



UDC 539.1

EDN YHMEJH

<https://www.doi.org/10.33910/2687-153X-2026-7-3-131-136>

Account of asymptotic couplings in collisional dynamics of H_2 quasimolecule

S. A. Yakovleva ¹, T. S. Maleeva¹, M. Yu. Yakovlev¹

¹ Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia

Authors

Svetlana A. Yakovleva, ORCID: [0000-0002-8889-7283](https://orcid.org/0000-0002-8889-7283), e-mail: sayakovleva@herzen.spb.ru

Tatiana S. Maleeva, ORCID: [0009-0000-7734-9444](https://orcid.org/0009-0000-7734-9444)

Maxim Yu. Yakovlev, ORCID: [0000-0002-1562-7370](https://orcid.org/0000-0002-1562-7370), e-mail: yakovlev.max2000@yandex.ru

For citation: Yakovleva, S. A., Maleeva, T. S., Yakovlev, M. Yu. (2026) Account of asymptotic couplings in collisional dynamics of H_2 quasimolecule. *Physics of Complex Systems*, 7 (3), 131–136. <https://www.doi.org/10.33910/2687-153X-2026-7-3-131-136> EDN YHMEJH

Received 12 May 2026; reviewed 15 June 2026; accepted 18 June 2026.

Funding: The research was supported by an internal grant of Herzen State Pedagogical University of Russia (project No. 46-VG).

Copyright: © S. A. Yakovleva, T. S. Maleeva, M. Yu. Yakovlev (2026). Published by Herzen State Pedagogical University of Russia. Open access under [CC BY License 4.0](https://creativecommons.org/licenses/by/4.0/).

Abstract. This work studies mutual neutralization processes in $H^- + H^+$ collisions using the reprojection method within the Born–Oppenheimer approach. This method enables nuclear dynamical calculations with non-vanishing radial couplings at large internuclear distances. Such calculations were performed for a mixed basis set of $^1\Sigma_g$ and $^1\Sigma_u$ molecular states with radial coupling matrix elements with analytically calculated asymptotic values. The partial mutual neutralization cross sections are calculated for a collision energy range from 0.001 to 100 eV.

Keywords: inelastic processes, nonadiabatic transitions, asymptotic couplings, mutual neutralization, cross sections, hydrogen

Introduction

The study of inelastic processes in collisions of hydrogen negative and positive ions is instrumental in analyzing the simplest electron transfer process in atomic collisions. Theoretical investigations into $H^- + H^+$ collisions are challenged by additional symmetry connected with the reflection of nuclei. This collisional system has scattering states of $^1\Sigma_g$ and $^1\Sigma_u$ molecular symmetries, and previous theoretical studies (Hörnquist et al. 2022; Nkambule et al. 2016; Stenrup et al. 2009) performed separate sets of calculations within each one of them. However, our analytical calculations show that several molecular states of different parity are coupled at large internuclear distances. Non-vanishing coupling matrix elements are fundamental to the Born–Oppenheimer approach, that is also called the electron translation problem, as non-adiabatic couplings in the asymptotic region induce transitions between different electronic molecular states at large internuclear distances. To solve this problem, the reprojection method was proposed in (Belyaev 2010) and later in (Yakovlev et al. 2018). However, it was used mostly in heteronuclear systems, and one study (Hedvall et al. 2024) applied the reprojection method to collisions of the same nuclei, namely $H^- + H^+$; nuclear dynamics was also treated separately for $^1\Sigma_g$ and $^1\Sigma_u$ states. This work aims to include the asymptotic values of radial couplings between $^1\Sigma_g$ and $^1\Sigma_u$ molecular states in calculations of non-adiabatic nuclear dynamics.

Theory

Mutual neutralization processes in $H^- + H^+$ collisions are investigated within the Born–Oppenheimer approach that divides the problem into two parts: electronic structure calculations and non-adiabatic nuclear dynamics study. The electronic structure of the H_2 quasimolecule is calculated in (Stenrup et al. 2009) and has information on adiabatic potential energies U_j and radial coupling matrix elements $\left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle$ as functions of internuclear distance R . Nuclear dynamics study focuses on solving the coupled channel equations system:

$$\begin{aligned} & \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 J(J+1)}{2M R^2} + U_j(R) - E \right) F_j = \\ & = \frac{\hbar^2}{M} \sum_{k \neq j} \left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle \frac{\partial F_k}{\partial R} + \frac{\hbar^2}{2M} \sum_k \left\langle \varphi_j \left| \frac{\partial^2}{\partial R^2} \right| \varphi_k \right\rangle F_k, \end{aligned} \quad (1)$$

where M — reduced mass of nuclei, J — total angular momentum quantum number, E — total energy, and F_j — radial wave functions of nuclei. Numerical solution of these equations gives matrix $\underline{\underline{R}}$, which can be used to calculate scattering matrix $\underline{\underline{S}}$ and transition probabilities and inelastic cross sections

$$\underline{\underline{S}} = (-1)^J \exp(-i\underline{\underline{K}}R_0) \underline{\underline{K}}^{-\frac{1}{2}} \left(\underline{\underline{t}}^- + i\underline{\underline{R}} \underline{\underline{t}}^- \underline{\underline{K}} \right) \left(\underline{\underline{t}}^+ + i\underline{\underline{R}} \underline{\underline{t}}^+ \underline{\underline{K}} \right)^{-1} \underline{\underline{K}}^{\frac{1}{2}} \exp(-i\underline{\underline{K}}R_0), \quad (2)$$

where matrices $\underline{\underline{t}}^\pm$ are introduced in the reprojection method (Belyaev 2010; 2022) as follows

$$t_{kj}^\pm = \delta_{kj} \pm \frac{iK_j \hbar^2}{M(U_k(\infty) - U_j(\infty))} \left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle_\infty, \quad (3)$$

and take into account that incoming and outgoing waves in a single atomic state must be distributed among all molecular states in the asymptotic region. Non-vanishing radial matrix elements at large internuclear distances arise since electronic structure calculations are usually performed in molecular coordinates. In the standard Born–Oppenheimer approach, asymptotic values of radial coupling matrix elements are neglected, which corresponds to setting $\underline{\underline{t}}^\pm$ to a unity matrix in equation (2).

Asymptotic values of radial coupling matrix elements can be calculated using asymptotic wave functions for different scattering states of the H_2 quasimolecule. At large internuclear distances, radial couplings can be expressed via atomic transition dipole matrix elements

$$\left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle_\infty = \gamma_k \frac{m}{\hbar^2} [U_j(\infty) - U_k(\infty)] \langle \varphi_j | z^{at} | \varphi_k \rangle_\infty, \quad (4)$$

where $U(\infty)$ is the asymptotic value of adiabatic potential energy, m — reduced mass of the electron and the nuclei, and factor $\gamma_k = M_{a,b}/(M_a + M_b)$ for nuclei a and b , which for the case of the H_2 quasimolecule has value $\gamma_k = 1/2$. Equation (4) shows that some of the matrix elements have zero values: these are matrix elements that correspond to transitions between degenerate states ($U_j(\infty) = U_k(\infty)$), between states where dipole transition is forbidden, and between covalent and ionic states.

Electronic structure

Calculations for the electronic structure of the H_2 quasimolecule that includes adiabatic potentials and coupling matrix elements for 13 scattering channels were presented in (Stenrup et al. 2009). This work was followed by (Hörnquist et al. 2022), with several higher-lying states added; however, they showed that cross sections to the scattering states $H(1s)+H(4l)$ are negligible. Ionic state $H^-(1s^2) + H^+$ produces $^1\Sigma_g$ and $^1\Sigma_u$ molecular symmetry, where subscripts g and u denote even and odd wave functions with respect to the reflection of nuclei. In our work we consider seven scattering states of $^1\Sigma_g$ molecular symmetry and six scattering states of $^1\Sigma_u$ symmetry, with each symmetry including one

ionic state. Scattering channels, their molecular terms, and asymptotic energies measured from the ground state are collected in Table 1. Adiabatic potential energies as functions of the internuclear distance R are shown in Fig. 1, with solid lines representing $^1\Sigma_g$ states and dashed lines — $^1\Sigma_u$ states. Table 1 and Fig. 1 demonstrate that scattering channels $H(1s)+H(nl)$ that have the same quantum number n are asymptotically degenerate, as well as two ionic states.

Table 1. Scattering channels for $H(1s) + H(nl)$ and $H^-(1s^2) + H^+$ that form $^1\Sigma_{g,u}$ molecular symmetry and their asymptotic energies with respect to the ground state

j	Scattering channel	Term	Asymptotic energy, a. u.
1	$H(1s) + H(1s)$	$1\ ^1\Sigma_g$	0.0
2	$H(1s) + H(2s)$	$2\ ^1\Sigma_g$	0.3748003
3	$H(1s) + H(2p)$	$3\ ^1\Sigma_g$	0.3748003
4	$H(1s) + H(3s)$	$4\ ^1\Sigma_g$	0.4442076
5	$H(1s) + H(3p)$	$5\ ^1\Sigma_g$	0.4442076
6	$H(1s) + H(3d)$	$6\ ^1\Sigma_g$	0.4442076
7	$H^-(1s^2) + H^+$	$7\ ^1\Sigma_g$	0.4997332
8	$H(1s) + H(2s)$	$1\ ^1\Sigma_u$	0.3748003
9	$H(1s) + H(2p)$	$2\ ^1\Sigma_u$	0.3748003
10	$H(1s) + H(3s)$	$3\ ^1\Sigma_u$	0.4442076
11	$H(1s) + H(3p)$	$4\ ^1\Sigma_u$	0.4442076
12	$H(1s) + H(3d)$	$5\ ^1\Sigma_u$	0.4442076
13	$H^-(1s^2) + H^+$	$6\ ^1\Sigma_u$	0.4997332

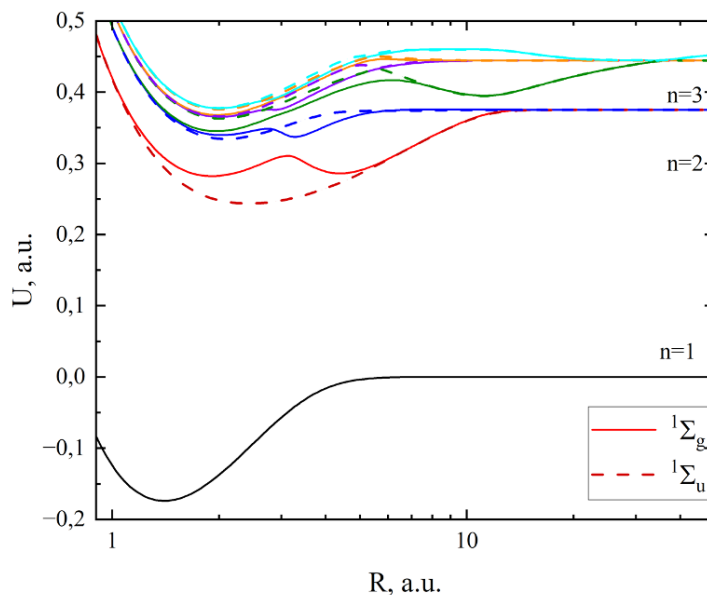


Fig. 1. Adiabatic potentials for H_2 quasimolecule $^1\Sigma_g$ states (solid lines) and $^1\Sigma_u$ states (dashed lines) as functions of internuclear distance

Asymptotic values of radial coupling matrix elements calculated using equation (4) are collected in Table 2. This table shows that besides zero values for transitions between degenerate states, ionic-covalent transitions, and optically forbidden transitions, radial couplings are zero in the asymptotic region for transitions between states of the same parity. However, the calculated radial matrix elements from (Stenrup et al. 2009) have non-zero asymptotic values for couplings between states of the same parity. This artifact may be attributed to the separate calculations for sets of $^1\Sigma_g$ and $^1\Sigma_u$ states.

Table 2. Asymptotic values for $\left\langle j \left| \frac{\partial}{\partial R} \right| k \right\rangle$ matrix elements, terms for molecular states correspond with Table 1

	$1^1\Sigma_g$	$2^1\Sigma_g$	$3^1\Sigma_g$	$4^1\Sigma_g$	$5^1\Sigma_g$	$6^1\Sigma_g$	$7^1\Sigma_g$	$1^1\Sigma_u$	$2^1\Sigma_u$	$3^1\Sigma_u$	$4^1\Sigma_u$	$5^1\Sigma_u$	$6^1\Sigma_u$
$1^1\Sigma_g$	—	0	0	0	0	0	0	0	−0.198	0	−0.094	0	0
$2^1\Sigma_g$	0	—	0	0	0	0	0	0	0	0	−0.061	0	0
$3^1\Sigma_g$	0	0	—	0	0	0	0	0	0	−0.019	0	−0.117	0
$4^1\Sigma_g$	0	0	0	—	0	0	0	0	0.019	0	0	0	0
$5^1\Sigma_g$	0	0	0	0	—	0	0	0.061	0	0	0	0	0
$6^1\Sigma_g$	0	0	0	0	0	—	0	0	0.117	0	0	0	0
$7^1\Sigma_g$	0	0	0	0	0	0	—	0	0	0	0	0	0
$1^1\Sigma_u$	0	0	0	0	−0.061	0	0	—	0	0	0	0	0
$2^1\Sigma_u$	0.198	0	0	−0.019	0	−0.117	0	0	—	0	0	0	0
$3^1\Sigma_u$	0	0	0.019	0	0	0	0	0	0	—	0	0	0
$4^1\Sigma_u$	0.094	0.061	0	0	0	0	0	0	0	0	—	0	0
$5^1\Sigma_u$	0	0	0.117	0	0	0	0	0	0	0	0	—	0
$6^1\Sigma_u$	0	0	0	0	0	0	0	0	0	0	0	0	—

Nuclear dynamics calculations

This work aims to incorporate asymptotic values of radial coupling matrix elements between $1^1\Sigma_g$ and $1^1\Sigma_u$ states, shown in Table 2, into non-adiabatic nuclear dynamics calculations. To include these analytical values of asymptotic radial coupling matrix elements in dynamical calculations, we modify quantum chemical data from (Stenrup et al. 2009) as follows: all radial couplings between states of the same parity are adjusted to reach zero in the asymptotic region; while radial couplings between states of the different parity are set to reach corresponding asymptotic values from Table 2 and have zero values at short and intermediate internuclear distances.

A system of coupled equations (1) is solved for 13 adiabatic states in Table 1 using modified matrix elements for collision energies from 0.001 to 100 eV. Calculated mutual neutralization cross sections are shown with solid lines in Fig. 2: the upper panel shows cross sections for transitions from the $7^1\Sigma_g$ ionic state to all covalent states ($1^1\Sigma_u - 5^1\Sigma_u$ and $1^1\Sigma_g - 6^1\Sigma_g$), and the lower panel — cross sections from the $6^1\Sigma_u$ ionic state. Dashed lines represent independent calculations within each molecular symmetry using initial quantum chemical data. Comparison of these two sets of data shows that cross sections for transitions from both ionic states $7^1\Sigma_g$ and $6^1\Sigma_u$ to the states of the same parity are not sensitive to the change in radial couplings: solid lines almost coincide with dashed lines in both panels of Fig. 2. Meanwhile, cross sections for transitions from each ionic state to the covalent states of different parity have generally much smaller values than to the states of the same parity, with the exception of the $7^1\Sigma_g \rightarrow 1^1\Sigma_g$ transition, which itself has a very small value due to the large energy gap between the $1^1\Sigma_g$ molecular term and other terms (see Fig. 1).

Fig. 3 shows the comparison of mutual neutralization cross sections calculated using the reprojection method and the standard Born–Oppenheimer approach with the upper panel showing transitions from the $7^1\Sigma_g$ state and the lower panel — from the $6^1\Sigma_u$ state; the dashed lines are used for calculations with the reprojection method while the solid lines correspond to calculations based on the standard approach. Cross sections for this figure are summed over final channels $H(1s)+H(nl)$ that have the same quantum number n . It is clearly seen that among mutual neutralization processes the effect of applying the reprojection method is the strongest for transition to the ground state $H(1s)+H(1s)$. These cross sections are in good agreement with the results described in (Stenrup et al. 2009).

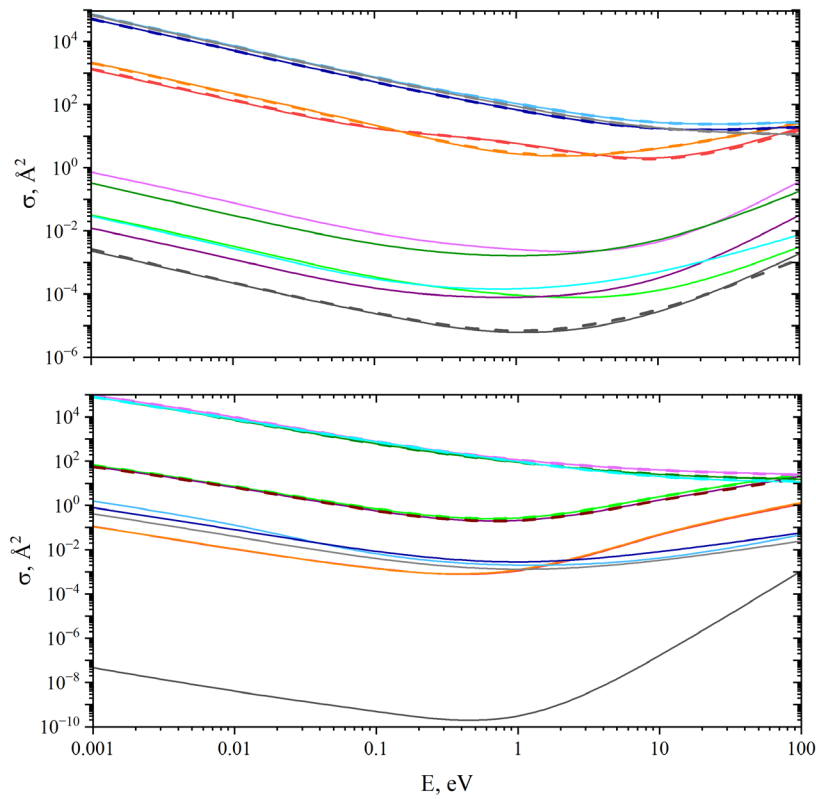


Fig. 2. Partial mutual neutralization cross sections from $7^1\Sigma_g$ state (upper panel) and from $6^1\Sigma_u$ state (lower panel). Solid lines represent calculation in mixed basis of 13 states, while dashed lines stand for calculations within $^1\Sigma_g$ and $^1\Sigma_u$ symmetries separately

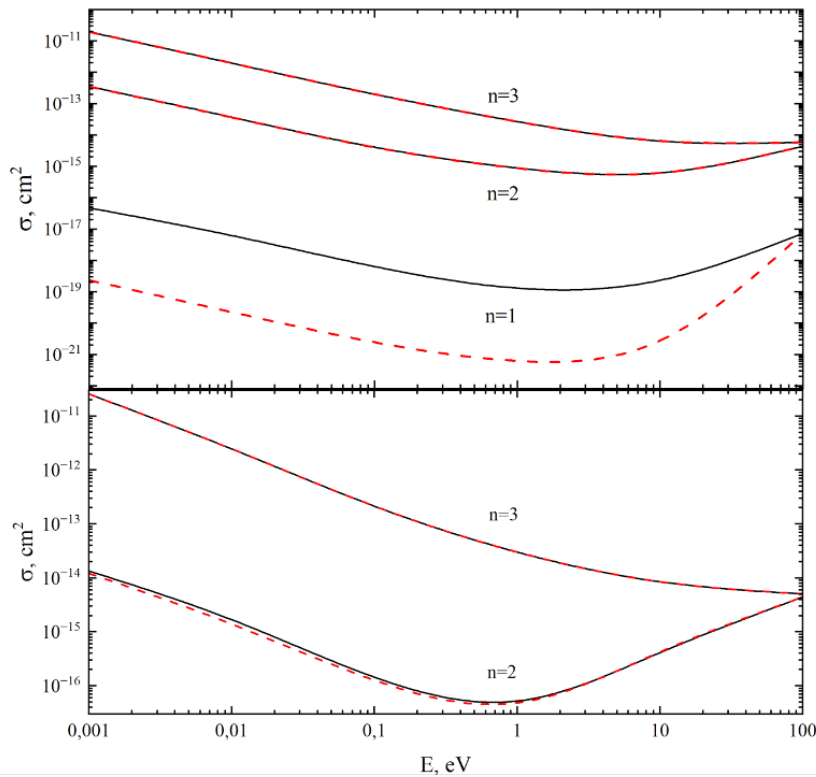


Fig. 3. Mutual neutralization cross sections from the $7^1\Sigma_g$ state (upper panel) and from the $6^1\Sigma_u$ state (lower panel) summed over final channels $H(1s)+H(nl)$ with the same n , calculated within the standard Born–Oppenheimer approach (solid lines) and using the reprojection method (dashed lines)

Conclusion

The mutual neutralization cross sections for $H^- + H^+$ collisions are calculated with the reprojection method that provides correct treatment of non-vanishing radial couplings at large internuclear separations. The basis set for nuclear dynamics consists of seven $^1\Sigma_g$ and six $^1\Sigma_u$ molecular states. Radial matrix elements are adapted for couplings between all 13 states with asymptotic calculated analytically. The analysis of calculated cross sections shows that the presence of asymptotic values couplings between states of different parity slightly redistributes partial mutual neutralization cross sections, though not changing total cross section. However, these asymptotic couplings may have a higher impact on the excitation and de-excitation cross sections.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Each of the authors contributed to the submission.

Acknowledgements

Authors extend their gratitude to Prof. Andrey K. Belyaev for fruitful discussions.

References

- Belyaev, A. K. (2022) Reprojection method for inelastic processes in atomic collisions within Born-Oppenheimer approach. *Physics of Complex Systems*, 3 (1), 25–36. <https://doi.org/10.33910/2687-153X-2022-3-1-25-36> (In English)
- Belyaev, A. K. (2010) Revised Born-Oppenheimer approach and a reprojection method for inelastic collisions. *Physical Review A*, 82, article 060701(R). <https://doi.org/10.1103/PhysRevA.82.060701> (In English)
- Hedvall, P., Hörnquist, J., Yakovlev, S. L. et al. (2024) Treatment of asymptotic non-adiabatic couplings with higher order reprojection method in the diabatic representation. *Journal of Chemical Physics*, 161 (5), article 054303. <https://doi.org/10.1063/5.0213714> (In English)
- Hörnquist, J., Hedvall, P., Larson, A. (2022) Mutual neutralization in $H^+ + H^-$ collisions: An improved theoretical model. *Physical Review A*, 106, article 062821. <https://doi.org/10.1103/PhysRevA.106.062821> (In English)
- Nkambule, S., Elander, N., Larson, Å. et al. (2016) Differential and total cross sections of mutual neutralization in low-energy collisions of isotopes of $H^+ + H^-$. *Physical Review A*, 93, article 032701. <https://doi.org/10.1103/PhysRevA.93.032701> (In English)
- Stenrup, M., Larson, A., Elander, N. (2009) Mutual neutralization in low-energy $H^+ + H^-$ collisions: A quantum *ab initio* study. *Physical Review A*, 79, article 012713. <https://doi.org/10.1103/PhysRevA.79.012713> (In English)
- Yakovlev, S. L., Yarevsky, E. A., Elander, N. O., Belyaev, A. K. (2018) Asymptotic solution of a multichannel scattering problem with a nonadiabatic coupling. *Theoretical and Mathematical Physics*, 195 (3), 874–885. <https://doi.org/10.1134/S0040577918060065> (In English)