RESEARCH ARTICLE

On the Bethe–Wigner–Shapiro limit of the rate coefficient for the capture of a rotating quadrupolar polarsable diatom by an ion

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Many channel character of capture shows itself in the dependence of the effective attractive potential on the intrinsic angular momentum of the diatom and in a nonadiabatic diagonal correction to the potential. The predicted energy dependence of the rate coefficients is compared with previous numerically accurate results for the capture of \( \text{H}_2 \) molecules by \( \text{H}_2^+ \) ions.

1. Introduction

In 1935, Bethe \cite{1} has shown that in the limit of low energies, when the scattering is dominated by \( s \)-waves, the inelastic (reactive) cross section is inversely proportional to the collision velocity \( v \). In 1948, Wigner \cite{2} discussed details of the threshold energy dependence of the partial inelastic amplitudes reviewed comprehensively in \cite{3}. As indicated by Shapiro \cite{4}, a certain property of the scattering amplitude allows one to derive the first general correction, in terms of the wave vector \( k \), to the \( 1/v \) behaviour of the reactive cross section. An elegant derivation of this result, based on the unitary property of the scattering matrix, is given in the Landau–Lifshitz textbook ((\textsuperscript{5}), Section 143). Written in terms of the energy-dependent reaction rate coefficient \( K(k) \) (the product of the velocity and the reaction cross section), the Bethe–Wigner (BW) and the Bethe–Wigner–Shapiro (BWS) results read

\begin{equation}
K(k)|_{k \to 0} \to K_{\text{BW}} = \frac{4\pi \hbar |a''|}{\mu},
\end{equation}

\begin{equation}
K(k)|_{k \ll 1} = K_{\text{BWS}}(k) = K_{\text{BW}}(1 - 2 |a''| k + O(|a''|^2 k^2)),
\end{equation}

where \( a'' \) is the (negative) imaginary part of the scattering length and \( \mu \) is the reduced mass of the collision partners. For the capture of isotropically polarsable neutrals by ions in the field of the charge-induced dipole (cid) potential

\begin{equation}
V_{\text{cid}}(R) = -\frac{q^2 \alpha}{2R^4}
\end{equation}

the quantity \( |a''| \) was calculated by Vogt and Wannier \textsuperscript{[}6\textsuperscript{]} (VW) as...
where $q$ is the charge of the ion and $\alpha$ is the polarisability of the neutral. It turns out that in this particular case the zero-energy BW rate coefficient is twice the high-energy Langevin (L) rate coefficient $K_L$, $K(k)|_{k=0} = K_L$, with

$$K_L = 2\pi \hbar R_{\text{VW}} / \mu = 2\pi \sqrt{q^2 \alpha / \mu}.$$ (1.4)

The aim of the present note is to generalise the expressions of Equation (1.1) for the capture of rotationally excited diatomic quadrupolar and polarisable molecules by ions and to compare the BWS linear $k$ dependence of the $K_{\text{BWS}}$ with previously calculated accurate data. Accordingly, the plan of this note is the following. Section 2 describes the basic assumptions underlying the calculation of the latter accounting for diagonal nonadiabatic corrections that arise from the dependence of the perturbed $s$-wave function on $R$. In Section 4, we compare the BWS linear rate coefficients with numerically accurate rate coefficients for the capture of $H_2$ ($j = 0, 1$) by $H_2^+$ [7,8] across the energy range where the difference between the results for $j = 0$ and $j = 1$ is clearly seen. Section 5 concludes this note.

2. General strategy for the calculation of $|a''|$.

In line with our previous work on the low-energy capture of molecules by ions at low energies [9], we adopt the following approximations:

1. We employ the perturbed rotor approximation. This is valid at collision energies much lower than the energy of the rotational excitation of the rotor. This approximation permits one to regard the quantum number $j$ of the intrinsic rotation of the diatom as a good quantum number, i.e. $j$ is assumed to be conserved during the capture event.

2. We also employ a perturbation approach with respect to the charge–quadrupole interaction in the capture channel with asymptotic orbital quantum number $\ell = 0$ of the relative rotational motion. This is valid at large distances between the partners $R$ where the incoming wave is increasingly reflected above the drop of the attractive interaction potential.

3. We also employ an adiabatic approximation with respect to the radial relative motion of the partners in the capture channel $\ell = 0$. This is valid because the nonadiabatic coupling with other channels $\ell > 0$ is weak at low collision energies. However, it does not imply that the diagonal nonadiabatic correction for the channel $\ell = 0$ is negligible.

4. As noted earlier [9], the effective long-range potential for the capture channel $\ell = 0$ is of $R^{-4}$ behaviour. We, therefore, use the results of Vogt and Wannier [6] who calculated the quantity $|a''|$ for this kind of interaction.

3. Bethe–Wigner and Bethe–Wigner–Shapiro limits of the rate coefficients.

For the case under discussion, the Hamiltonian of the collision partners, besides $\mu, \alpha, q$, depends also on the quadrupole moment $Q$ of the diatom. The interaction energy reads

$$V(R, \vartheta) = V_{\text{cid}}(R) + V_{\text{cq}}(R, \vartheta).$$ (3.1)

Here, $V_{\text{cid}}(R)$ is given by Equation (1.2) and the charge–quadrupole (cq) interaction $V_{\text{cq}}(R, \vartheta)$ is equal to

$$V_{\text{cq}}(R, \vartheta) = (qQ/2R^3) (3\cos^2 \vartheta - 1),$$ (3.2)

where $\vartheta$ is the angle between the collision and the diatom axes in the body-fixed (BF) frame. In general, the potential $V(R, \vartheta)$ should be supplemented by an anisotropic $V_{\text{cid}}(R)$ interaction. We ignore it here because the anisotropic part of the $V_{\text{cid}}(R)$ interaction proportional to $R^{-4}$, being handled here in the second order with respect isotropic to relative motion in the field of isotropic potential (see below), results in the correction proportional to $R^{-6}$ which is neglected in comparison to $V_{\text{cid}}(R) \propto R^{-4}$.

On the basis of free functions $|J, j, \ell; \Xi\rangle$ (where $J$ is the total angular momentum of the collision complex and $\Xi$ is the set of angles describing the orientation of the collision and the rotor axis axes in a space-fixed (SF) frame), the adiabatic approximation with respect to the radial relative motion is defined through the perturbed second-order functions $|J, j, \ell; \Xi, R\rangle$. In particular, for the perturbed state with asymptotic quantum number $\ell = 0$, the perturbed function (accurate through second order in the perturbation parameter $\xi_j(R)$) reads

$$\begin{aligned}
|J, j, \ell; \Xi, R\rangle|_{\ell=0, \ell=0, j=j} &= \left(1 - \xi_j^2(R)/2\right)|J, j, \ell; \Xi\rangle|_{\ell=0, j=j} \\
&+ \xi_j(R)|J, j, \ell; \Xi\rangle|_{\ell=2, j=j},
\end{aligned}$$ (3.3)

where

$$\xi_j(R) = \frac{|J, j, \ell; \Xi\rangle|_{\ell=0, j=j} V_{\text{cq}}(R, \vartheta)|J, j, \ell; \Xi\rangle|_{\ell=2, j=j}}{\Delta E_{\ell\ell}(R)}$$ (3.4)
\[
\Delta E_{02}(R) = 3\hbar^2 / \mu R^2. \tag{3.5}
\]

The numerator in Equation (3.4) represents the off-diagonal element of the cq interaction and the denominator is the difference in the relative rotational energy for the \( \ell = 0 \) and \( \ell = 2 \) zero-order states. Since the former is proportional to \( R^{-3} \), and the latter to \( R^{-2} \), the perturbation parameter \( \zeta_j(R) \propto 1/R \). The matrix element in the numerator of the right-hand side of Equation (3.4), in which the functions \( [J, j, \ell; \Xi] \) are defined in an SF frame while the cq interaction depends on the angle in a BF frame, can be calculated by standard formulae [10]. The effective \( j \)-dependent interaction potential \( V_{\text{eff}}^{(j)}(R) \) that corresponds to the wave function in Equation (3.3) equals the expectation value of the Hamiltonian at fixed \( R \) that consists of the relative rotational energy, the interaction potential and the diagonal nonadiabatic correction, i.e.

\[
V_{\text{eff}}^{(j)}(R) = \langle J, j, \ell; \Xi, R | \xi_{\ell=0, j} [3 \hbar^2 / 2 \mu R^2 + V(R, \theta)] - (\hbar^2 / 2 \mu) (\partial^2 / \partial R^2) | J, j, \ell; \Xi, R \rangle | \xi_{\ell=0}. \tag{3.6}
\]

After integrating with respect to the four angular coordinates that enter into the set \( \Xi \), we get

\[
V_{\text{eff}}^{(j)}(R) = V_{\text{eld}}(R) - \Delta E_{02}(R) \xi_j^2(R) + (\hbar^2 / 2 \mu) (d\xi_j(R) / dR)^2 \nabla^2 + (\hbar^2 / 2 \mu) (d\xi_j(R) / dR)^2. \tag{3.7}
\]

Taking into account that \( \xi_j \propto 1/R \), we have \( (\xi_j / R)^2 = (d\xi_j / dR)^2 \), so that the last term at the right-hand side of Equation (3.7) equals \(-1/6 \) of the middle term (this is already seen from the ratio of numerical factors in front of these two terms). Moreover, the \( R \)-dependence of these terms is the same as that of the first term. This implies that the effective potential can be written as

\[
V_{\text{eff}}^{(j)}(R) = -q^2 \alpha / 2R^4 - (3\hbar^2 / \mu R^2) \xi_j^2(R) + (\hbar^2 / 2 \mu) (d\xi_j(R) / dR)^2. \tag{3.8}
\]

where \( \beta = Q^2 \mu / \alpha \hbar^2 \). Comparing Equation (3.8) with Equation (1.2) leads to the following generalisation of \( R_{\text{VW}} \):

\[
R_{\text{VW}} \rightarrow R_{\text{VW}}^{(j)}.
\]

\[
R_{\text{VW}}^{(j)} = R_{\text{VW}} \sqrt{1 + \beta j(j+1) / 9(2j-1)(2j+3)}. \tag{3.9}
\]

with \( R_{\text{VW}}^{(j)}|_{j=0} = R_{\text{VW}} \), which corresponds to the absence of the cq interaction in the spherically symmetrical state \( j = 0 \). For a rotationally excited diatom \( (j \geq 1) \), \( R_{\text{VW}}^{(j)} \) decreases with increasing \( j \), tending, for \( j \gg 1 \), to the fly-wheel (FW) limit that corresponds to the interaction of an ion with a space-fixed (i.e. stationary) axially symmetric quadrupolar field [11]. The latter is created by a fast rotation of the diatom about the space-fixed classical vector \( \mathbf{J} = \mathbf{J} \). The respective FW potential \( V_{\text{eq}}^{\text{FW}}(R, \theta) \) reads

\[
V_{\text{eq}}^{\text{FW}}(R, \theta) = - (qQ / 4R^3) (3\cos^2 \theta - 1), \tag{3.10}
\]

where \( \theta \) is the angle between the vectors \( \mathbf{R} \) and \( \mathbf{J} \). The correspondence between \( V_{\text{eq}}^{\text{FW}}(R, \theta) \) and \( V_{\text{eq}}(R, \theta) \) is established in reference configuration, when the diatom classically rotates about \( \mathbf{R} \) (i.e. \( \theta = \pi / 2 \)) which coincides with \( \mathbf{J} \) (i.e. \( \theta = 0 \)):

\[
V_{\text{eq}}(R, \theta)|_{\theta=\pi/2} = V_{\text{eq}}^{\text{FW}}(R, \theta)|_{\theta=0}. \tag{3.11}
\]

Corresponding to the expressions in Equations (3.9), the BW and the BWS rate coefficients are

\[
K_{\text{BW}}^{(j)} = \frac{4\pi \hbar R_{\text{VW}}^{(j)}}{\mu},
\]

\[
K_{\text{BWS}}^{(j)}(k) = K_{\text{BW}}^{(j)} \left( 1 - 2R_{\text{VW}}^{(j)} k + O(R_{\text{VW}}^{(j)} k^2) \right). \tag{3.12}
\]

4. Comparison of the Bethe–Wigner–Shapiro approximation with accurate results for \( \text{H}_2 \) \( (j = 0, 1) \) capture by \( \text{H}_2^+ \)

In a comparison of the BWS limit with accurate numerical results, it is simpler to use the capture rate coefficients \( K^{(j)}(k) \) \( (j = 0, 1) \) scaled to the Langevin rate coefficient \( K_L \) and consider the ratios \( \chi^{(j)} = K^{(j)} / K_L \) as functions of the scaled wave vector \( \kappa = R_{\text{VW}} k \). Then, the expressions of Equation (3.10) assume the form

\[
\chi_{\text{BW}}^{(j)} = \rho_{\text{BW}}^{(j)},
\]

\[
\chi_{\text{BWS}}^{(j)}(\kappa) = \rho_{\text{BW}}^{(j)} \left( 1 - \rho_{\text{BWS}}^{(j)} \kappa \right), \tag{4.1}
\]

where

\[
\rho_{\text{BW}}^{(j)} = 2R_{\text{VW}}^{(j)} / R_{\text{VW}} = 2 \sqrt{1 + \beta j(j+1) / 9(2j-1)(2j+3)}. \tag{4.2}
\]

The comparison of \( \chi_{\text{BW}}^{(j)}(\kappa) \) with accurate values \( \chi_{\text{L}}^{(j)}(\kappa) \) for \( \text{H}_2 \) \( (j = 0, 1) \) capture by \( \text{H}_2^+ \) is illustrated in Figure 1. The relevant parameters for the two processes are \( R_{\text{VW}} = 100.2 \) a.u. = 52.9 Å and \( \beta = 75.7 \) which leads
(1) The BWS approximation in the limit $\kappa \to 0$ performs excellent for $j = 0$ and quite satisfactory for $j = 1$. A slight difference in $\chi_{\text{BWS}}^{(j=1)}(\kappa)$ (dashed line) and $\chi_{\text{acc}}^{(j=1)}(\kappa)$ (full line) in this limit may be due to the neglect of the interchannel nonadiabatic coupling and the incipient breakdown of the second-order approximation for the cq interaction. At low temperatures, $\chi_{\text{BWS}}^{(j=1)}(\kappa)$ is noticeably larger than $\chi_{\text{BWS}}^{(j=0)}(\kappa)$ because, in the former case, the cq interaction increases the attraction of the collision partners.

(2) The larger deviation (with increasing $\kappa$) of BWS rate coefficients from their accurate counterparts for $j = 1$ compared to $j = 0$ is due to an earlier contribution of higher partial waves to the $\chi_{\text{acc}}^{(j=0)}$. For $\chi_{\text{acc}}^{(j=0)}$, a noticeable contribution from $p$-waves occurs beyond the upper limit of the $\kappa$-scale shown; this explains the drop of $\chi_{\text{acc}}^{(j=0)}$ in this limit below its asymptotic Langevin value. At low temperatures, $\chi_{\text{BWS}}^{(j=1)}(\kappa)$ decreases more rapidly than $\chi_{\text{BWS}}^{(j=0)}(\kappa)$ with increasing temperature in accord with the fundamental BWS relation (Equation (4.1)).

(3) The effect of the radial diagonal nonadiabatic correction to the capture potential in the case $j = 1$ is demonstrated by the comparison of the dashed straight line (correction included) with the dotted line (correction disregarded).

(4) Across the energy range of Figure 1, the SACM approximation fails badly for $j = 1$ (see Figure 7 from [7]) since it ignores the rotational non-adiabatic coupling. In the present treatment, it is included in the zero-order approximation.

5. Conclusion

The calculation of the generalised VW radii $R_{\text{VW}}^{(j)}$ shows that the rotation of the diatom has a modest effect on the BWS rate coefficients which change from $R_{\text{VW}}^{(j=1)} = 2\sqrt{1 + 2\beta/45}$ down to $R_{\text{VW}}^{(j=1)} = 2\sqrt{1 + \beta/36}$. These two values bracket the BWS coefficients in a rather narrow range. The dependence of the BWS rate coefficient on $j$ across this range reflects the multistate character of capture; a further manifestation of the latter is the modification of the attractive capture potential that arises from the diagonal non-adiabatic correction. This $s$-wave limit at zero energy and the classical Langevin limit at high energies provide a useful estimation of the possible variation of the capture rate coefficients for different $j$ across a broad range of collision energies. Finally, we note that the energy range where the BWS approximation still satisfactorily performs for $H_2$ ($j = 0,1$) capture by $H_2^+$ corresponds to $E/k_B < 10^{-3}$ K for $j = 0$ and $E/k_B < 10^{-4}$ K for $j = 1$. These temperatures, however, are still much lower than attainable experimentally [12] in studying bimolecular chemical reactions dynamics.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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