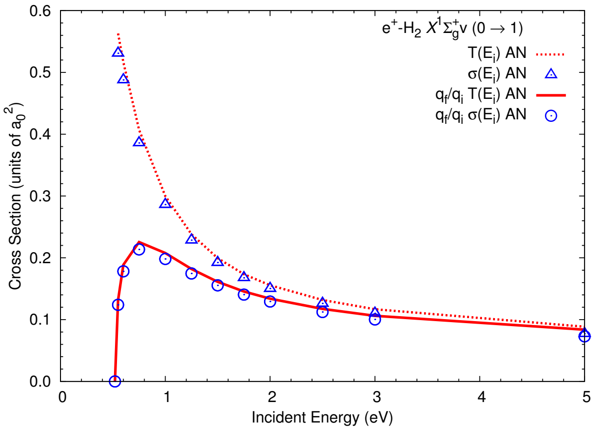

FIG. 16: Positron scattering from the ground state of $H_2$ vibrational 0 → 1 excitation cross section. Refer to the text for details of the present models.

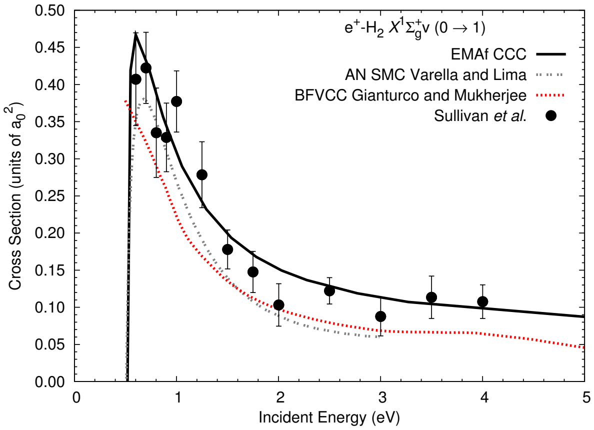

FIG. 17: Positron scattering from the ground state of $H_2$ vibrational 0 → 1 excitation cross section. The energy-modified adiabatic flux (EMAf) corrected convergent close-coupling (CCC) results are compared with the adiabatic-nuclei (AN) Schwinger multichannel (SMC) calculations of Varella and Lima [72], body-frame vibrational close-coupling (BFVCC) calculations of Gianturco and Mukherjee [64] and the measurements of Sullivan *et al.* [19].

## IV. CONCLUSION

The single-centre CCC method has been applied to positron scattering from $H_2$ in the electronic ground, $v_i = 0$ and $v_i = 1$ vibrational states. The reasonably large difference between results for scattering from the $v_i = 0$ and $v_i = 1$ vibrational states indicate that inclusion of these processes maybe important in transport modelling. Results were presented for the scattering length and the elastic scattering, total ionisation, vibrational excitation and grand total cross sections. In addition the present elastic DCS were used to "correct" the low-energy GTCS measurements of Zecca *et al.* [12] for the forward angle scattering effect. Here the fixed-nuclei CCC calculations explicitly demonstrate convergence in the close-coupling (target-state) and projectile partial-wave expansions. We estimate that the major integrated cross sections are accurate to within ±5% in the fixed-nuclei approximation. In general comparison with experiment is good.

However there is still some discrepancy between the CCC results and recent low-energy measurements of the GTCS [12, 13]. This is surprising as we have explicitly demonstrated convergence and the fixed-nuclei (ground state) scattering length obtained here ($A = -2.65\ a_0$) is in excellent agreement with accurate calculations [58, 61] ($A = -2.71\ a_0$). We also find that the GTCS is in excellent agreement with measurements in the intermediate-energy region, which indicates that calculations have accurately accounted for Ps-formation. In addition the present EMAf $0 \to 1$ vibrational excitation cross section is calculated from the low-energy GTCS and is in excellent agreement with the experiment of Sullivan *et al.* [19]. This serves as an independent check in support of our GTCS. We are confident with the EMAf method as the basis of this method (EMAP) also worked very well when applied to electron-$H_2$ scattering [68]. Hence calculations can only rigorously be improved by coupling electronic and nuclei motion. However, at these energies (4-8 eV) this coupling is not expected to play a significant role.

In the near future we will present results on the positron-$H_2$ electronic and rotational excitation cross sections. Our long term goal is to extend the single-centre CCC method to positron scattering from arbitrary diatomic molecules.

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