Theoretical physics.
Physics of atoms and molecules

UDC 539.1

EDN WTKYUL
https://www.doi.org/10.33910/2687-153X-2025-6-3-150-154

Pseudopotential method for coupling matrix element calculations

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For citation: Yakovleva, S. A., Vahrushev, V. A., Stepanov, I. G., Belyaev, A. K. (2025) Pseudopotential method for coupling matrix elements calculations. *Physics of Complex Systems*, 6 (3), 150–154. https://www.doi.org/10.33910/2687-153X-2025-6-3-150-154 EDN WTKYUL

Received 20 May 2025; reviewed 27 June 2025; accepted 1 July 2025.

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

Abstract. This work derives electronic Hamiltonian matrix elements in diabatic representation using an asymptotic approach. Off-diagonal matrix elements which couple different covalent excited states of a LiH quasi-molecule with an ionic molecular state are calculated. Electronic wave functions of different lithium states are determined by both the Discrete Variable Representation (DVR) and pseudopotential methods. Electronic wave functions of a hydrogen negative ion are obtained by the complex rotation method.

Keywords: inelastic processes, nonadiabatic transitions, pseudopotential, electronic Hamiltonian, hydrogen negative ion

Introduction

There is a wide variety of methods for calculating the electronic structure of a quasi-molecule. Both adiabatic and diabatic representations can be used. In adiabatic representation, eigenfunctions of the electronic Hamiltonian ψ_j^{ad} are used to determine the eigenvalues of the electronic Hamiltonian $\left\langle \psi_j^{ad} \left| \widehat{H}_j \right| \psi_k^{ad} \right\rangle$ as well as non-adiabatic coupling matrix elements $\left\langle \psi_j^{ad} \left| \frac{\partial}{\partial R} \right| \psi_k^{ad} \right\rangle$, $\left\langle \psi_j^{ad} \left| L_x^2 + L_y^2 \right| \psi_k^{ad} \right\rangle$ and so on. In diabatic representation, the basis of diabatic functions ψ_j^{di} is used to determine the diagonal and off-diagonal matrix elements of the electronic Hamiltonian $\left\langle \psi_j^{di} \left| \widehat{H}_j \right| \psi_k^{di} \right\rangle$. The aforementioned quantities are used in the studies of nuclear dynamics of colliding systems in terms of the Born–Oppenheimer approach. The choice of electronic basis functions (adiabatic or diabatic) defines the system of coupled channel differential equations for nuclear wave functions.

This paper proposes a method based on the asymptotic approach for calculating the electronic Hamiltonian matrix elements in diabatic representation for collisions of atoms and positive ions of different chemical elements with atoms and negative ions of hydrogen. The main focus of this work is calculating the off-diagonal matrix element of the electronic Hamiltonian that corresponds to the interaction

of ionic and covalent configurations. Molecular wave functions of the covalent states are constructed using the one-electron wave functions computed on Discrete Variable Representation (DVR) basis functions with the pseudopotential method. Hydrogen negative ion wave function calculated using the complex rotation method (Yarevsky 2016) is used as the ionic state wave function.

Theory

The asymptotic approach was proposed for studying inelastic processes in (Belyaev 2013). The electron structure of a quasimolecule formed in collisions of atoms and ions of various elements with atoms and ions of hydrogen is modeled by constructing the electronic Hamiltonian matrix in diabatic representation. An important step is the calculation of the off-diagonal matrix elements which define interactions between different states of the quasimolecule. In terms of the asymptotic approach, only the ion-covalent couplings are taken into account, and for determining the off-diagonal matrix elements charge exchange formula (Olson et al. 1971) is used. This paper proposes calculating the matrix elements of ion-covalent interaction by use of asymptotic expressions for covalent state wave functions of the quasimolecule and negative hydrogen ion wave function calculated using the complex rotation method.

To model the electronic structure of a LiH quasimolecule using the asymptotic approach, we consider several covalent states $Li(1s^2nl^2L) + H(1s^2S)$ and one ionic state $Li^+(1s^2\,{}^1S) + H^-(1s^2\,{}^1S)$, including only $^1\Sigma^+$ molecular states. The electronic hamiltonian for this system reads

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\Delta_{\vec{r}_1} - \frac{\hbar^2}{2m_e}\Delta_{\vec{r}_2} - \frac{Ze^2}{4\pi\varepsilon_0 r_{1H}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{1Li}} - \\ - \frac{Ze^2}{4\pi\varepsilon_0 r_{2H}} - \frac{Ze^2}{4\pi\varepsilon_0 r_{2Li}} + \frac{Ze^2}{4\pi\varepsilon_0 R} + \frac{Ze^2}{4\pi\varepsilon_0 r_{12}}, \tag{1}$$

where electron coordinates $\vec{r}_1$ and $\vec{r}_2$ are measured from the center of the nuclear mass, R is internuclear distance, r_{1H}, r_{2H}, r_{1Li}, r_{2Li} are the distances from the first or second electron to the hydrogen or lithium core, and r_{12} is the distance between two electrons.

The asymptotic molecular wave function $|L\tilde{\Lambda}SM_S\rangle$ for covalent $^1\Sigma^+$ ($\tilde{\Lambda}$ = 0, S = 0, M_S = 0) molecular states of LiH is constructed using one-electron atomic wave functions using the expression from (Nikitin, Umanskii 1984) and reads:

$$|L000\rangle = \hat{A}\sum_{m_{s1},m_{s2}} C^{0\,0}_{1\,\frac{1}{2}m_{s1}\frac{1}{2}m_{s2}}\,\varphi^{Li}_{nl0}(\vec{r})\chi_{\frac{1}{2}m_{s1}}(\sigma)\cdot\varphi^{H}_{100}(\vec{r}')\chi_{\frac{1}{2}m_{s2}}(\sigma'), \tag{2}$$

where $\hat{A}$ is an antisymmetrization operator, $C^{JM}_{j_1 m_1\, j_2 m_2}$ denotes Clebsch–Gordan coefficients, and $\varphi^{\alpha}_{nlm}(\vec{r})Xsm_s(\sigma)$ is the wave function of an electron centered on the hydrogen or lithium core (α being H or Li). The antisymmetric wave function if the ionic state is expressed as follows:

$$|0000\rangle = \frac{1}{\sqrt{2}}\psi_{H^-}(r_{1H}, r_{2H}, cos\,\Theta_{12})\left(\chi_{\frac{1}{2}\frac{1}{2}}(\sigma_1)\chi_{\frac{1}{2}-\frac{1}{2}}(\sigma_2) - \chi_{\frac{1}{2}-\frac{1}{2}}(\sigma_1)\chi_{\frac{1}{2}\frac{1}{2}}(\sigma_2)\right), \tag{3}$$

where $\Psi_H - (r_{1H}, r_{2H}, cos\theta_{12})$ is the wave function of two electrons in the negative hydrogen ion, θ_{12} being the angle between $\vec{r}_{1H}$ and $\vec{r}_{2H}$.

Using these molecular wave functions, the off-diagonal matrix element of the electronic Hamiltonian (1) can be expressed via coordinate one-electron atomic functions and the function of the hydrogen negative ion:

$$\langle L000|\hat{H}_e|0000\rangle = \frac{1}{2\sqrt{2(1+s^2)}}\left[2\left(E_{H^-} + \frac{Ze^2}{4\pi\varepsilon_0 R}\right)S - \right. \\ - \frac{e^2}{4\pi\varepsilon_0}\left(\left\langle\varphi_{100}(\vec{r}_{2H})\varphi_{nl0}(\vec{r}_{1Li})\right|\frac{1}{r_{1Li}} + \frac{1}{r_{2Li}}\left|\psi_{H^-}(r_{1H}, r_{2H}, cos\,\Theta_{12})\right\rangle + \\ \left. + \left\langle\varphi_{100}(\vec{r}_{1H})\varphi_{nl0}(\vec{r}_{2Li})\right|\frac{1}{r_{1Li}} + \frac{1}{r_{2Li}}\left|\psi_{H^-}(r_{1H}, r_{2H}, cos\,\Theta_{12})\right\rangle\right)\Big] \tag{4}$$

where s and S are overlap integrals:

$$s = \langle \varphi_{nl0}(\vec{r}_{1Li}) | \varphi_{100}(\vec{r}_{2H}) \rangle = \langle \varphi_{nl0}(\vec{r}_{2Li}) | \varphi_{100}(\vec{r}_{1H}) \rangle,$$

$$S = \langle \varphi_{100}(\vec{r}_{2H}) \varphi_{nl0}(\vec{r}_{1Li}) | \psi_{H^-}(r_{1H}, r_{2H}, cos\ \Theta_{12}) \rangle =$$

$$\langle \varphi_{100}(\vec{r}_{1H}) \varphi_{nl0}(\vec{r}_{2Li}) | \psi_{H^-}(r_{1H}, r_{2H}, cos\ \Theta_{12}) \rangle.$$

To find the actual values of the off-diagonal matrix element (4), one needs to calculate several similar 6-dimensional integrals. In the present work we perform integration over the coordinates of two electrons, measured from the hydrogen core as follows:

$$\langle \varphi_{100}(\vec{r}_{2H}) \varphi_{nl0}(\vec{r}_{1Li}) | \frac{1}{r_{1Li}} | \psi_{H^-}(r_{1H}, r_{2H}, cos\ \Theta_{12}) \rangle =$$

$$= \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \frac{\varphi_{100}(\vec{r}_{2H}) \varphi_{nl0}(\vec{r}_{1Li}) \psi_{H^-}(r_{1H}, r_{2H}, cos\ \Theta_{12})}{r_{1Li}} \cdot \tag{5}$$

$$\cdot r_{1H}^2\ sin\ \theta_{1H} dr_{1H} d\theta_{1H} d\varphi_{1H} r_{2H}^2\ sin\ \theta_{2H} dr_{2H} d\theta_{2H} d\varphi_{2H}$$

In order to use the wave function of the hydrogen negative ion, we define $cos\theta_{12}$ from the scalar product of $\vec{r}_{1H}$ and $\vec{r}_{2H}$; the distance r_{1Li} is defined via r_{1H} and R.

These equations make it possible to calculate the off-diagonal matrix element of the electronic Hamiltonian in diabatic representation for a particular internuclear distance R. In order to study non-adiabatic nuclear dynamics — for example, using the multichannel Landau–Zener model — one needs to know both diagonal and off-diagonal matrix elements for a range of internuclear distances.

Results

In this work we consider the following excited states of Li(2s, 2p, 3s, 3p, 4s, 4p) for molecular wave functions of the covalent states Li($1s^2$nl ^{2}L) + H(1s ^{2}S) defined by Eq. (2). The wave function of one electron centered on the lithium core is calculated by expanding it over the basis of DVR functions with the use of a pseudopotential. The dependence of the pseudopotential on r is calculated using the tabulated wave function of a 2s-electron in a Li atom from (Clementi, Roetti 1974). The wave function of two electrons in the hydrogen negative ion is calculated by the complex rotation method (Yarevsky 2016).

Fig. 1 shows the probability density of two electrons as a function of two distances from the nucleus to both electrons ($\vec{r}_1$ and $\vec{r}_2$) for a fixed angle between these radius vectors. The upper panel depicts the case of equal distances ($r_1 = r_2$) for two geometries of the particles: the angle between electron radius vectors equals 0 and π. The electron correlation is clearly seen. The lower panel demonstrates the dependence of the electronic probability density on the distance from the nucleus to one electron while the distance to another electron is fixed. We can see that the maximum of the density corresponds to the case when both electrons are close to the nucleus (both distances are around 1–3 a. u.) and the two-electron wave function can be represented as a product of two equivalent single-electronic wave functions. When one of the electrons moves away, the electronic configuration changes and the two-electronic wave function becomes a product of two non-equivalent single-electronic wave functions.

Finally, the off-diagonal matrix elements of the electronic Hamiltonian are calculated using Eq. (4). The comparison of the calculated data with the values from quantum chemical calculations (Croft et al. 1999) and given by a semi-empirical formula for one electron charge transfer (Olson et al. 1971) is presented in Fig. 2.

The graphs demonstrate the general agreement of the off-diagonal Hamiltonian matrix elements calculated in the present work with the results of the previous calculations for a LiH molecule (Croft et al. 1999) as well as the semi-empirical estimates (Olson et al. 1971). These dependences have the exponential form that agrees with the asymptotic theory. The difference of the data calculated in the present work from the results of quantum chemical calculations can be related to the fact that the pseudopotential is obtained using the wave function of the 2s-electron. It is worth noting that for calculations of the wave functions for higher excited states of the Li atom, the larger basis of DVR functions should be used, which can also lead to deviations of the obtained results from the quantum chemical data.

 https://www.doi.org/10.33910/2687-153X-2025-6-3-150-154

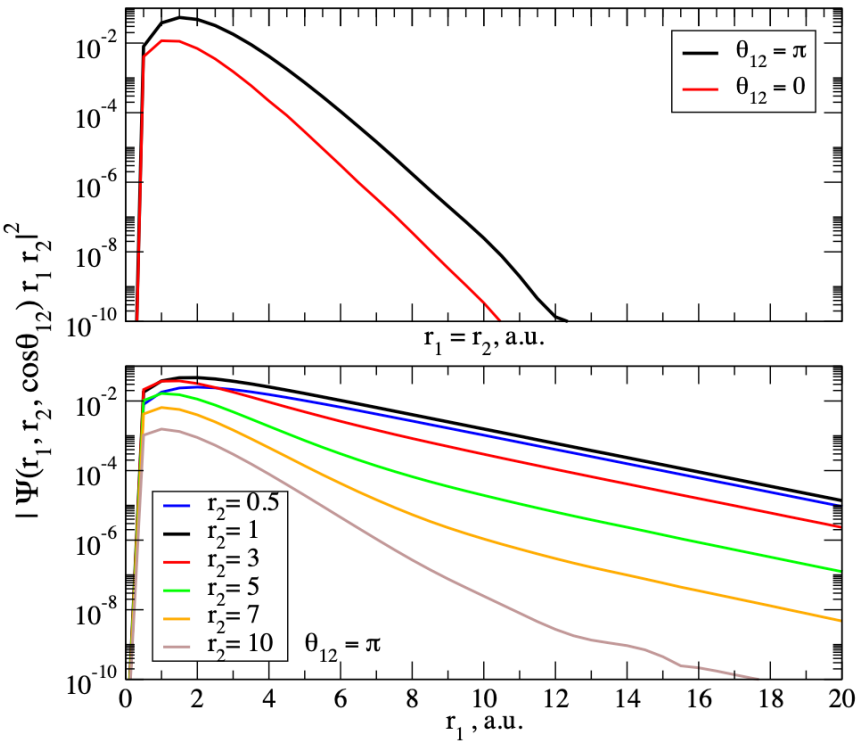

Fig. 1. The probability density of two electrons in a negative hydrogen ion calculated by the complex rotation method

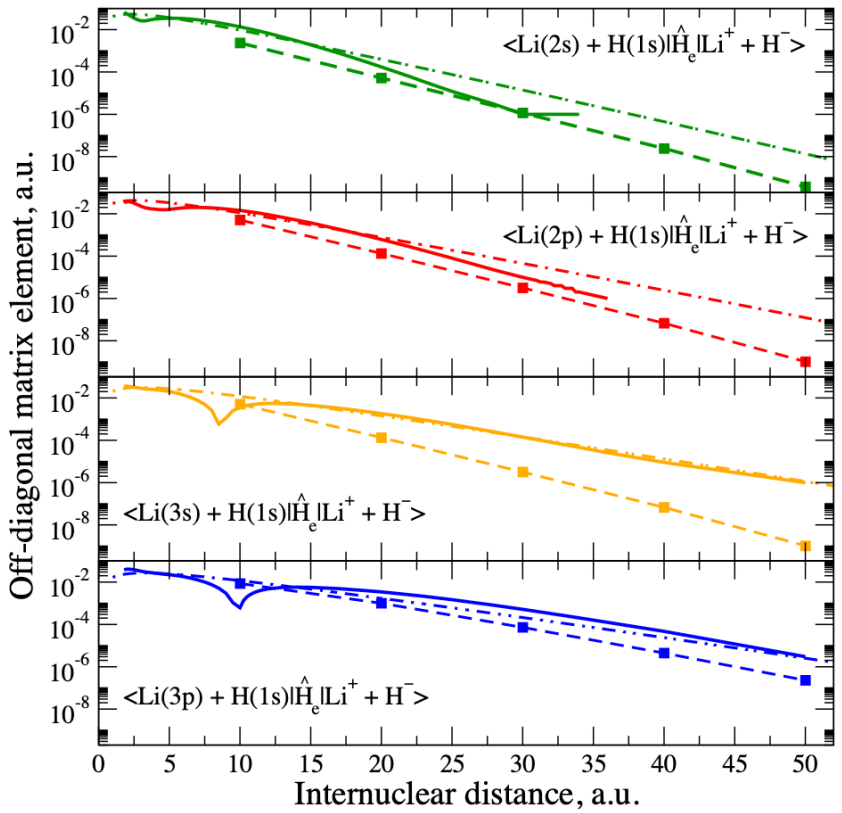

Fig. 2. The off-diagonal matrix element for LiH calculated in this work (dotted line with squares), by a semi-empirical formula (dash-dotted line) and in quantum chemical calculations (solid line) for 2s (upper panel), 2p (second from the top panel), 3s (second from the bottom panel), and 3p (bottom panel) electron in a Li atom

Conclusion

The off-diagonal electronic Hamiltonian matrix elements are calculated using the accurate wave function of the two electrons in the hydrogen negative ion and the wave functions of the six excited states of the lithium atom, calculated by means of the DVR basis functions and the pseudopotential taken from the accurate ab initio Hartree–Fock calculations. The calculated matrix elements can be used for accurate nuclear dynamics studies determining the non-adiabatic transition probabilities and inelastic cross sections in the lithium-hydrogen collisions, by means of the wave packet method (Yakovlev, Belyaev 2024), the reprojection method (Belyaev 2022), and probability currents method (Stepanov, Belyaev 2024).

Conflict of Interest

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

Author Contributions

Each of the authors has contributed to the submission.

Acknowledgements

The authors gratefully acknowledge the assistance with obtaining the wave function of the hydrogen negative ion provided by Dr. E. Yarevsky in private communication.

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