Simple Closed-Form Expression for Penning Reaction Rate Coefficients for Cold Molecular Collisions by Non-Hermitian Time-Independent Adiabatic Scattering Theory

Mariusz Pawlak,*,†[iD] Anael Ben-Asher,‡ and Nimrod Moiseyev‡,¶

†Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland
‡Schulich Faculty of Chemistry, Technion—Israel Institute of Technology, Haifa 32000, Israel
¶Faculty of Physics, Technion—Israel Institute of Technology, Haifa 32000, Israel

ABSTRACT: We present a simple expression and its derivation for reaction rate coefficients for cold anisotropic collision experiments based on adiabatic variational theory and time-independent non-Hermitian scattering theory. We demonstrate that only the eigenenergies of the resulting one-dimensional Schrödinger equation for different complex adiabats are required. The expression is applied to calculate the Penning ionization rate coefficients of an excited metastable helium atom with molecular hydrogen in an energy range spanning from hundreds of kelvins down to the millikelvin regime. Except for trivial quantities like the masses of the nuclei and the bond length of the diatomic molecule participating in the collision, one needs as input data only the complex potential energy surface (CPES). In calculations, we used recently obtained ab initio CPES by D. Bhattacharya et al. (*J. Chem. Theory Comput.* **2017**, *13*, 1682−1690) without fitting parameters. The results show good accord with current measurements (*Nat. Phys.* **2017**, *13*, 35−38).

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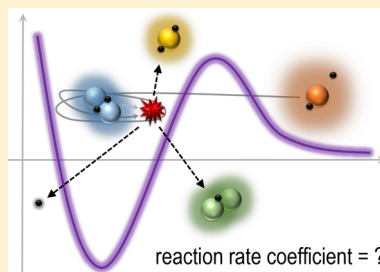
1. INTRODUCTION

The great progress of advanced experimental techniques has enabled the study of the Penning ionization (PI) at very low temperatures.[1−9] In such a reaction, an electron is transferred from the collision partner (usually an atom or a molecule) to the partially empty orbital of metastable atom A* and the initially excited electron of A* is ejected to the continuum. This is very efficient, in particular, in a head-on collision when the projectile and the target get close to each other. A recent experiment revealed the role of anisotropy in the subkelvin regime when the PI occurs.[4] It was demonstrated how the change from spherical to nonspherical symmetry qualitatively affects the collision dynamics. Thus, a theoretical description is strongly desired. There are several quantum mechanical scattering techniques currently being used to calculate reaction rate coefficients (or cross sections) for cold molecular collisions. Jankunas and co-workers investigated the PI of polyatomic molecules by metastable helium and neon within the framework of the multichannel quantum defect model,[5−9] whereas Klein et al. performed close-coupling quantum scattering computations for collisions of an excited He atom with molecular hydrogen.[4] In quantum mechanical scattering theory, the cross sections can be calculated in a nontrivial way based on phase shifts determined from asymptotic solutions of the time-independent Schrödinger equation, as was recently done for atom−diatom low-temperature collisions.[2,10,11] It is necessary to develop models and formulas that are adequate to account for process complexity yet straightforward enough for implementing and understanding experimental findings.

In this paper, we present a new uncomplicated expression and its derivation for the reaction rate coefficients based on adiabatic variational theory[10,11] and time-independent non-Hermitian scattering theory as previously developed by Moiseyev and colleagues for atomic and molecular scattering from solid surfaces,[12−16] to electron scattering from molecules,[17−20] and to interatomic/intermolecular Coulombic decay (ICD).[21] We show that it is not required to take into consideration in the calculations the different products of the reaction involving real potential energy surfaces (PESs). It makes the calculations much more simple. Moreover, the eigenenergies from the radial Schrödinger equation for different adiabats are only necessary. Consequentially, the reaction rate expression can be easily implemented by experimentalists. All computations and results are presented here without any fitting and scaling. We state that our approach for determining rate coefficients can be favorably applied for studying cold anisotropic collision reactions of different complexes when also other types of ionization occur (ICD,[22] Auger decay, etc.).

2. THEORETICAL BACKGROUND

We show the derivation and the final expression for the reaction rate coefficient of an atom (A) colliding with a diatomic molecule (M), where the interaction is described by the complex potential energy surface (CPES). As an illustrative numerical example, we consider the PI reaction that has been recently measured[1,2,4]

$$A^* + M \rightarrow [A^*-M] \rightarrow A + M^+ + e^- \tag{1}$$
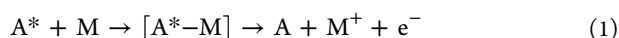
where A^* denotes excited metastable helium atom (1s2s, triplet S), whereas M denotes H_2. The reactants form a quasi-bound complex in a resonance state that decays upon collision. Because the state of the system He^*-H_2 is embedded in the continuum above the ionization threshold of the system $He-H_2^+$, the PES for the reactants is not real but complex. The complex intermolecular interaction potential V_C for an open-shell atom in an S state interacting with a molecule expanded in Legendre polynomials is[23,24]

$$V_C(R, \Theta) = \mathrm{Re}[V_C(R, \Theta)] - i\frac{\Gamma_C(R, \Theta)}{2}$$
$$= \sum_k V_k^C(R) P_k(\cos \Theta) \tag{2}$$

where R is the distance between the atom and the center of mass of the diatom, Θ is the angle between the molecular bond and $\vec{R}$, and Γ_C is the rate of decay from the neutral-excited state to the cationic one.

We consider the Hamiltonian assuming the stiffness of the molecule to make our approach simpler. It means that we treat the diatomic molecule to be a rigid rotor (the bond length r_0 is kept fixed). This approximation results from the fact that the vibrational molecular frequencies are much higher than the intermolecular ones. Thus

$$\hat{H} = -\frac{\hbar^2}{2\mu_{AM}}\partial_R^2 + \frac{\hat{l}^2}{2\mu_{AM}R^2} + \frac{\hat{j}^2}{2\mu_M r_0^2} + V_C(R, \Theta) \tag{3}$$

where μ_M is the reduced mass of the diatomic molecule, μ_{AM} is the reduced mass of the van der Waals complex, and $\hat{j}^2$ and $\hat{l}^2$ are the squared angular momentum operators associated with diatomic and with the atom–diatom relative rotations, respectively. The components of $\vec{R} = (R, \theta_1, \phi_1)$ point to the atom from the center of mass of the diatomic molecule, $\mathrm{d}\vec{R} = \sin\theta_1\, \mathrm{d}R\, \mathrm{d}\theta_1\, \mathrm{d}\phi_1$, and the angles θ_2 and ϕ_2 show the orientation of molecular bond in the same laboratory coordinate frame.

We split the many-dimensional problem into many subproblems by applying the adiabatic variational theory.[10,11] First, we construct the potential matrix with products of spherical harmonics as basis functions for a given intermolecular separation. We treat R as a parameter (and not as a dynamical variable). The matrix is

$$V_{q',q}^{var}(R) = \left\langle \psi_{q'} \left| \frac{\hat{l}^2}{2\mu_{AM}R^2} + \frac{\hat{j}^2}{2\mu_M r_0^2} + V_C(R, \Theta) \right| \psi_q \right\rangle \tag{4}$$

where $\psi_q(\theta_1, \phi_1, \theta_2, \phi_2) = Y_{l,m_l}(\theta_1, \phi_1) Y_{j,m_j}(\theta_2, \phi_2)$ and q denotes a superindex containing quantum numbers l, m_l, j, m_j ($l = 0, 1, ..., l_{max}$; $m_l = 0, \pm 1, ..., \pm l$; $j = 0, 1, ..., j_{max}$; $m_j = 0, \pm 1, ..., \pm j$). The form of the matrix more suitable for implementation is as follows[11]

$$V_{q',q}^{var}(R) = V_0^C(R)\delta_{q',q} + V_1^C(R)\langle \psi_{q'}|\cos\Theta|\psi_q\rangle$$
$$+ V_2^C(R)(3\langle \psi_{q'}|\cos^2\Theta|\psi_q\rangle - \delta_{q',q})/2$$
$$+ \frac{\hbar^2 l(l+1)}{2\mu_{AM}R^2}\delta_{q',q} + \frac{\hbar^2 j(j+1)}{2\mu_M r_0^2}\delta_{q',q} \tag{5}$$

The angle Θ can be written as[10] $\Theta(\theta_1, \phi_1, \theta_2, \phi_2) = \arccos(\sin\theta_1 \cos\phi_1 \sin\theta_2 \cos\phi_2 + \sin\theta_1 \sin\phi_1 \sin\theta_2 \sin\phi_2 + \cos\theta_1 \cos\theta_2)$. All analytical expressions for angular parts in eq 5 are presented in the Supporting Information of ref 11 in a simple form. The next step is to diagonalize the potential matrix obtaining complex eigenvalues, $\mathcal{V}_q(R)$, where $q = 1, 2, ..., (l_{max} + 1)^2(j_{max} + 1)^2$. We repeat this procedure for different values of R. The eigenvalues provide $j_{max} + 1$ families of effective one-dimensional potentials. Each family is well-separated and asymptotically corresponds to a specific rotational state of the molecule; here we denote these states as j_{th} ("j threshold"). In other words, one can write schematically $\{\mathcal{V}_q(R)\} = \{\mathcal{V}_\alpha^{j_{th}}(R)\}_{j_{th}=0,1,...,j_{max}}$, where $\alpha = 1, 2, ...$ and $\mathcal{V}_\alpha^{j_{th}}(R \rightarrow \infty) = \hbar^2 j_{th}(j_{th} + 1)/(2\mu_M r_0^2) + V_C(R \rightarrow \infty, \Theta)$.

It should be noted that because we do not use the Clebsch–Gordan coefficients, our potential matrix (eq 5) includes different values of total angular momentum. By proper transformation, the matrix can be represented as uncoupled block matrices. Then, each block is associated with different total angular momentum J and different project on the z-axis M that varies from $-J$ to J. Our approach is motivated by the fact that in the experiment of the Narevicius group[1−4] the different values of J and M are involved in the reaction; thus, we need to take sufficiently many J and M quantum numbers to get converged results. The number of states that is needed to get converged results depends on the temperature, which is controlled in the experiment by the angle of two supersonic beams that collide.

Within the framework of the adiabatic variational theory, the Hamiltonian depends on one variable: R. The Schrödinger equation for reactants that has to be solved for each adiabatic effective potential (adiabat) is

$$\left(-\frac{\hbar^2}{2\mu_{AM}}\partial_R^2 + \mathcal{V}_\alpha^{j_{th}}(R)\right)\Psi_{\alpha,\nu}^{j_{th}}(R) = \left(\varepsilon_{\alpha,\nu}^{j_{th}} - i\frac{\gamma_{\alpha,\nu}^{j_{th}}}{2}\right)\Psi_{\alpha,\nu}^{j_{th}}(R) \tag{6}$$

where ν is associated with the vibrational mode of the α-surface and $(\varepsilon_{\alpha,\nu}^{j_{th}} - i\gamma_{\alpha,\nu}^{j_{th}}/2)$ are complex eigenenergies. For practical reasons, each adiabat is shifted up to set the dissociation threshold at zero, i.e., $\mathcal{V}_\alpha^{j_{th}}(R \rightarrow \infty) \rightarrow 0$.

3. REACTION RATE COEFFICIENTS FOR ANISOTROPIC MOLECULAR COLLISIONS AT VERY LOW TEMPERATURES

Inspired by previous works,[25,26] we attempt to find a simple form of the reaction rate expression that is easy to implement. For this purpose, we define the dimensionless ionization probability containing the transition matrix elements from reactants to products in the following form

$$P^{j_{th}}(E_{col}) = \frac{1}{2j_{th} + 1}$$
$$\times \sum_{\alpha,\nu} \sum_{\beta,\xi} |(\Phi_{\beta,\xi}^{j_{th}}(R)|\sqrt{\Gamma_\alpha^{j_{th}}(R)}|\Psi_{\alpha,\nu}^{j_{th}}(R))|^2 \rho(\varepsilon_{\alpha,\nu}^{j_{th}})\delta_{\varepsilon_{\alpha,\nu}^{j_{th}}, E_{col}} \tag{7}$$

where $\Gamma_\alpha^{j_{th}}(R) = -2\mathrm{Im}[\mathcal{V}_\alpha^{j_{th}}(R)]$, ρ stands for the density of continuum states, and $\delta_{\varepsilon_{\alpha,\nu}^{j_{th}}, E_{col}}$ is the Kronecker delta. Of course, the Schrödinger equation solutions for $He-H_2^+$, $\Phi_{\beta,\xi}^{j_{th}}(R)$ and $\epsilon_{\beta,\xi}^{j_{th}}$, are real. Because the problem is non-Hermitian, the c-

product $(\cdots|\cdots)$ has to be used rather than the usual scalar product $\langle\cdots|\cdots\rangle$, where $(f|g) = \langle f^*|g\rangle$ (see chapter 6 in ref 27 and references therein). One does not take the complex conjugate of the terms in the "bra" state. The collision energy, E_{col}, has to be positive, and therefore, only the dissociative states of the quasi-bound system He*–H_2 play a role, namely, $\varepsilon_{\alpha,\nu}^{j_{th}} > 0$. The system can autoionize only when its energy $\varepsilon_{\alpha,\nu}^{j_{th}}$, which equals to E_{col}, is greater than the product system energy $\epsilon_{\beta,\xi}^{j_{th}}$, taking also into account the differences between the asymptotes of the resonance potential and the product potential. Note that the quantity $(E_{col} - \epsilon_{\beta,\xi}^{j_{th}})$ constitutes the kinetic energy of an electron.

Because $\Phi_{\beta,\xi}^{j_{th}}$ is real, $(\Phi_{\beta,\xi}^{j_{th}}| = \langle\Phi_{\beta,\xi}^{j_{th}}|$. Then, one can simplify the expression by assuming that $\sum_{\beta,\xi}|\Phi_{\beta,\xi}^{j_{th}}\rangle\langle\Phi_{\beta,\xi}^{j_{th}}|$ is equal to unity. The probability can be written by means of the scalar product as follows

$$P^{j_{th}}(E_{col}) = \frac{1}{2j_{th} + 1}$$
$$\times \sum_{\alpha,\nu}\langle\Psi_{\alpha,\nu}^{j_{th}}(R)|\Gamma_{\alpha}^{j_{th}}(R)|\Psi_{\alpha,\nu}^{j_{th}}(R)\rangle\rho(\varepsilon_{\alpha,\nu}^{j_{th}})\delta_{\varepsilon_{\alpha,\nu}^{j_{th}},E_{col}}$$

(8)

where the information about products is not necessary. The wave function $\Psi_{\alpha,\nu}^{j_{th}}(R)$ is complex. By definition, the expectation value of $-\Gamma_{\alpha}^{j_{th}}(R)/2$ is equal to the imaginary part of proper eigenenergy (with accuracy of normalization), i.e., $-\gamma_{\alpha,\nu}^{j_{th}}/2$. To show it, let us consider the expectation value of the complex Hamiltonian in the form $\hat{\mathcal{H}}_{\alpha}(R) = \hat{\mathcal{H}}_{\alpha}^{Re}(R) - i\Gamma_{\alpha}(R)/2$ in the basis set of eigenvalues (including normalization): $\langle\Psi_{\alpha,\nu}(R)|\hat{\mathcal{H}}_{\alpha}(R)|\Psi_{\alpha,\nu}(R)\rangle/\langle\Psi_{\alpha,\nu}(R)|\Psi_{\alpha,\nu}(R)\rangle = \mathcal{E}_{\alpha,\nu}$. Then, one can write $\langle\Psi_{\alpha,\nu}|\hat{\mathcal{H}}_{\alpha}^{Re}|\Psi_{\alpha,\nu}\rangle - i\langle\Psi_{\alpha,\nu}|\Gamma_{\alpha}|\Psi_{\alpha,\nu}\rangle/2 = \mathcal{E}_{\alpha,\nu}\langle\Psi_{\alpha,\nu}|\Psi_{\alpha,\nu}\rangle$. Expectation values of real operators are always real, and therefore, $\langle\Psi_{\alpha,\nu}|\Gamma_{\alpha}|\Psi_{\alpha,\nu}\rangle = -2\text{Im}[\mathcal{E}_{\alpha,\nu}]\langle\Psi_{\alpha,\nu}|\Psi_{\alpha,\nu}\rangle = \gamma_{\alpha,\nu}\langle\Psi_{\alpha,\nu}|\Psi_{\alpha,\nu}\rangle$. Consequently

$$P^{j_{th}}(E_{col}) = \frac{1}{2j_{th} + 1}\sum_{\alpha,\nu}\gamma_{\alpha,\nu}^{j_{th}}N_{\alpha,\nu}\rho(\varepsilon_{\alpha,\nu}^{j_{th}})\delta_{\varepsilon_{\alpha,\nu}^{j_{th}},E_{col}}$$

(9)

where $N_{\alpha,\nu}$ guarantees the normalization of the function $\Psi_{\alpha,\nu}$ with respect to the scalar product, $N_{\alpha,\nu} = \langle\Psi_{\alpha,\nu}|\Psi_{\alpha,\nu}\rangle$. This quantity may be neglected when Γ_C is small because $N_{\alpha,\nu} \simeq 1$. As one can see above, in order to find the ionization probability, the product of $\gamma_{\alpha,\nu}^{j_{th}}$ and the energy density of states for $\varepsilon_{\alpha,\nu}^{j_{th}} = E_{col}$ has to only be calculated. All components are known from the solution of the Schrödinger eq 6. This one-dimensional equation can be solved using any known technique (e.g., such as in refs 28−31). The complex eigenvalues are only required.

By multiplying eq 9 by the relative velocity of colliding exited atoms with diatomic molecules and by dividing by square of the wavenumber for reactants, we ensure the proper units, i.e., cm³ s⁻¹. Thus, we obtain a simple expression for the total ionization rate coefficient asymptotically correlated with a well-defined rotational state of the molecule

$$\mathcal{R}^{j_{th}}(E_{col}) = P^{j_{th}}(E_{col})\frac{v_{col}}{k_{col}^2}$$

(10)

where $v_{col} = \sqrt{2E_{col}/\mu_{AM}}$ and $k_{col}^2 = 2\mu_{AM}E_{col}/\hbar^2$. Finally, we have

$$\mathcal{R}^{j_{th}}(E_{col}) = \frac{\hbar^2}{2j_{th} + 1}\frac{\sum_{\alpha,\nu}\gamma_{\alpha,\nu}^{j_{th}}N_{\alpha,\nu}\rho(\varepsilon_{\alpha,\nu}^{j_{th}})\delta_{\varepsilon_{\alpha,\nu}^{j_{th}},E_{col}}}{\sqrt{2\mu_{AM}^3 E_{col}}}$$

(11)

The above equation is an explicit expression for reaction rate coefficients in terms of E_{col}, $\varepsilon_{\alpha,\nu}^{j_{th}}$, $\rho(\varepsilon_{\alpha,\nu}^{j_{th}})$, $\gamma_{\alpha,\nu}^{j_{th}}$, $N_{\alpha,\nu}$, μ_{AM}, and j_{th}. One can see that here we do not have to calculate the complex phase shifts determined from asymptotic forms of the wave functions of the Schrödinger equation, which is usually done by means of Bessel-like functions as was performed in our previous approaches.[10,11] Because the continuum is discretized in the nonexact numerical solutions of the Schrödinger equation, the Kronecker delta determines interpolation for the numerator in eq 11.

To demonstrate the quality and reliability of our method, we calculated the reaction rate coefficients for the collision pairs He*–para-H_2 ($j = 0$) and He*–ortho-H_2 ($j = 1$) in the temperature range spanning from room temperature down to the millikelvin regime. The CPES was taken from ref 26. The surface was generated on the basis of ab initio coupled-cluster calculations and the resonances via the Padé (RVP) method that was recently developed by the authors of refs 26 and 32. Isotropic and anisotropic radial interaction terms, V_0^C ($=\text{Re}[V_0^C(R)] - i\Gamma_0^C(R)/2$) and V_2^C ($=\text{Re}[V_2^C(R)] - i\Gamma_2^C(R)/2$), respectively, were included in our computations. Due to the symmetry reason (the diatom is homonuclear), V_1^C vanishes. The eigenenergies (from eq 6) were determined using the sin-DVR method with 1500 basis functions and the box size $L = 500$ au. According to ref 33, the density of states in the discretized continuum was found from the following formula: $\rho(\varepsilon_{\alpha,\nu}^{j_{th}}) = 2/|\varepsilon_{\alpha,\nu+1}^{j_{th}} - \varepsilon_{\alpha,\nu-1}^{j_{th}}|$. The results are presented in Figure 1 together with the newest molecular beam PI experimental measurements.[4] The agreement is very satisfactory. The peaks of resonances are slightly shifted to smaller energies. Note that we did not scale the potential surface as was done by us in refs 10 and 11 and other authors in refs 2, 34, and 35 to fit the calculated reaction rate coefficients to the experimental results. Moreover, we did not use any fitting parameters as in refs 5−7 and did not impose short-range and asymptotic boundary conditions as was done in the applied technique in ref 4. The input data are the masses, the bond length (the expectation value of the interatomic distance in the ground vibrational state: $r_0 = 1.4487$ au[4]), and l_{max} (here we took $l_{max} = 18$, although the choice $l_{max} = 12$ is sufficient to get converged results). The measured quantity is not the reaction rate coefficient at a definite value of the collision energy but the energy-averaged reaction rate coefficient. Therefore, the theoretical results are convoluted with the experimental energy spread using a Gaussian distribution with 10 m/s width. The convolution, $\int\mathcal{R}(E'_{col})G(E'_{col} - E_{col})\,dE'_{col}$, was computed numerically, $\sum_i\mathcal{R}(E'_{col,i})G(E'_{col,i} - E_{col})\Delta E'_{col,i}$. The structures of observed resonances are very well reconstructed by the theory (see Figure 1). Our results with respect to absolute numbers for the reaction rate coefficients are within the uncertainty of experimental findings[4] due to the large systematic error in normalization according to the rate
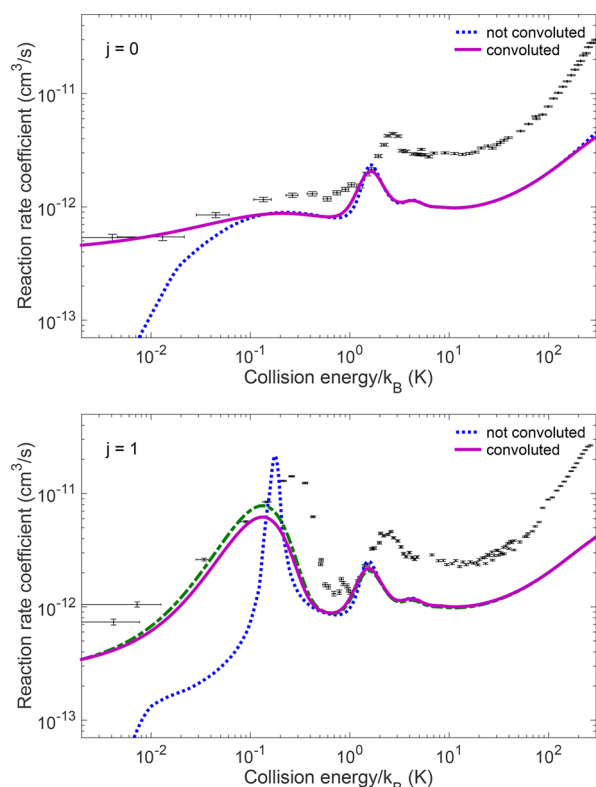
Figure 1. Reaction rate coefficients of an excited metastable helium atom (1s2s, triplet S) with *para*-H_2($j = 0$) [upper panel] and *ortho*-H_2 ($j = 1$) [lower panel]. The reaction rate coefficients have been calculated using our new expression (eq 11) [dotted blue curve]. Then, the theoretical results have been convoluted with the experimental resolution [solid purple curve]. The CPES has been taken from ref 26. No scaling and fitting parameters have been used in our calculations. The black points with error bars are the latest experimental data.[4] The convoluted results excluding $\text{Im}[V_2^C]$ in calculations are represented by the dashed−dotted green curve [lower panel].

measurements at 300 K by Veatch and Oskam.[36] The discrepancies between theoretical and experimental data in positions of resonances occur on account of the imperfect CPES that is very hard to calculate accurately because the state of He*−H_2 is embedded in the continuum of scattering states of He−H_2^+. Usually, enormous problems with the convergence of results and linear dependencies arise.

So far, we know how crucial the anisotropic radial potential is in computations. In ref 11, it is shown that the picture of the reaction rate coefficient can be incomplete when only the isotropic radial potential is taken into consideration. Some resonances can be missed. However, we still do not know what the effect of the neglect of $\text{Im}[V_2^C]$ (which is equal to $-\Gamma_2^C/2$) is on the rate coefficient. This information may be significant because the imaginary parts of nonisotropic interaction potentials frequently are not available in the literature. For this purpose, we repeated calculations here without $\text{Im}[V_2^C]$ for He*−*ortho*-H_2. Note that the potential V_2^C does not contribute to the reaction when the diatomic molecule is in the ground rotational state ($j = 0$) due to vanishing all matrix elements of $(3\langle \psi_{q'}|\cos^2\Theta|\psi_q\rangle - \delta_{q',q})/2$ in eq 5. The results are presented in the lower panel of Figure 1 (see the dashed−dotted green curve). The effect is surprisingly minor and concerns the low-temperature peak. It turned out that the qualitative explanation

why only lower-energy resonance is affected is very simple. Only below 1 K does the anisotropic term in the potential multipole expansion become important. This is exposed in the inset in Figure 2. Note that the Γ_2^C in some sense is the second-
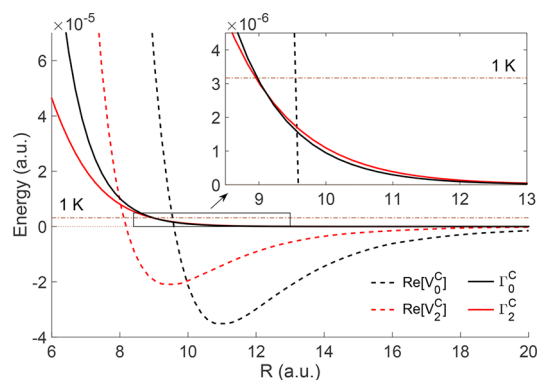

Figure 2. Isotropic and anisotropic radial interaction potentials of excited metastable helium atom (1s2s, triplet S) colliding with molecular hydrogen, $V_0^C(R)$ (=$\text{Re}[V_0^C(R)] - i\Gamma_0^C(R)/2$) and $V_2^C(R)$ (=$\text{Re}[V_2^C(R)] - i\Gamma_2^C(R)/2$), respectively. The horizontal dashed−dotted line corresponds to the collision energy at 1 K. The complex potential energy surface has been taken from ref 26.

order correction to the Γ_0^C; thus, modification of the resonant structures cannot be dramatic. Moreover, from Figure 1 [lower panel], one can see that the measured quantity at room temperature is not changed by taking $\Gamma_2^C = 0$. Indeed, at high energies, Γ_2^C is large for small R, but it does not affect the final results because it is much smaller than Γ_0^C and especially due to the repulsive branches of the potentials. This is clearly seen in Figure 2.

4. CONCLUDING REMARKS

In summary, on the basis of the adiabatic variational theory and the non-Hermitian scattering theory, we have found a new simple closed-form expression for the low-energy Penning reaction rate coefficients of diatomic molecules by excited atoms. We have demonstrated that only the eigenenergies of the resulting radial Schrödinger equation for different complex adiabats are required. Moreover, information about products is superfluous. The presented expression can be of great interest for experimentalists because of its ease of implementation. The expression has been applied to calculate the anisotropic reaction rate coefficients of the excited metastable helium atom with H_2 in the temperature range from 300 K down to a few dozen millikelvins. The results show good accord with recent experimental findings. No scaling and fitting parameters have been used in any of our calculations. We should put emphasis on the fact that our expression is applicable not only to collisions of atoms with diatoms but to a large variety of atomic and molecular systems where the interaction is described by the CPES. Definitely, the expression can be used beyond the adiabatic approach, but then, the problem becomes more complicated. Of course, for a 1D Hamiltonian, there is no need for the adiabatic approximation and the expression can be directly applied to colliding atoms, for example, for ultracold mixtures of metastable helium or neon and alkali metal atoms or noble gas atoms. Moreover, our rate coefficient expression is not restricted to the PI process; it can be used for studies of other ionization mechanisms such as

intermolecular Coulombic decay, which is intensively investigated now.[37]

AUTHOR INFORMATION

Corresponding Author

*E-mail: teomar@chem.umk.pl.

ORCID ⊙

Mariusz Pawlak: 0000-0002-2200-8287

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