Multichannel quantum-defect theory for ultracold atom–ion collisions

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Abstract. We develop an analytical model for ultracold atom–ion collisions using the multichannel quantum-defect formalism. The model is based on analytical solutions of the $r^{-4}$ long-range potential and on the application of a frame transformation between asymptotic and molecular bases. This approach allows the description of atom–ion interaction in the ultracold domain in terms of only three parameters: the singlet and triplet scattering lengths, assumed to be independent of the relative motion angular momentum, and the lead dispersion coefficient of the asymptotic potential. We also introduce corrections to the scattering lengths that improve the accuracy of our quantum-defect model for higher-order partial waves, a particularly important result for an accurate description of shape and Feshbach resonances at finite temperature. The theory is applied to the system composed of a $^{40}$Ca$^+$ ion and a Na atom, and compared with numerical coupled-channel calculations carried out using ab initio potentials. For this particular system, we investigate the spectrum of bound states, the rate of charge-transfer processes and the collision rates in the presence of magnetic Feshbach resonances at zero and finite temperature.

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1. Introduction

The successful realization of systems combining ultracold atoms and ions is stimulating increased interest in the physics of atom–ion collisions at very low collision energy. Recent experiments either are focused on the properties of clouds of atoms and ions stored in hybrid dual charged–neutral traps at milli-kelvin temperatures [1–4], or consist in immersing single ions in Bose–Einstein condensates in the micro- and nano-Kelvin temperature domain [5–7]. Understanding atom–ion collisions in the quantum regime is an essential elementary step before a more complete many-body description of these systems can be developed. While atom–ion collision properties are well known for high collision energies [8, 9], a theoretical description in the ultracold domain is still under development [10–13]. Atom–ion and neutral atom scattering are significantly different, mainly due to the relatively long-range character of the polarization interaction between atom and ion. Beyond the fundamental interest in their collision properties, these systems are also very attractive for quantum information processing [14, 15]. Hybrid architectures may profit from advantages offered by both ionic and atomic species, namely a short computation time for charged particles and a long coherence time for neutral atoms.
Ultracold charged-neutral systems are also expected to exhibit interesting many-body effects, including for instance non-trivial modifications of the condensate wave function in the presence of ionic impurities [16] or the creation of mesoscopic-size molecular ions [17].

The objective of this paper is to provide a simple framework for describing cold atom–ion collisions by expanding our previous treatment of $^{40}\text{Ca}^+–^{23}\text{Na}$ collisions [12]. This framework is based on the very powerful technique of multichannel quantum-defect theory (MQDT) [18–20], which gives the complex near-threshold bound and scattering states of such atomic systems in terms of a few physically meaningful parameters and the properties of the long-range potential. The essential simplification of MQDT is the separation of the physics into long-range and short-range parts. The latter is fully determined by known solutions of the power-law long-range potential having the form $-C_n/R^n$, where $n=4$ for atom–ion collisions and $n=6$ for atom–atom collisions. The generally unknown short-range part is parameterized by an MQDT phase parameter for each potential that is related to the s-wave scattering length of the potential. These phases are then subjected to determination by fitting experimental data. This MQDT theory has been applied to collisions of two alkali-metal atoms, where, as for $^{40}\text{Ca}^+–^{23}\text{Na}$ collisions, the entire near-threshold bound state spectrum, scattering phase shift and magnetic field variation of the Feshbach resonance spectrum are determined from a knowledge of only the $C_n$ coefficient of the long-range potential and two phase parameters for the singlet and triplet Born–Oppenheimer potentials for two ground state atoms [21]. This MQDT method is also similar to the techniques pioneered by the Vehaar group for alkali-metal atom scattering [22, 23]. The separation of length and energy scales between long and short range has recently been applied in an MQDT framework to explain threshold reaction rates of ultracold molecules [24–28].

In a previous paper [12], we have studied the basic properties of atom–ion scattering and bound states, using $^{40}\text{Ca}^+–^{23}\text{Na}$ [29] as a reference system. We have developed an effective atom–ion collision model by applying MQDT to the polarization potential, which scales as $r^{-4}$ at large atom–ion distance $r$. We have verified that the MQDT model predicts very accurately all atom–ion scattering properties at ultracold temperatures by comparing with numerical close-coupled (CC) calculations performed on \textit{ab initio} $^{40}\text{Ca}^+–^{23}\text{Na}$ potentials. In the literature, the MQDT approach has already been applied to describe scattering and bound states in electron–ion cores [18], electron–atom [30], neutral atom systems [21, 31–33] and ultracold molecular collisions [24–28]. Our model of atom–ion collisions combines knowledge of the analytical solutions for the $r^{-4}$ asymptotic potential [13, 30, 34–37] with the idea of a frame transformation [21, 31–33, 38, 39,]. The latter, applied at small distances, allows a reduction of the number of quantum-defect parameters needed to represent the effect of the short-range interaction potential. In this way, all the scattering properties of atom–ion systems can be predicted from the quantum-defect model and the analytical solutions, without the need to resort to more computationally demanding CC calculations.

In [12], we have applied MQDT to the study of magnetic Feshbach resonances and radiative charge-exchange processes, including the effects of Feshbach and shape resonances. In this paper, we present a detailed derivation of our atom–ion model, based on the Mies formulation of MQDT [20]. We consider the simple problem of the collision of an ion with an atom in free space. Future work will build on this MQDT framework to incorporate the effect of ion or atom trapping potentials and ion micromotion. We begin by introducing the quantum-defect approach, and discuss the properties of analytical solutions of the $r^{-4}$ asymptotic potential. We derive asymptotic expansions of the model quantum-defect functions, valid for
energies below a characteristic quantity $E^*$ defined in terms of the atom–ion interaction strength. For energies above $E^*$, an efficient numerical algorithm to determine the characteristic exponent and the solutions of the Mathieu equation needed for the MQDT is proposed. Knowledge of the quantum-defect parameters is crucial for understanding atom–ion collisions in the ultracold domain, and allows us to derive several nontrivial analytical results concerning the behavior of weakly bound states, s-wave magnetic Feshbach resonances and radiative charge-transfer probabilities. In comparison to the model presented in [12], we introduce an angular-momentum-dependent correction that improves the accuracy of MQDT for high-order partial waves. This modification allows the regime of applicability of our model to be extended up to millikelvin temperatures. Using this revised model and numerical CC calculations, the effect of finite energy Feshbach resonances on elastic and charge-transfer collision rates is investigated as a function of the magnetic field.

In this paper, we also include details on the semiclassical description of radiative charge-transfer rates. A combination of the semiclassical approximation and MQDT scaling functions allows us to represent the charge-exchange loss rate as the product between the classical Langevin result and a universal quantum correction dependent only on a single parameter, the short-range phase. In [12], we discovered that the main product of a charge-transfer process for $^{40}\text{Ca}^+–^{23}\text{Na}$ is molecular ions. Here we present a more detailed analysis by analyzing the population of vibrational states formed after the electron transfer. A semiclassical formula describing this distribution is derived. The very good accuracy of our MQDT analytical results is tested by comparison with the numerical solution of the CC Schrödinger equation for the $^{40}\text{Ca}^+–^{23}\text{Na}$ system.

The paper is organized as follows. Section 2 introduces the MQDT formalism. Section 3 discusses the properties of scattering and bound states for a single-channel potential, based on analytical solutions for the polarization potential. In particular, section 3.1 derives the analytical solutions, and section 3.2 presents the results of the scattering states and analyzes the applicability of the semiclassical description. Section 3.3 presents the analytical results for weakly bound states, and section 3.4 studies the low-energy behavior of the MQDT functions. The idea of frame transformation is discussed in section 4, using a particular example of an alkali atom and an alkali-earth ion. Section 4.1 generalizes the frame transformation to the presence of a magnetic field, and section 4.2 derives the corrections to the quantum-defect matrix for higher partial waves. Section 5 describes the radiative charge transfer: the perturbative approach based on the Fermi golden rule and the semiclassical description of the charge-transfer probability at short range. The theoretical model is applied to the $^{40}\text{Ca}^+–^{23}\text{Na}$ system in section 6. Section 7 presents the conclusions, and five appendices give some technical details related to the derivation of analytical solutions and the multichannel calculations of radiative charge transfer.

2. Multichannel formalism and quantum-defect theory

In this section, we summarize the basic formalism of the MQDT, adopting the formulation introduced by Mies in [20]. Atom–ion collisions are described by an $N$-channel CC radial Schrödinger equation

$$\frac{\partial^2 F}{\partial r^2} + \frac{2\mu}{\hbar^2} (E - W(r)) F(r) = 0.$$  \hspace{1cm} (1)
Here $\mu = m_pm_n/(m_i + m_j)$ denotes the reduced mass, and $W(r)$ and $F(r)$ are $N \times N$ matrices representing the interaction and the radial solutions, respectively. A general solution to the $N$-channel scattering problem is given by a set of $N$ linearly independent wave functions

$$\Psi_i(r) = \sum_{j=1}^{N} |\Phi_j\rangle Y_{\ell j}(\hat{r}) F_{ji}(r)/r, \quad i = 1, \ldots, N,$$

(2)

where $|\Phi_j\rangle$ are channel states describing the internal spin degrees of freedom and $Y_{\ell j}(\hat{r})$ denotes the angular part of the solution (spherical harmonic) for channel $j$. The interaction matrix is asymptotically diagonal,

$$W_{ij}(r) \to \infty \left[ E_i^\infty + \frac{\hbar^2 \ell_i(\ell_i + 1)}{2\mu r^2} - \frac{C_4}{r^4} \right] \delta_{ij},$$

(3)

where $E_i^\infty$ are the threshold energies for molecular dissociation, $\ell_i$ is the partial wave quantum number of channel $i$ and $C_4 = \alpha e^2/2$ with $\alpha$ denoting the static dipolar polarizability of the atom and $e$ the ion charge. Here we neglect the contribution of higher-order dispersion terms to the long-range potential, which give relatively small corrections in atom–ion scattering [12].

Given the total energy $E$, the channel states can be classified as open for $E > E_i^\infty$ or closed for $E < E_i^\infty$. In the former case the asymptotic wave number $k_i = \sqrt{2\mu(E - E_i^\infty)/\hbar^2}$ is real and positive, whereas in the latter it is purely imaginary, $k_i = e^{i\pi/2}|k_i|$. The solution matrix $F(r)$ can be split into blocks,

$$F(r) = \begin{pmatrix} F_{oo}(r) & F_{oc}(r) \\ F_{co}(r) & F_{cc}(r) \end{pmatrix},$$

(4)

corresponding to $N_o$ open and $N_c$ closed channels. Imposing appropriate asymptotic boundary conditions on the closed channel components, $F_{ij} \to 0(r \to \infty)$ for $i = N_o + 1, \ldots, N$, the physically meaningful part of $F(r)$ is contained in the block $(N \times N_o)$. Observable properties of the atom–ion system result from the asymptotic behavior of the open–open block $F_{oo}(r)$, which at large distances yields the reactance matrix $K_{oo}$:

$$F_{oo}(r) \to \infty [J(r) - N(r)K_{oo}] A_{oo}.$$

(5)

Here, $J_{ij}(r) = \delta_{ij} \sin(k_{i}r - \ell_{i}\pi/2)/\sqrt{k_{i}}$ and $N_{ij}(r) = -\delta_{ij} \cos(k_{i}r - \ell_{i}\pi/2)/\sqrt{k_{i}} (r \to \infty)$ exhibit asymptotic behavior associated with the spherical Bessel functions $j_{i}(kr)$ and $n_{i}(kr)$. The constant matrix $A_{oo}$ depends on the boundary conditions at $r \to \infty$. In particular, the choice $A_{oo} = (1 - iK_{oo})^{-1}$ corresponds to the usual incoming-wave boundary conditions, where the amplitude of the outgoing wave is determined by the scattering matrix $S_{oo} = (1 + iK_{oo})(1 - iK_{oo})^{-1}$.

The basic idea of the quantum-defect theory is to introduce a set of parameters describing the short-range behavior of the wave function, which weakly depend on total energy $E$ and can be used to predict the system properties as $E$ crosses the dissociation thresholds of individual channels. As we will show later, in the ultracold domain the quantum-defect parameters for atom–ion collisions are also weakly dependent on the relative orbital angular momentum $\ell$ and can be taken as constant, at least for the lowest partial waves.

We now adapt the formulation of MQDT developed by Mies for atomic collisions [20] to our atom–ion system. The starting point is the choice of a set of reference potentials $\{V_j(r)\}$ that should reproduce the asymptotic behavior of the interaction matrix at large distances.
$V_j(r) \xrightarrow{r \to \infty} W_{jj}(r)$ but can otherwise be arbitrary. One associates with the reference potentials $V_i(r)$ a pair of linearly independent solutions $\hat{f}_i(r)$ and $\hat{g}_i(r)$ that are normalized according to the Wentzel–Kramers–Brillouin (WKB) approximation:

(6a)
$$\hat{f}_i(r) = \alpha_i(r) \sin \beta_i(r),$$

(6b)
$$\hat{g}_i(r) = \alpha_i(r) \cos \beta_i(r).$$

The amplitude $\alpha_i(r)$ fulfills the inhomogeneous Milne equation, $[d^2/dr^2 + k_i(r)^2]\alpha_i(r) = \alpha_i^{-1}(r)$ [40], with the local wave vector $k_i(r) = \sqrt{2\mu(E - V_i(R))/\hbar}$, while the phase $d\beta_i/dr = 1/\alpha_i^2$. Since the reference potentials $\{V_j(r)\}$ reproduce the asymptotic behavior of $W(r)$, the exact solution to equation (1) can be expressed at large distances in terms of a pair of functions $\hat{f}(r) \equiv \{\delta_{ij}\hat{f}_i(r)\}$ and $\hat{g}(r) \equiv \{\delta_{ij}\hat{g}_i(r)\}$:

(7)
$$F(r) \xrightarrow{r \to \infty} [\hat{f}(r) + \hat{g}(r)Y]\hat{A}.$$ 

Here, $Y$ is the quantum-defect matrix that plays a central role in the MQDT analysis. In contrast to the $S$- and $K$-scattering matrices, $Y$ remains analytic across the thresholds, and has in general only a weak dependence on energy.

The observable properties depend on the asymptotic behavior of solutions at large distance. It is therefore convenient to introduce another pair of solutions, $f_i(r)$ and $g_i(r)$, together with the physically well-behaved solution $\phi_i(r)$ for the closed channels, that have energy-like normalization as $r \rightarrow \infty$:

(8a)
$$f_i(r) \equiv k_i^{-1/2} \sin(k_i r - \ell_i/2 + \xi_i), \quad E \geq E_i^\infty,$$

(8b)
$$g_i(r) \equiv k_i^{-1/2} \cos(k_i r - \ell_i/2 + \xi_i), \quad E \geq E_i^\infty,$$

(8c)
$$\phi_i(r) \equiv \frac{1}{2k_i^{-1/2}} e^{-|k_i|r}, \quad E \leq E_i^\infty.$$

The factor $\frac{1}{2}$ in the last equation is introduced for convenience in order to simplify the value of Wronskian [20]. Here, $\xi_i$ is the scattering phase shift for channel $i$. The MQDT functions $C_i(E), \tan \lambda_i(E)$ and $v_i(E)$ relate solutions (8) to (6), and are defined as follows:

(9a)
$$f_i(r) = C_i^{-1}(E) \hat{f}_i(r), \quad E \geq E_i^\infty,$$

(9b)
$$g_i(r) = C_i(E)[\hat{g}_i(r) + \tan \lambda_i(E) \hat{f}_i(r)], \quad E \geq E_i^\infty,$$

(9c)
$$\phi_i(r) = N_i(E)[\cos v_i(E) \hat{f}_i(r) - \sin v_i(E) \hat{g}_i(r)], \quad E \leq E_i^\infty.$$

Now, when all the channels are open, $\forall_i E \geq E_i^\infty$, the solution $F(r)$ at $r \to \infty$ can be expressed in terms of $f(r) \equiv \{\delta_{ij}f_i(r)\}$ and $g(r) \equiv \{\delta_{ij}g_i(r)\}$:

(10)
$$F(r) \xrightarrow{r \to \infty} [f(r) + g(r)R(E)]A.$$

Using relationships (9a)–(9c), one can show that

(11)
$$R(E) = C^{-1}(E) \left[ Y^{-1}(E) - \tan \lambda(E) \right]^{-1} C(E),$$

where $C(E) \equiv \{\delta_{ij}C_i(E)\}$ and $\lambda(E) \equiv \{\delta_{ij}\lambda_i(E)\}$. At high energies the WKB approximation is valid at all distances, and the functions $\hat{f}, \hat{g}$ become identical to $f$ and $g$, respectively. Therefore, in this situation the MQDT parameters behave like $C_i(E) \to 1$ and $\tan \lambda_i(E) \to 0$, and equation (11) reduces to $R(E) \equiv Y(E)$.
Next, with the help of equation (5) one can relate the reactance matrix \( \mathbf{K} \) and the scattering matrix \( \mathbf{S} \) to matrix \( \mathbf{R} \):

\[
\mathbf{K} = [\sin(\xi) + \cos(\xi)\mathbf{R}][\cos(\xi) - \sin(\xi)\mathbf{R}]^{-1},
\]

\[
\mathbf{S} = e^{i\xi} [1 + i\mathbf{R}] [1 - i\mathbf{R}]^{-1} e^{i\xi},
\]

with \( \xi(E) \equiv \{ \delta_{ij}\xi_i(E) \} \).

The current derivation has to be modified in the presence of closed channels: \( E < E_i^\infty \) for \( i = N_0 + 1, \ldots, N \). In this case, we impose the requirement that the wave function of the closed channels decays exponentially for large \( r \), i.e. the closed-channel wave functions are proportional to \( \phi_i(r) \). This results in the renormalization of the open–open block of the quantum-defect matrix [20]

\[
\mathbf{Y}_{oo} = \mathbf{Y}_{oo} - \mathbf{Y}_{cc} [\tan(\psi_{cc}) + \mathbf{Y}_{cc}]^{-1} \mathbf{Y}_{co},
\]

where \( \psi(E) \equiv \{ \delta_{ij}\psi_i(E) \} \). The scattering matrices can now be calculated from equations (11)–(13), applied only to the open–open block, where one substitutes \( \mathbf{Y}_{oo} \) in place of \( \mathbf{Y}_{oo} \). Finally, when all the channels are closed (\( N_c = N \)), the wave functions of all the channels must be proportional to \( \phi_i(r) \) at large \( r \), and the energies of the bound states are determined by the condition

\[
|\mathbf{Y}(E) + \tan \psi(E)\rangle = 0.
\]

3. Long-range atom–ion interaction

3.1. Analytical solutions

Here we focus on the Schrödinger equation for a single channel where we include only the long-range part of the atom–ion interaction and the centrifugal barrier for partial wave \( \ell \):

\[
\frac{\partial^2 F}{\partial r^2} + \frac{2\mu}{\hbar^2} \left( E - \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} - \frac{C_4}{r^4} \right) F(r) = 0.
\]

In the following, we work in dimensionless units, where length is expressed in units of \( R^* \equiv \sqrt{2C_4\mu/\hbar^2} \) and energy in units of \( E^* \equiv \hbar^2/[2\mu (R^*)^2] \). Table 1 presents the characteristic lengths \( R^* \) and energies \( E^* \) for some sample combination of alkali atoms and alkali-earth ions. Figure 1 shows the long-range atom–ion potentials for the lowest partial waves, where squares mark the top of centrifugal barriers occurring at \( r_{\text{max}} = \sqrt{2}/\sqrt{\ell(\ell + 1)} R^* \) with energy \( E_{\text{max}} = \frac{1}{4} \ell^2 (\ell + 1)^2 E^* \). Equation (16) in characteristic units of \( R^* \) and \( E^* \) takes the form

\[
\frac{\partial^2 F}{\partial r^2} + \left( E - \frac{\ell(\ell + 1)}{r^2} + \frac{1}{r^4} \right) F(r) = 0.
\]

This equation can be solved analytically [34, 35, 41] by substituting \( F(r) = \psi(r)r^{1/2} \) and \( r = e^{2E^{1/4}} \), which yields Mathieu’s equation of imaginary argument:

\[
\frac{d^2 \psi}{dz^2} - [a - 2q \cosh 2z] \psi = 0,
\]

with \( a = (\ell + \frac{1}{2})^2 \) and \( q = \sqrt{E} \). Although Mathieu’s equation is well known in mathematical physics (see e.g. [42, 43]), we include a brief derivation of its basic properties in appendix A. The appendix also discusses the basic methods we applied for its numerical solution.
Table 1. Characteristic distance \( R^* \) and characteristic energy \( E^* / h \) (kHz) for some selected atom–ion systems.

| System         | \( R^* (a_0) \) | \( E^* / h \) |
|----------------|-----------------|---------------|
| \(^{40}\)Ca\(^+\) + \(^{23}\)Na | 2081            | 28.56         |
| \(^{40}\)Ca\(^+\) + \(^{87}\)Rb | 3989            | 4.143         |
| \(^{135}\)Ba\(^+\) + \(^{87}\)Rb | 5544            | 1.111         |
| \(^{172}\)Yb\(^+\) + \(^{87}\)Rb | 5793            | 0.9313        |

Figure 1. Long-range atom–ion potentials for the few lowest partial waves scaled by the characteristic distance \( R^* \) and the characteristic energy \( E^* \).

We denote two linearly independent solutions to equation (17) by \( T_\nu(r) \) and \( T_{-\nu}(r) \), where \( \nu \) is the complex number called the characteristic exponent (see appendix A for definition). In view of the asymptotic properties of \( T_\nu(z) \) discussed in appendix A, we can construct two solutions \( \hat{f}(r) \) and \( \hat{g}(r) \) defined by equations (6):

\[
\hat{f}(r) = A_\nu(\phi)T_\nu(r) + A_{-\nu}(\phi)T_{-\nu}(r),
\]

\[
\hat{g}(r) = A_\nu(\phi + \pi/2)T_\nu(r) + A_{-\nu}(\phi + \pi/2)T_{-\nu}(r),
\]

where

\[
A_\nu(\phi) = \frac{\sin(\phi - \nu\pi/2 + \pi/4)}{\sin(\pi\nu)}
\]

and \( \phi \) is some parameter that can be interpreted as the short-range phase. As can be easily verified, \( \hat{f}(r) \) and \( \hat{g}(r) \) exhibit, at distances \( r \ll 1 \), semiclassical behavior given by equations (6) with \( \alpha(r) \cong r \) and \( \beta(r) \cong -1/r \):

\[
\hat{f}(r) \xrightarrow{r \to 0} r \sin(-1/r + \phi),
\]

\[
\hat{g}(r) \xrightarrow{r \to 0} r \cos(-1/r + \phi).
\]
The asymptotic behavior given by equations (22) can also be obtained by directly solving equation (17), with centrifugal and energy terms neglected. Since \( r \sin(-1/r + \phi) \) is an exact solution of (16) for \( \ell = 0 \) and \( E = 0 \), it can be used to derive a simple relation between the short-range phase \( \phi \) and the s-wave scattering length of the channel:

\[
a = \cot \phi.
\]

The formula follows from the asymptotic behavior of the \( \hat{f}(r) \) function: \( \hat{f}(r) \rightarrow r \sin \phi - \cos \phi \) \((r \rightarrow \infty)\). The long-range behavior of the general scattering wave function at \( E = 0 \) and for \( \ell = 0 \) is given by \( F(r) \sim r - a (r \rightarrow \infty) \), which leads to equation (23).

At large distances, solutions \( \hat{f}(r) \) and \( \hat{g}(r) \) behave according to

\[
\hat{f}(r) \xrightarrow{r \to \infty} C_v(\phi)\sqrt{q}r_j(qr) - D_v(\phi)\sqrt{q}r_n(qr), \quad (24a)
\]

\[
\hat{g}(r) \xrightarrow{r \to \infty} C_v\left(\phi + \frac{\pi}{2}\right)\sqrt{q}r_j(qr) - D_v\left(\phi + \frac{\pi}{2}\right)\sqrt{q}r_n(qr), \quad (24b)
\]

where

\[
C_v(\phi) = A_v(\phi)m_v \cos \eta - (-1)^\ell A_{-v}(\phi)m_{-v} \sin \eta, \quad (25a)
\]

\[
D_v(\phi) = (-1)^\ell A_{-v}(\phi)m_{-v} \cos \eta - A_v(\phi)m_v \sin \eta. \quad (25b)
\]

Here, \( \eta = \frac{\pi}{2}(\nu - \ell - \frac{1}{2}) \), \( m_v = S_v(4/q)^\nu \) and \( S_v \) is a function of \( \nu \), which is defined in terms of a continued fraction (see appendix A for the definition).

Making use of the asymptotic behavior (24), one can find the phase shift \( \xi \),

\[
\tan \xi = D_v(\phi)/C_v(\phi), \quad (26)
\]

and all MQDT functions defined in (9a)–(9c),

\[
C(E) = C_v(\phi)/\cos \xi, \quad (27)
\]

\[
\tan \lambda(E) = C^{-2}(E) \tan^{-1}(\xi - \tilde{\xi}), \quad (28)
\]

\[
\tan \nu(E) = \frac{A_v(\phi) + A_{-v}(\phi)S_v^{-2}(\chi/4)^{2\nu}}{A_v(\phi + \frac{\pi}{2}) + A_{-v}(\phi + \frac{\pi}{2})S_v^{-2}(\chi/4)^{2\nu}}, \quad (29)
\]

where \( \chi = \sqrt{-E} \) and \( \tilde{\xi} \) is the phase shift of a second short-range normalized solution \( \hat{g}(r) \),

\[
\tan \tilde{\xi} = \frac{D_v(\phi + \pi/2)}{C_v(\phi + \pi/2)}. \quad (30)
\]

Finally, we point out that formulas (24) describing the asymptotic behavior of \( \hat{f}(r) \) and \( \hat{g}(r) \) can be used to determine the scattering matrix \( K \) directly from the quantum-defect matrix \( Y \):

\[
K = [Y(\phi)C_v(\phi + \pi/2) - D_v(\phi + \pi/2)]^{-1} [Y(\phi)C_v(\phi) - D_v(\phi)], \quad (31)
\]

where \( C_v(\phi) = \{\delta_{ij}C_{v(i)}(\phi)\} \) and \( D_v(\phi) = \{\delta_{ij}D_{v(i)}(\phi)\} \). We note that, in principle, the parameterization in terms of the quantum-defect matrix \( Y(\phi) \) depends on the short-range phase \( \phi \) that is fixed by the choice of the reference potentials. In contrast, the scattering matrix \( K \) will depend only on the actual scattering lengths associated with the scattering channels and should be independent of a particular set of reference functions that determine specific \( \phi \) for that choice.
3.2. Scattering states and semiclassical approximation

Using equation (26) and the small-$q$ expansions presented in section A.4, one can derive the well-known threshold behavior of the phase shifts in the polarization potential [35, 41]:

\[
\tan \xi_0(q) = -aq - \frac{\pi}{2} q^2 + O(q^3),
\]

(32)

\[
\tan \xi_\ell(q) = \frac{\pi q^2}{8(\ell - \frac{1}{2})(\ell + \frac{1}{2})(\ell + \frac{3}{2})} + O(q^3), \quad \ell > 0.
\]

(33)

Here, we have used relation (23) between the short-range phase $\phi$ and the scattering length $a$ of the reference potentials, in order to express all the formulas in terms of $a$. We note that for $\ell > 0$ the threshold behavior of the phase shifts is dominated by the quadratic term originating from the polarization potential. Figure 2 shows the energy-dependent scattering length $a(k) = -\tan \xi_0/k$ as a function of $\phi$ for different values of the energy. The limit $k \to 0$ corresponds to $a = \cot \phi$. This definition of an energy-dependent scattering length generalizes the standard definition of the scattering length, and is preferable to the effective range expansion, which is not useful for very long-range potentials like $r^{-4}$. It was introduced to model collisions at finite energies in terms of a contact pseudo-potential [44, 45], which is valid as long as the range of the potential is smaller than the size of the trap. The threshold relations at $E = 0$, in particular equation (23), significantly change as the energy varies away from the $E = 0$ limit. In the case of atom–ion interactions, the characteristic energy for the polarization potential is relatively low, of the order of microkelvin or lower; hence the energy-dependent corrections are likely to be important in experiments.

At sufficiently high energies the scattering can be described using the semiclassical approximation. To identify the crossover from the quantum to the semiclassical regime, we plot in figure 3 the quantity $\lambda'(r)/2\pi$, where $\lambda(r)$ is the local de Broglie wavelength. A necessary condition for the applicability of the WKB approximation can be expressed in terms of the

Figure 2. Energy-dependent scattering length $a(k)$ as a function of the short-range phase $\phi$ for different values of the collision energy.
Figure 3. Derivative of the local de Broglie wavelength $\lambda'(r)$ giving the condition for the applicability of the WKB approximation plotted for different energies.

Figure 4. Exact wave function (black solid line) compared with the WKB wave function (red solid line) and with small- and large-$r$ asymptotic approximations, given by equations (22a) and (24a), respectively (blue dotted and dashed lines), for energy $kR^* = 1$ and $\phi = 0$. The figure also shows the derivative of the local wavelength $\lambda'(r)$ (green dot-dashed line), representing the condition for the applicability of the WKB approximation.

local wavelength: $\lambda'(r) \ll 2\pi$ [46]. We observe that this condition is first violated at distances comparable to $R^*$, while the WKB approximation remains valid at small and large distances. We have verified that to a good approximation the wave function can be calculated within the semiclassical approximation when $\lambda'(r)/2\pi \lesssim 1/2$, which is fulfilled for energies $E \gtrsim 25E^*$. Figures 4 and 5 compare predictions of the WKB method with the exact wave functions $\hat{f}(r)$ for two values of energy: $E = E^*$ and $E = 100E^*$. In addition, they show the small-$r$ and
large-$r$ asymptotic formulae (22a) and (24a), respectively, and the derivative of the local wavelength: $\lambda'(r)/2\pi$.

3.3. Bound states

The bound-state spectrum for a reference potential characterized by the scattering length $a$ can be calculated from the condition $\tan \nu(E) = 0$ [20]. In this case, the bound-state wave function $\phi(r)$ of equation (9c) contains only the $\tilde{f}(r)$ component, with the short-range phase $\phi$ given in terms of the scattering length of the reference potential by equation (23). Using equation (29) the condition determining the energy of a bound state can be rewritten as

$$\sin \left[ \frac{\pi}{2} \nu(E) - \phi - \frac{\pi}{4} \right] = -\frac{E}{16} \nu(E) S_{\nu}^{-2}(E),$$

with $S_{\nu}(E)$ defined in section A.3. Figure 6 shows energies of the bound states versus the short-range phase $\phi$ for the lowest partial waves, where we assume that $\phi$ is $\ell$-independent. The short-range phases set the threshold crossing points of bound states of different symmetries, and thus values of $B$-fields of Feshbach resonances and positions of shape resonances in the charge-exchange rates. The short-range phases can only be determined experimentally for the atom–ion systems of interest and cannot be predicted theoretically based on the current ab initio calculations. Thus, in figure 6 we only show the pattern of bound-state energies for all possible values of the short-range phases. In future, an experiment will pick a particular value of the phase, and the bound-state spectrum can be deduced from the presented pattern. We observe that for even $\ell$ the bound states cross the threshold at $\phi = 0$ ($a = \pm\infty$), while for odd $\ell$ this happens for $\phi = \pi/2$ ($a = 0$). Thus, for a polarization potential there is an $\ell = 2$ periodicity in the values of $\phi$ at the threshold, which is reminiscent of $\ell = 4$ periodicity for van der Waals potential [47].

The energies of the bound states for $a = \pm\infty$ and for different partial waves are shown in figure 7. For even $\ell$ this defines characteristic energy bins, which determine the positions of the last bound states in the spectrum. For instance, the last s-wave bound state is located in the energy range $E/E^* = [-106, 0]$.

Figure 5. Same as figure 4, but for energy $E = 100E^*$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Same as figure 4, but for energy $E = 100E^*$.}
\end{figure}
Applying small-\(q\) expansions of \(v\) and \(S_\nu\) (see section A.4), one can expand the right-hand side of equation (34), which yields for s-waves
\[
\frac{1}{a} = \kappa - \frac{\pi}{3} \kappa^2 + \mathcal{O}(\kappa^3), \quad \ell = 0,
\]
and for p-waves
\[
\kappa = -\frac{\pi}{15} \kappa^2 - \frac{\kappa^3}{9} + \mathcal{O}(\kappa^4), \quad \ell = 1,
\]
with \(\kappa = \sqrt{-E}\). Inverting the former equation, we can write the energy of s-wave bound states in powers of \(1/a\):
\[
E = -\frac{1}{a^2} + \frac{2\pi}{3} \frac{1}{a^3} + \mathcal{O}(1/a^4), \quad \ell = 0.
\]
The exact results of equation (34) (black solid line) are compared with the universal law \( \frac{E}{E^*} = -\left(\frac{R^*}{a}\right)^2 \) (red dotted line) and with approximation (37), including terms up to the order of \( 1/a^3 \) (red dashed line).

The first term on the right-hand side is the universal energy of a weakly bound state, and the higher-order term represents the correction that is specific for \( 1/r^4 \) potential. Figure 8 shows the binding energy for an s-wave bound state versus the inverse of the scattering length. We observe that the range of the applicability of the universal formula \( E = -1/a^2 \) is very narrow. Inclusion of the higher-order correction in \( 1/a \) given by equation (37) improves the agreement with the exact result. In fact, approximation (37) works reasonably well for \( |E| \lesssim 0.5E^* \).

3.4. Behavior of multichannel quantum-defect theory functions for polarization potential

Figures 9–11 show the \( C(E) \), \( \tan \lambda(E) \) and \( \tan \nu(E) \) functions for angular momenta \( \ell = 0 \) and 2 determined from equations (27)–(29) for different values of the s-wave scattering length \( a \), i.e. choice of \( \phi \) in figure 2. Calculations are performed under the assumption that the short-range phase \( \phi \) does not depend on \( \ell \), such that all the MQDT functions can be parameterized with a single \( \ell \)-independent \( \phi \). Substituting the small-\( q \) expansions given in (A.4) into equations (27) and (28), one obtains

\[
C^2(E) \underset{E \to 0^+}{\sim} \frac{\Gamma \left(\ell + \frac{3}{2}\right)^2}{\Gamma \left(\frac{1}{2} - \ell\right)^2} \sin^2 \left(\phi + \ell \frac{\pi}{2}\right) \left(\frac{4}{q}\right)^{2\ell+1} + \delta_{\ell,0} q \cos^2 \phi + O(q^2), \quad (38a)
\]

\[
\tan \lambda(E) \underset{E \to 0^+}{\sim} - \cot \left(\phi + \ell \frac{\pi}{2}\right) + \delta_{\ell,0} q^2 \cot \phi \sin^2 \phi + O(q^3), \quad (38b)
\]

\[
\tan \nu(E) \underset{E \to 0^-}{\sim} \tan \left(\phi + \ell \frac{\pi}{2}\right) + \delta_{\ell,0} \frac{\kappa (\kappa \tan \phi - 1)}{\cos^2 \phi} - \frac{\pi \kappa^2}{8(\ell - \frac{1}{2})(\ell + \frac{1}{2})(\ell + \frac{3}{2})} + O(q^3). \quad (38c)
\]
Figure 9. $C(E)$ function versus energy for partial waves $\ell = 0$ (upper panel) and $\ell = 2$ (bottom panel), calculated for different values of scattering length $a$.

Figure 10. $\tan \lambda(E)$ function versus energy for partial waves $\ell = 0$ (upper panel) and $\ell = 2$ (bottom panel), calculated for different values of scattering length $a$. 

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Figure 11. $\tan \nu(E)$ function versus energy for partial waves $\ell = 0$ (upper panel) and $\ell = 0$ (bottom panel), calculated for different values of scattering length $a$.

Here, $\delta_{\ell,0} = 1$ for $\ell = 0$ and is zero otherwise. At sufficiently large energy, the semiclassical solution begins to be valid at all distances, implying $C(E) \to 1$ and $\tan \lambda(E) \to 0$. One can verify that the MQDT functions presented in figures 9–11 exhibit the small-$q$ and large-$q$ asymptotic behavior given by equations (38). For nonzero angular momenta, one can observe the existence of sharp peaks in the function $C(E)$, corresponding to shape resonances, that appear due to the presence of quasi-bound states behind the centrifugal barrier.

4. Frame transformation

In the ultracold regime, variations of the total energy $E$ are typically much smaller than the depth of the potential at short range, where matrix $Y$ is defined. Therefore, one can neglect the dependence of $Y(E)$ on energy and set $Y(E) \equiv Y$. In this way, matrix $Y$ can be determined at a single value of energy, for instance from the reaction or scattering matrices $K$ or $S$ by applying formulae (12) and (13), respectively. An alternative way is to apply the frame transformation technique [31, 48] that provides a very convenient way of parameterizing the short-range matrix $Y$ in terms of a few parameters, e.g. scattering lengths.

In this paper, we focus on the collisions of an alkali atom with an alkali-earth ion in their electronic ground states. Hence, the asymptotic channel states can be characterized by the hyperfine quantum numbers $f_1$, $m_{f_1}$, and $f_2$, $m_{f_2}$ for ion and atom, respectively, and by the angular-momentum quantum numbers $\ell$ and $m_\ell$ of the relative motion of the atom and ion centers of mass. We label the internal quantum numbers in the asymptotic basis...
by $\alpha = \{f_1 f_2 m_f, m_f\}$; hence, the asymptotic channels are characterized by $i = |\alpha \ell m_i|$. At short distances, it is more convenient to characterize the channel states in terms of the total electron spin $S = s_1 + s_2$ and total nuclear spin $I = i_1 + i_2$, where $s_1$ and $s_2$ are electron spin of ion and atom, respectively, and $i_1$ and $i_2$ denote their nuclear spins, respectively. This basis is characterized by two additional quantum numbers, the total hyperfine angular momentum $F = f_1 + f_2 = I + S$ and its projection $M_f$ on the axis of quantization. We denote the internal quantum numbers in the molecular basis by $\beta = |ISFM_F\rangle$, so the molecular channel states are characterized by $j = |\beta \ell m_i\rangle$. The frame transformation is a unitary transformation between channels $\alpha$ and $\beta$, which can be written as

$$U_{\alpha \beta} = (f_1 f_2 m_f | ISFM_F) = \sum_F (m_f | ISFM_F)(f_1 f_2 | IS).$$

(39)

Here, for simplicity we have omitted the quantum numbers $\ell$ and $m_\ell$ that are conserved if one neglects weak dipolar interactions. Symbol $(m_f | ISFM_F)$ stands for the usual Clebsch–Gordan coefficient,

$$(m_f | ISFM_F) = (-1)^{f_1 - f_2 + M_F} \sqrt{2F + 1} \begin{pmatrix} f_1 & f_2 \\ m_f & m_f \end{pmatrix}^F_{M_F},$$

(40)

while

$$(f_1 f_2 | IS) = \sqrt{(2f_1 + 1)(f_2 + 1)(2I + 1)(2S + 1)} \begin{pmatrix} i_1 & s_1 & f_1 \\ i_2 & s_2 & f_2 \\ I & S & F \end{pmatrix}$$

(41)

is the transformation between $f_1 f_2$ and $IS$ coupling schemes, given in terms of the Wigner $9j$ symbol.

Knowledge of the analytical solutions for the polarization potential suggests that the reference potentials can be chosen to contain only the diagonal long-range part of the interaction matrix:

$$V_i(r) = E_i^\infty + \frac{\hbar^2 \ell_i (\ell_i + 1)}{2\mu r^2} - \frac{C_4}{r^4}. \quad (42)$$

According to equations (22a) and (22b), the wave functions in pure polarization potential are singular at $r \to 0$. In this case, the standard boundary condition $F(r) \to 0$ ($r \to 0$) that is imposed on the physically meaningful solution has to be replaced by the boundary condition (22a) with some short-range phase $\phi_i$.

4.1. Angular-momentum-insensitive quantum-defect matrix

The exchange interaction that mixes asymptotic channel states $\alpha$ takes place usually in some range of distances $R_0$ of the order of a few tens of $a_0$. At such distances the interaction potential between species is much larger than the hyperfine or Zeeman splittings in the presence of an external magnetic field. Therefore, it is convenient to define matrix $Y$ at distances $r \gtrsim R_0$, where the exchange interaction is negligible, and $W_{ij}(r) \approx \delta_{ij} C_4 r^4$ for $R_0 \lesssim r \ll R^*$. This approximation relies on the fact that for $r \ll R^*$ one can safely neglect the centrifugal potential, the asymptotic kinetic energy and hyperfine splittings. On the other hand, it also ignores the higher-order dispersion terms $C_6/r^6, C_8/r^8, \ldots$, which only give relatively small corrections.

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for the specific atom–ion system considered in this paper \cite{12}. Hence, for \(R_0 \lesssim r \ll R^*\) the single-channel wave function is given by the linear combination of the two WKB solutions (22).

Based on the arbitrariness of the reference potentials, we can choose values \(\phi_i\) at our convenience. This stems from the fact that in MQDT the scattering properties are determined simultaneously by the scattering lengths (short-range phases) of the reference potentials, and the elements of the quantum-defect matrix \(Y\). Thus, different choices of the reference potentials and the quantum-defect matrix can describe the same physical situation. Hence, we can select a particular choice for its convenience in analysis. For the following choice of short-range phases,

\[
\phi_i = 0,
\]

the quantum-defect matrix takes a particularly simple form in the molecular \((IS)\) basis,

\[
Y^{(IS)}_{\beta\beta'} = \delta_{\beta\beta'} [a_{S(\beta)}]^{-1},
\]

where \(S(\beta) = 0, 1\) denotes the total electron spin in channel \(\beta\), and \(a_0 = a_s\) and \(a_1 = a_t\) are the singlet and triplet s-wave scattering lengths, respectively. We note that the singlet and triplet scattering lengths refer to the scattering lengths of the real physical channels and not to the reference potentials. By using the unitary transformation (39), we find the quantum-defect matrix \(Y\) in the basis of the asymptotic channel states,

\[
Y = U Y^{(IS)} U^\dagger.
\]

In the presence of an external magnetic field \(B\), the total transformation matrix is a product of \(U\) and an additional unitary matrix \(Z(B)\) relating the bare \((B = 0)\) and dressed \((B \neq 0)\) channel states \(|\Psi_\alpha(B)\rangle\):

\[
|\Psi_\alpha(B)\rangle = \sum_{\alpha'} Z_{\alpha\alpha'}(B) |\Psi_\alpha'(B = 0)\rangle.
\]

In this case, the quantum-defect matrix reads

\[
Y = Z(B) U Y^{(IS)} U^\dagger Z^\dagger(B).
\]

Apart from the shifts of the internal hyperfine states of the atom and ion, the magnetic field in general also affects the motion of the ion as a charged particle. This leads to the Landau quantization of ion motion \cite{46} and can result in several interesting scattering effects resembling collisions in the quasi-one-dimensional (1D) confinements \cite{49}. There are, however, two limits when ion cyclotron motion can be neglected: firstly, when the characteristic size of the Landau orbit \(a_L = \sqrt{\hbar/m_i\Omega}\), with \(\Omega = eB/m_i\) and \(e\) denoting the ion charge, is much smaller than \(R^*\); secondly, when the ion is confined in the radio-frequency (RF) trap, which is typically much tighter than the size of the Landau states. This second case is, however, beyond the scope of the present analysis, and in the following we assume that the former condition applies.

### 4.2. Corrections to the quantum-defect matrix for higher partial waves

According to the arguments presented in section 4, at distances \(R_0 \ll R^*\) one can expect the dependence of the quantum-defect matrix \(Y\) on \(\ell\) to be negligible. However, as we will show later with the example of a Na atom and a Ca\(^+\) ion, this approximation works well only for the few lowest partial waves. Already for \(\ell \gtrsim 4\) one starts to observe some deviations of the quantum-defect parameter from the exact numerical solutions for a realistic potential. In order
to improve the accuracy of the quantum-defect model, we introduce a correction of the short-range phase $\phi$ for nonzero relative angular momenta $\ell$. Such correction can be obtained within the semiclassical theory, since the modification of $\phi$ arises at distances where the real potential $W_{ii}(r)$ differs from $V_i(r)$, a region well described in the semiclassical approximation. We start from the semiclassical formula for the radial wave function $\tilde{f}_i(r)$ calculated in potential $W_{ii}(r)$:

$$\tilde{f}_i(r) \approx \tilde{k}_i(r)^{-1/2} \sin \tilde{\beta}_i(r),$$

(48)

where $\tilde{k}_i(r) = \sqrt{2\mu(E_i^\infty - W_{ii}(R))/\hbar}$ is the local wave vector, $\tilde{\beta}_i(r) = \frac{\pi}{4} + \int_{r_T}^r dx \tilde{k}_i(x)$ is the WKB phase and $r_T$ is the classical turning point. Here, we neglect the contribution from the asymptotic kinetic energy, taking $E = E_i^\infty$. Equation (48) can be rewritten as

$$\tilde{f}_i(r) \approx \tilde{k}_i(r)^{-1/2} \sin [\beta_i(r) + \Delta_i(r)],$$

(49)

where

$$\Delta_i(r) = \tilde{\beta}_i(r) - \beta_i(r),$$

(50)

$k_i(r) = \sqrt{2\mu(E_i^\infty - V_i(R))/\hbar}$ and $\beta_i(r) = \frac{\pi}{4} + \int_{r_T}^r dx k_i(x)$. At sufficiently large distances, where the potential takes its asymptotic form (3), but still within the semiclassical regime $r \ll R^*$, we require that the phases of $\tilde{f}_i(r)$ and of the solution $\hat{f}_i(r)$ calculated for $V_i(r)$ be equal. At large $r$, $\Delta_i(r) \rightarrow \Delta_i(\infty) = \text{const}$, and this happens already within the semiclassical domain $r \ll R^*$, since the potentials $W_{ii}(r)$ and $V_i(r)$ have the same long-range asymptotics. The $\ell$-dependent shift can be obtained by comparing the $\Delta_i(\infty)$ computed for $\ell = 0$ and $\ell > 0$:

$$\delta \phi_i(\ell) = \Delta_i(\infty)|_{\ell} - \Delta_i(\infty)|_{\ell=0}.$$  

(51)

In this formula, $\Delta_i|_{\ell}$ is calculated for the actual value of $\ell$, while $\Delta_i|_{\ell=0}$ represents a shift that can be incorporated into the definition of the short-range phase $\phi$. By treating the centrifugal barrier in the expressions for $k_i(r)$ and $\tilde{k}_i(r)$ as a perturbation to the interaction potential, we find a particularly simple result containing partial-wave quantum number $\ell$ only in the prefactor of an integral

$$\delta \phi_i(\ell) = \frac{\ell_i(\ell_i + 1) \hbar}{2\sqrt{2\mu}} \int_{r_T}^\infty dx \frac{1}{x^2} \left( \frac{1}{\sqrt{C_4/x^2}} - \frac{1}{\sqrt{U_i(r)}} \right),$$

(52)

where $U_i(r) = W_{ii}(r) - E_i^\infty - \ell_i(\ell_i + 1)/(2\mu r^2)$.

5. Radiative charge transfer

In this section, we develop a quantum mechanical description of the radiative charge-exchange process $A + B^+ \rightarrow A^+ + B + h\nu$ with emission of a photon of frequency $\nu$. Since the probability of charge exchange in heteronuclear atom–ion collisions is small, the quantum transition rates can be described in the distorted-wave Born approximation (DWBA) [50] treating the molecular dynamics exactly and the interaction with the radiation field as a perturbation. If weak dipolar interactions are neglected, molecular dynamics conserves the quantum numbers $\ell$ and $m_\ell$ of the orbital angular momentum of atomic fragments in both the initial and final molecular states. Radiative transitions are induced to first order by electric dipole coupling, provided that the variation $|\Delta \ell| = 1$. 

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We ignore at first nuclear spins, such that the collision only involves two coupled molecular channels. After angular integrals have been performed analytically using standard angular momentum techniques, the radiative charge-exchange decay rate reads (see e.g. [51])

\[
A(E) = \frac{64\pi^4}{3hc^3} \left\{ \sum_\ell \int d(h\nu) \nu^3 \left[ (\ell + 1) |(E'\ell + 1)|d(r)|E\ell\rangle|^2 + \ell |(E'\ell - 1)|d(r)|E\ell\rangle|^2 \right] + \sum_{\ell'} \nu_{\ell'}^3 \left[ (\ell + 1) |(\ell' + 1)|d(r)|E\ell\rangle|^2 + \ell |(\ell' - 1)|d(r)|E\ell\rangle|^2 \right] \right\}. \tag{53}
\]

This equation is expressed in terms of reduced dipole matrix elements for free–free \( \langle E'\ell'|d(r)|E\ell\rangle \) transitions, in which the atom and the ion remain unbound, and free–bound \( \langle \ell'\ell|d(r)|E\ell\rangle \) transitions, in which the colliding pair forms a molecular ion.

The \( |E\ell\rangle \) scattering state is energy-normalized with incoming wave boundary conditions in the entrance potential of the \( AB^+ \) state. The primed quantities \( |E'\ell'\rangle \) and \( |\ell'\ell\rangle \) represent, respectively, energy-normalized scattering states with outgoing wave boundary conditions and unit normalized bound states of the \( A^+B \) molecular complex. Energy conservation requires \( h\nu = E - E' + \delta \) and \( h\nu_{\ell'} = E - E_{\ell'} + \delta \) for free–free and free–bound transitions, where \( \delta \) is the difference of ion and atom ionization potentials.

While this approach is physically transparent and has the advantage of providing detailed information on the products of the charge-exchange process, the generation of dipole moments as a function of photon energy and of free–bound matrix elements for all ro-vibrational levels is computationally costly. A significantly simpler approach discussed in [52] approximates the sum over all continuum and bound transitions with a simple average of a space-varying Einstein coefficient for spontaneous emission over the initial scattering wave function:

\[
A(E) = \sum_\ell (2\ell + 1)|E\ell|\bar{A}(r)|E\ell\rangle, \tag{54}
\]

with

\[
\bar{A}(r) = \frac{64\pi^4 v^3(r)d^2(r)}{3hc^3}. \tag{55}
\]

Equation (54) is inspired by the exact quantum-mechanical closure relation over scattering and bound states in the final channel, and by the classical Franck–Condon principle relating the potential energy difference with the energy of a photon emitted at interatomic separation \( r \), \( h\nu(r) = W_i(r) - W_f(r) \) [52]. In the next subsection, we cast this equation in a particularly expressive form using a combination of semiclassical and MCQDT approaches.

### 5.1. Semiclassical model

Radiative charge transfer takes places at relatively short distances, where the electronic wave functions of the atom and ion start to overlap and the dipole matrix element is non-negligible. At such distances, one can calculate the matrix element of \( \bar{A}(r) \) in the semiclassical approximation

\[
\langle E\ell|\bar{A}(r)|E\ell\rangle \approx \frac{2}{\hbar} C^{-2}(E, \ell) \int_{R_{\text{min}}}^\infty dr \frac{\bar{A}(r)}{v(r)}. \tag{56}
\]
Here, $R_{\text{min}}$ denotes the classical turning point in the potential $U(r)$ of the entrance channel, and

$$v(r) = \sqrt{\frac{2}{\mu} \left(E - U(r) - \frac{\hbar^2 (\ell + \frac{1}{2})^2}{2\mu r^2}\right)}$$  \hspace{1cm} (57)$$
is the classical velocity of a particle in the entrance channel at distance $r$. The MQDT function $C^{-2}(E, \ell)$ provides the proper scaling of the semiclassical wave function at short distances, with respect to its long-range asymptotic behavior, given by the energy-normalized functions $|E\ell\rangle$.

The total cross-section for the charge exchange can be calculated from

$$\sigma_{\text{tr}} = \frac{2\pi}{k^2} h A(E).$$  \hspace{1cm} (58)$$

In the regime of ultracold energies, one can neglect the contribution of energy $E$ to $v(r)$ at distances where the radiative charge transfer occurs. Similarly, one can also omit the contribution from the centrifugal barrier. In this approximation, $v(r) \approx \sqrt{-2U(r)/\mu}$, and the energy and angular momentum dependence enters only through the MQDT function $C^{-2}(E, \ell)$:

$$\langle E\ell|\tilde{A}(r)|E\ell\rangle \approx \frac{1}{\hbar} C^{-2}(E, \ell) P_{\text{tr}}.$$  \hspace{1cm} (59)$$

Here, $P_{\text{tr}} = 2 \int_{R_{\text{min}}}^\infty dr \frac{\tilde{A}(r)}{v(r)}$ is the probability of photon emission during a single collision, which in our approximation is a constant. In this way the cross-section for the charge-transfer event $\sigma_{\text{tr}}$ can be written as

$$\sigma_{\text{tr}}(E) = \frac{2\pi}{k^2} P_{\text{tr}} \sum_{\ell} (2\ell + 1) C^{-2}(E, \ell).$$  \hspace{1cm} (60)$$

It is instructive to investigate the classical, high-energy limit of the charge-transfer rate, where we expect Langevin theory to be applicable. Starting from equation (54) with the semiclassical approximation (56), setting $C^{-2}(E, \ell) \approx 1$ at $E \gg E^*$, and replacing summation over $\ell$ by integration over impact parameter $b = (\ell + \frac{1}{2})/k$, we obtain [29]

$$\sigma_{\text{tr}}^{\text{class}}(E) = 2\pi \sqrt{2\mu} \int_0^\infty db \int_{R_{\text{min}}}^\infty dr \frac{\tilde{A}(r)}{\sqrt{E - U(r) - Eb^2/r^2}}.$$  \hspace{1cm} (61)$$

Equation (61) can be further simplified, first by replacing the inner integral by a constant probability $P_{\text{tr}}$ and then by performing the remaining integral over $b$. We perform the integration over $b$ to some maximal value of the impact parameter $b_{\max}$, given by the height of the centrifugal barrier $E_{\max}(\ell) = \frac{1}{4} E^* (\ell + 1)^2$. Thus, the particle can penetrate the inner part of the potential only for $E > E_{\max}$, which imposes the upper bound on $b$: $b_{\max} = \sqrt{2R^*/k}$. This yields for the cross-section

$$\sigma_{\text{tr}}^{\text{class}}(E) = \frac{2\pi R^*}{k} P_{\text{tr}},$$  \hspace{1cm} (62)$$

and for the charge-transfer collision rate $K_{\text{tr}} = \sigma_{\text{tr}}(E)v$

$$K_{\text{tr}}^{\text{class}} = \frac{hR^*}{\mu} P_{\text{tr}} = 2\pi \sqrt{\frac{2C_4}{\mu}} P_{\text{tr}}.$$  \hspace{1cm} (63)$$
Figure 12. Thermally averaged quantum contribution $\langle Q(E) \rangle_{th}$ to the charge-transfer rate versus temperature for selected values of the short-range phase.

At large energies the charge-transfer rate acquires a constant value. The latter formula agrees with predictions of Langevin theory, assuming that all the classical trajectories that fall down on the scattering center lead to a reaction [34]. In our case, the probability of a reaction in a single collision event is given by $P_{tr}$, whereas in the case of homonuclear collisions, where the resonant charge transfer takes place, $P_{tr} = \frac{1}{2}$ [2].

It is convenient to express the charge-transfer rate in the quantum regime in terms of $K_{tr}^{\text{class}}$:

$$K_{tr}(E) = K_{tr}^{\text{class}} Q(E),$$

In this form, the charge-transfer rate is a product of a constant classical rate that depends on the particular atom–ion system, and a quantum factor $Q(E)$ that is universal and depends only on the specific atom–ion combination through the characteristic energy $E^*$ and the short-range phase $\phi$. In this way, the whole energy dependence will be given by $Q(E)$. In the limit of high energy ($E \to \infty$), $Q(E) \to 1$. In the limit of small energies ($E \to 0$), only the s-wave contributes and $Q(E) \to \frac{1}{2} (1 + \cot^2 \phi)$.

In figure 12, we show $Q(E)$ averaged over thermal distribution:

$$\langle Q(E) \rangle_{th} = \frac{2}{\sqrt{\pi} (k_B T)^{3/2}} \int_0^{\infty} dE \ Q(E) \sqrt{E} e^{-E/k_B T}$$

for selected values of the short-range phase. We observe that even at large energies $E \sim 10^4 E^*$, $\langle Q(E) \rangle \neq 1$, due to the contribution of shape resonances. The detailed structure of resonances, however, is washed out by the thermal average.
6. Results for $^{40}$Ca$^+$ and $^{23}$Na

We now apply our model to $^{40}$Ca$^+$ and $^{23}$Na, a system whose ab initio potential energy curves are known [29]. Molecular states relevant to the present work are the two NaCa$^+(A^1\Sigma, a^3\Sigma)$, and the Na$^+Ca(X^1\Sigma)$ terms. The corresponding potential energy curves used in our calculation are built at short range by a spline interpolation of the ab initio points reported in [29]. Such short-range potentials are smoothly connected to the long-range analytical form $-C_4/r^4$ characteristic of ion–neutral atom interactions, with $C_4 = 81.35$ (au) [29]. In a similar manner, the transition electric dipole moment between the $A^1\Sigma$ and $X^1\Sigma$ terms is obtained at each value of the internuclear distance by interpolation of the data points of [29]. The potentials built in this way are finally integrated in the coupled-channel Schrödinger equation (1).

We note that in MQDT only two aspects of each potential are important: the long-range form of the MQDT reference function and the short-range phase that parameterizes the value of the scattering length. Consequently, we can make small variations in the short-range potential to select a ‘typical’ value of the scattering length.

In our calculations, the scattering lengths were selected and made the same in the CC and MQDT calculations. The scattering lengths determine the positions of specific bound states and resonances, which vary as the scattering lengths (QDT parameters) vary. Here, we present results obtained for the scattering lengths equal in magnitude to the characteristic length of the potential $R^*$. We have verified that other values give similar patterns, but shifted. In fact, only an experiment can determine the actual values of the scattering lengths, which set the actual positions of the bound states and the magnetic fields of Feshbach resonances. We are now in a position to compare the full solution obtained by numerically solving the resulting multichannel equation with our analytical approach.

6.1. Channel states

The $^{40}$Ca ion has vanishing nuclear spin ($i_1 = 0, s_1 = 1/2$). We label its ground-state sublevels in an external magnetic field in increasing energy $|a_1\rangle = |f = 1/2, m_f = -1/2\rangle$ and $|b_1\rangle = |f = 1/2, m_f = 1/2\rangle$. $^{23}$Na has nuclear spin $i_2 = 3/2$; hence its hyperfine angular momentum can take values $f = 1$ and $2$. The hyperfine structure of $^{23}$Na is shown in figure 13. The figure adopts the standard $|a_2\rangle, |b_2\rangle, \ldots$ notation to label states in increasing energy in the magnetic field, where in the weak field limit one has the identification $|a_2\rangle = |f = 1, m_f = 1\rangle, |b_2\rangle = |f = 1, m_f = 0\rangle, \ldots$. In the presence of an external magnetic field, only the projection $M_j$ of the total angular momentum $J = \sum f_i + a_2 + l$ is conserved during a collision. However, if we ignore small anisotropic spin–spin interactions giving rise to the long-range dipole–dipole force, states with different angular momentum $L$ will not be coupled, and both $\ell$ and $m_\ell$ will be conserved. Hence, $M_F$ will also be conserved and we can restrict our discussion to subspaces of constant $M_F$. In most of our calculations, we will consider collisions within the subblock of $M_F = 1/2$, which contains the lowest energy channel state $|a_1a_2\rangle$. For $M_F = 1/2$ there are four possible scattering channels, listed in table 2 together with their threshold energies at $B = 0$. Table 3 lists the channel states in the molecular basis.
Figure 13. Hyperfine structure of $^{23}\text{Na}$. Zeeman sublevels versus magnetic field $B$ are shown.

Table 2. Scattering channels of $^{40}\text{Ca}^+$ and $^{23}\text{Na}$ for $M_F = 1/2$ in the asymptotic representation.

| $\alpha$ | $|f_1, m_{f_1}, f_2, m_{f_2}\rangle$ | $E_\infty^\alpha / h$ (GHz) |
|---|---|---|
| 1 | $|a_1, a_2\rangle$ | 0 |
| 2 | $|b_1, b_2\rangle$ | 0 |
| 3 | $|a_1, g_2\rangle$ | 1.77163 |
| 4 | $|b_1, f_2\rangle$ | 1.77163 |

The quantum-defect matrix $Y$ in the molecular $\{IS\}$ basis is diagonal and for the assumed channel numbering reads as

$$Y^{(IS)} = \begin{pmatrix} (a_1)^{-1} & 0 & 0 & 0 \\ 0 & (a_1)^{-1} & 0 & 0 \\ 0 & 0 & (a_1)^{-1} & 0 \\ 0 & 0 & 0 & (a_1)^{-1} \end{pmatrix}$$

(67)

Using frame transformation (39), one can easily find $Y$ in the asymptotic channel representation:

$$Y = \begin{pmatrix} 1 + \frac{1}{8a_c} & \frac{\sqrt{2}}{8a_c} & -\frac{\sqrt{3}}{8a_c} & \frac{\sqrt{2}}{8a_c} \\ \frac{\sqrt{2}}{8a_c} & 1 + \frac{1}{4a_c} & -\frac{\sqrt{6}}{8a_c} & \frac{1}{4a_c} \\ -\frac{\sqrt{3}}{8a_c} & -\frac{\sqrt{6}}{8a_c} & 1 + \frac{3}{8a_c} & -\frac{\sqrt{6}}{8a_c} \\ \frac{\sqrt{2}}{8a_c} & \frac{1}{4a_c} & -\frac{\sqrt{6}}{8a_c} & 1 + \frac{1}{4a_c} \end{pmatrix}$$

(68)
with \( 1/a_c = 1/a_s - 1/a_t \) is the coupling parameter characterizing the strength of coupling between channels. We note that for similar triplet and singlet scattering lengths \( 1/a_c = 0 \), the channels are uncoupled, and no interchannel resonances occur.

In the presence of a magnetic field, the energies of the hyperfine states of Na atom are given by the Breit–Rabi formula [54]

\[
E^{(Na)}_{f m_f}(B) = \frac{E_{hf}}{2} + (-1)^f \frac{1}{2} \sqrt{\left( \frac{E_{hf}}{2} + x \right)^2 + y^2}
\]

with

\[
x = g \mu_B B m_f \frac{1}{1 + 2i} \sqrt{(i + \frac{1}{2})^2 - m_f^2}
\]

\[
y = (-1)^{2(i+m_f)} g \mu_B B \frac{1}{1 + 2i}.
\]

where \( g \) is the Landé factor and \( \mu_B \) is the Bohr magneton. By including in the Hamiltonian additional small couplings of the magnetic field to the nuclear spin, \( H(B) = H(0) + \mu_B \mathbf{B}(g_s \mathbf{j} + g_i \mathbf{i}) \), the effective \( g \)-factor is given by \( g = g_j - g_i \), and the levels acquire an additional \( B \)-dependent shift \( \Delta E^{(Na)}_{f m_f}(B) = g_i \mu_B B m_f \). Here, \( g_j \) and \( g_i \) are Landé factors for the total orbital angular momentum \( \mathbf{j} = \mathbf{L} + \mathbf{s} \) and the nuclear spin \( \mathbf{i} \), respectively. In Ca ion, which has no hyperfine structure, the levels shift according to the standard Zeeman formula

\[
E^{(Ca)}_{f m_f}(B) = \mu_B B g_j m_f.
\]

The transformation matrix \( \mathbf{Z} \) from the bare \((B = 0)\) to the dressed channel states \((B \neq 0)\) can be easily found from the transformation matrices \( \mathbf{Z}^{(k)} \), connecting bare and dressed states of ion \((k = 1)\) and atom \((k = 2)\). For the ion we simply have \( \mathbf{Z}^{(1)} = \mathbf{1} \), whereas for the atom

\[
\mathbf{Z}^{(2)}(B) = \frac{1}{w} \left( \begin{array}{cc} x + E^{(Na)}_{f m_{f_2}}(B) & -y \\ y & x + E^{(Na)}_{f m_{f_2}}(B) \end{array} \right),
\]

where \( f_2 = i_2 + 1/2 = 2 \) and \( w = \sqrt{y^2 + (x + E^{(Na)}_{f m_{f_2}})^2} \). Then the total transformation matrix \( \mathbf{Z} \)

---

Table 3. Scattering channels of \(^{40}\text{Ca}^+\) and \(^{23}\text{Na}\) for \( M_F = 1/2 \) in the molecular \([I S]\) representation.

| \( \beta \) | \( [F, M_F, I, S] \) |
|---|---|
| 1 \( \frac{1}{\sqrt{2}}[a_1 b_2] + \frac{1}{\sqrt{2}}[b_1 b_2] - \sqrt{\frac{5}{2}}[a_1 g_2] + \frac{1}{\sqrt{2}}[b_1 f_2] \) | \( \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, 0 \) |
| 2 \( \sqrt{\frac{5}{2}}[a_1 b_2] - \frac{1}{\sqrt{2}}[b_1 b_2] \) | \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1 \) |
| 3 \( \sqrt{\frac{5}{2}}[a_1 b_2] + \frac{1}{\sqrt{2}}[b_1 b_2] - \sqrt{\frac{5}{2}}[a_1 g_2] - \frac{1}{\sqrt{2}}[b_1 f_2] \) | \( \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, 1 \) |
| 4 \( \sqrt{\frac{5}{2}}[a_1 b_2] + \sqrt{\frac{5}{2}}[b_1 f_2] \) | \( \frac{5}{2}, \frac{1}{2}, \frac{1}{2}, 1 \) |
Figure 14. Energies of the bound states versus the short-range phase $\phi$ in the triplet channel $a^3\Sigma^+$ for the few lowest partial waves. The numerical results obtained by solving the Schrödinger equation with the \textit{ab initio} potential of \cite{29} (solid lines) are compared with predictions of MQDT assuming angular-momentum-insensitive short-range phase (dotted lines), and with MQDT including the $\ell$-dependent correction \cite{51} to the short-range phase (dashed lines). The inset zooms in the region around $\phi = 0$.

for the assumed channel numbering reads

$$Z = \begin{pmatrix}
\tilde{Z}^{(2)}_{11} & 0 & \tilde{Z}^{(2)}_{12} & 0 \\
0 & \tilde{Z}^{(2)}_{11} & 0 & \tilde{Z}^{(2)}_{12} \\
\tilde{Z}^{(2)}_{21} & 0 & \tilde{Z}^{(2)}_{22} & 0 \\
0 & \tilde{Z}^{(2)}_{21} & 0 & \tilde{Z}^{(2)}_{22}
\end{pmatrix}. \quad (72)$$

6.2. Bound states

In this section, we discuss the properties of bound states in a single scattering channel. Figure 14 shows a sample bound-state spectrum for $a^3\Sigma^+$ molecular potential. Numerical calculations based on the \textit{ab initio} Na–Ca$^+$ potentials of \cite{29} with the quantum-defect theory with and without the $\ell$-dependent correction \cite{51} to the short-range phase are compared. For simplicity, in the numerical calculation we neglect the higher-order dispersion terms in the potential so as to isolate the effect of the centrifugal barrier, in particular for high-order partial waves. We note that the quantum-defect model assuming the same short-range phase $\phi$ for all partial waves starts to deviate already for $\ell = 3$, whereas the inclusion of correction \cite{51} greatly improves the agreement between the MQDT model and the numerical solution. The inset shows magnification of the region around $\phi = 0$. For $\ell = 4$ still some small discrepancy between the numerical and corrected MQDT results can be observed. The latter may originate from effects going beyond the WKB approximation, which was assumed to hold in the derivation of equation \cite{51}. Although the $\ell$-dependent corrections are small, we note that they may correspond to large shifts.
in resonance positions or binding energies, in comparison to the expected precision in measuring these quantities. In current experiments, the resonance positions or binding energies can be measured with relative precision of the order of $10^{-3}$ or better; thus $\ell$-dependent corrections are necessary to predict the right relative positions of resonances for different partial waves.

6.3. Radiative charge transfer

In the case of Na–Ca$^+$ collisions, the charge-transfer process occurs due to transitions from a singlet $A^1\Sigma$ channel to the absolute ground molecular term NaCa$^+(A^1\Sigma) \rightarrow$ Na$^+$Ca$(X^1\Sigma)$. For its description we first use the DWBA leading to equation (53), which allows the final states of the charge-exchange process to be individually identified. In order to calculate the free–free transition dipole elements, a two-coupled channel model is set up, comprising $W_{\ell}(r) = V(A^1\Sigma)$ and $W_{\ell'}(r) = V(X^1\Sigma)$ diagonal molecular potentials with $\ell$ and $\ell'$ centrifugal barriers, coupled by a $\xi d(r)$ term, with $\xi$ a parameter to be optimized. In a field-dressed approach, a vertical energy shift is introduced so as to guarantee total, photons plus atoms, energy conservation. If the $\xi$ parameter is chosen so as to ensure the validity of first-order perturbation theory, in the DWBA the required reduced matrix element is simply proportional to the transition scattering matrix element $s_\xi = s(E\ell' \leftarrow E\ell; \xi)$ obtained numerically:

$$s_\xi = -2\pi i \xi \langle E\ell'|d(r)|E\ell \rangle. \tag{73}$$

The free–bound reduced dipole elements are obtained following a different method. As a first step, the vibrational wave functions of the $X^1\Sigma$ potential are generated for each angular momentum $\ell'$ using a grid method. To this aim, use of the step-adaptive approach of [55] is essential. In fact, due to the long-range character of $r^{-4}$ interaction, numerical convergence of near-threshold levels is attained for a grid extending to large distances. To keep the number of grid points reasonable ($\sim 5000$), the local step size is made to vary over five orders of magnitude from the potential well to the asymptotic region using an appropriate scaling function [55]. Figure 15 shows, for instance, the last rotationless vibrational wave function for $a = 5R_s$, as well as the convergence rate of the corresponding eigenenergy for two different step sizes $\delta r$ of the numerical grid near the potential minimum. Note that for this specific molecular level, convergence begins to be attained for a box of $10^5 a_0$ size. The relative energy accuracy is of the order of $10^{-2}$ for $\delta r = 0.2 a_0$, and increases by one order of magnitude for $\delta r = 0.1 a_0$. As a second step, the overlap $\langle \psi\ell'|d(r)|E\ell \rangle$ with the initial scattering wave function of angular momentum $\ell$ is computed using a standard propagation code. The number of needed $\ell$ values is determined by numerical convergence.

In the alternative approach based on the approximate sum rule equation (54), the expectation value $\langle E\ell|\hat{A}(r)|E\ell \rangle$ is extracted numerically from the elastic scattering matrix element $s_\xi = s(E\ell \leftarrow E\ell; \xi)$ for a single-channel potential $W_{\ell}$ with angular momentum $\ell$ perturbed by a $\xi \hat{A}(r)$ term. The scaling parameter $\xi$ has to be chosen so as to be in the linear regime. With this proviso, letting $s_0$ be the scattering matrix for the unperturbed $W_{\ell}$ potential, the needed matrix element is determined from the DWBA as

$$s_0^*(s_\xi - s_0) = -2\pi i \xi \langle E\ell|\hat{A}(r)|E\ell \rangle. \tag{74}$$

The prefactor $s_0^*$ arises from the fact that the expectation value on the right-hand side has to be evaluated between scattering states with outgoing boundary conditions, whereas transition matrix elements in the DWBA present incoming wave boundary conditions in the exit channel.
Figure 15. The closest to threshold \( \ell = 0 \) vibrational wave function for s-wave scattering length \( a = 5R^* \) (lower panel) showing the points of the adaptive numerical grid. Convergence of molecular energy is also shown (upper panel) as a function of the numerical grid size for two values of the radial step \( \delta r \) near the potential minimum (see text).

The charge-transfer rates we obtain are shown in figure 16 as a function of the collision energy for a sample value of the singlet scattering length, \( a_s = R^* \). This figure compares the numerical result calculated by summing contributions from all free–free and free–bound transitions equation (53) with the MQDT model assuming the semiclassical charge-transfer probability equation (64). In the former case, we additionally plot separately contributions from free–free and free–bound transitions. The MQDT calculation includes the \( \ell \)-dependent correction (51). We observe that at energies larger than 10 \( \mu \)K, the rate of charge exchange exhibits several peaks due to the shape resonances. The MQDT model agrees well with the full numerical calculations, except in the millikelvin regime where high-order partial waves are contributing. In this range of energies, the discrepancy is due to the corrections to the short-range phase for large \( \ell \) that are beyond the applicability of the semiclassical formula (51). Finally, the approximation based on equation (54) is in full agreement with the numerically exact result and is not shown in the figure.

6.4. Population of vibrational states in the charge-transfer process

According to figure 16, the main outcome of the charge-transfer process is molecular ions. It is interesting to analyze the dependence of the charge-exchange rate on the vibrational quantum number of the molecule, i.e. the vibrational distribution of product molecular ions. In the full quantum treatment based on the numerical calculation of initial and final wave functions, such distribution is proportional to the transition matrix elements in equation (53). In the MQDT approach, it can be obtained using the semiclassical approximation, in analogy with the derivation presented in section 5.1. We start from equations (54) and (56), and obtain the probability of the charge-transfer process normalized per vibrational quantum number \( \vartheta \) in...
Figure 16. Rates of radiative charge transfer due to transitions between $A^1\Sigma^+$ and $X^1\Sigma^+$ states versus energy for the single scattering length $a_s = R^*$. The full numerical calculation based on the Fermi golden rule equation (53) (triangles) is compared with the quantum-defect model assuming semiclassical description of the charge-transfer process (solid line). In addition, we show the contribution from free–free (squares) and free–bound (circles) transitions obtained from the numerical calculation, the thermal average obtained from the quantum-defect model (dashed line) and the charge-transfer rate given by Langevin theory (gray solid line).

the final state:

$$
\frac{dA}{d\theta}(E') = \frac{1}{\rho(E')} \left| \left. \frac{dU}{dr}(E') \right| \right|_2 \frac{2 A(r)}{\hbar v(r)} \sum_J (2J + 1) C^{-2}(E, J).
$$

(75)

Here, $\rho(E) = \frac{d\rho}{dE}$ is the density of states in the exit channel and $V(r) = W_i(r) - W_f(r)$ is the difference between interaction potentials of the entrance (initial) and exit (final) channels. The distance $r$ at which all $r$-dependent quantities are calculated is related to the final energy by the Franck–Condon principle: $E + \delta - E' = h\omega(r) = V(r)$, with $\delta = E_\infty^i - E_\infty^f$ denoting the difference of the dissociation energies of the entrance and exit channels, respectively. The density of states $\rho(E)$ can be calculated from the LeRoy–Bernstein formula [56]. In the case of $r^{-4}$ potential, it yields

$$
\rho(E) = \frac{d\rho}{dE} = \frac{1}{E^*} \frac{\Gamma(\frac{1}{4})}{2 \sqrt{\pi} \Gamma(\frac{3}{4})} \left( -\frac{E}{E^*} \right)^{-3/4}.
$$

(76)

In figure 17, we show the charge-transfer rate from the $A^1\Sigma^+$ channel to the bound states of the $X^1\Sigma^+$ channel, calculated numerically in the DWBA from equation (53). Numerical points are obtained for two values of singlet scattering length: $a_s = \pm R^*$. The solid line shows the prediction of equations (75), with the total cross-section related to probability $A$ by equation (58). We note that the full quantum result predicts oscillations of the distribution over final states, whereas the semiclassical theory leads to smooth behavior, which can be interpreted as the distribution averaged over the quantum oscillations. The oscillations in the charge-transfer rate per vibrational state are due to variation of the Franck–Condon
Figure 17. Rates of radiative charge transfer due to transitions between $A^1\Sigma^+$ and $X^1\Sigma^+$ states versus energy of the vibrational state in the exit channel, for two values of the singlet scattering length $a_s$ (lines with symbols). The solid line shows the semiclassical result obtained from equation (75), while the dashed line is the same result multiplied by two, which gives approximately the amplitude of the quantum oscillations.

overlap factors between initial and final wave functions and are sensitive to wave function phase. The semiclassical theory neglects the phase of the initial and final state wave functions and only calculates the amplitude of the emission per final state based on the Franck–Condon principle; see equations (54)–(56). As a consequence, the oscillations are not present in the semiclassical formula. In the quantum calculations, the dipole matrix elements entering equation (53) are calculated with the actual wave functions of the initial and final states.

6.5. Magnetic Feshbach resonances at zero energy

In this section, we analyze magnetic Feshbach resonances in the limit of zero energy when only s-wave scattering is present. We neglect the effects of the magnetic field on translational ion motion. For the Na–Ca$^+$ system of interest, the radius of the Landau orbit $a_L$ becomes equal to $R^*$ at $B_L = 1086$ G. Hence, the presented analysis is valid as long as $B \ll B_L$.

Figure 18 shows the variation of the s-wave scattering length versus magnetic field for two sample values of the singlet and triplet scattering lengths: $a_s = R^* = 2081 a_0$ and $a_t = -R^* = -2081 a_0$, respectively. The resonances can be assigned to the particular bound state crossing the threshold of the $\alpha = |a_1 a_2\rangle$ channel, as one can verify by inspection of the bound-state energies in the bottom panel. The resonances are labeled by capital letters from A to E. The middle panel shows a close-up of the bound-state spectrum just below threshold. Because of the long-range character of the polarization potential, the last s-wave bound state is always located relatively close to the threshold, with the binding energy $E_b \leqslant 106 E^* = 3.02$ MHz. As one can observe in this figure the last bound state in the open channel can be strongly coupled to the other bound states crossing the threshold, giving rise to relatively strong avoided crossing, as in the case of...
Figure 18. Scattering length (upper panel) and energies of the s-wave bound states (middle and lower panels) versus magnetic field strength $B$ for collisions of Na with $^{40}\text{Ca}^+$ calculated using the MQDT model for some typical singlet and triplet scattering lengths: $a_s = R^* = 2081\, a_0$ and $a_t = -R^* = -2081\, a_0$, respectively. The capital letters in the upper panel label the Feshbach resonances.

resonance $E$. In contrast, very close to threshold the energy of the bound state bends and follows universal behavior $E = -\hbar^2 (2\mu a^2)$.

An approximate but highly accurate description of Feshbach resonances can be developed using a two-channel description based on the CI (configuration interaction) model of a Feshbach resonance, where a single closed channel represents the effects of all the closed channels contributing to a resonance [57]. In the case of a single open and a single closed channel, the application of MQDT is straightforward, and after some simple algebra (see for instance [58]), one obtains the following expression for the phase shift $\xi(E, \ell)$ in the open channel [59]:

$$\xi(E, \ell) = \xi_{bg}(E, \ell) - \tan^{-1}\left(\frac{\Gamma C^{-2}(E, \ell)}{E - E_n + \frac{\Gamma}{2} \tan \lambda(E, \ell)}\right).$$

(77)

The first term $\xi_{bg}(E, \ell)$ is the background phase shift, describing the scattering from the open channel only and incorporating effectively the influence of closed channels for magnetic fields far from the resonance. The second term describes the resonant contribution resulting from a bound state in the closed channel with energy $E_n$, crossing the threshold of the open channel. An energy-dependent width of the resonance is given by a constant width $\Gamma$ multiplied by the MQDT function $C^{-2}(E, \ell)$, which accounts for proper threshold behavior as $k \to 0$. 

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In the two-channel model, one assumes that the energy of a bound state varies approximately linearly with the magnetic field \( B \):

\[
E_n(B) = \delta \mu (B - B_n),
\]

where \( B_n \) is the magnetic field at which the bound state crosses the threshold of the open channel and \( \delta \mu \) is the difference of magnetic moments between the open and closed channels. The second MQDT function \( \tan \lambda(E) \) in the denominator of \( \xi_{\text{res}} \) describes the shift of the resonance position from the bare value \( B_n \), which is due to the coupling between the open and closed channels.

In the following, we will focus on s-wave Feshbach resonances, considering the zero-energy limit. According to the results of sections 3.2 and 3.4, for \( \ell = 0 \) the phase shift and MQDT functions exhibit the following threshold behavior:

\[
\tan \xi(E) \stackrel{E \to 0}{\sim} -ka - \frac{\pi}{3} (kR^*)^2,
\]

\[
C^{-2}(E) \stackrel{E \to 0}{\sim} kR^*(1 + s^2) - (kR^*)^3 s^2(1 + s^2),
\]

\[
\tan \lambda(E) \stackrel{E \to 0}{\sim} -s + (kR^*)^2 s(1 + s^2),
\]

where \( s = a/R^* \). The connection to the standard theory of magnetic Feshbach resonances can be done by introducing the width of magnetic Feshbach resonance \( \Delta \),

\[
\lim_{E \to 0} \frac{\Gamma}{2 \tan \xi_{\text{bg}}(E)} = -\delta \mu \Delta,
\]

and the resonance position \( B_0 \), that is shifted from \( B_n \) due to the coupling between the open and closed channels,

\[
B_0 = B_n + \frac{\Gamma}{2\delta \mu} \lim_{E \to 0} \tan \lambda(E).
\]

Now, substituting equations (78), (82), (83) into (77) in the limit of zero kinetic energy one retrieves the standard expression

\[
a(B) = a_{\text{bg}} \left[ 1 - \frac{\Delta}{B - B_0} \right].
\]

Making use of the MQDT expansions equations (79)–(81), one can express \( \Gamma \) and \( B_n \) in terms of parameters \( a_{\text{bg}}, \Delta, B_0 \) and \( \delta \mu \), which can be directly measured in experiments:

\[
B_n = B_0 + \frac{s_{\text{bg}}^2}{1 + s_{\text{bg}}^2} \Delta, \quad \Gamma = \frac{2s_{\text{bg}}}{1 + s_{\text{bg}}^2} \delta \mu \Delta.
\]

Here, \( s_{\text{bg}} = a_{\text{bg}}/R^* \).

Another important parameter characterizing Feshbach resonances is the fraction of the closed channel in the weakly bound molecular state at large and positive values of the scattering length [60]:

\[
Z(B) = \frac{1}{\delta \mu} \frac{\partial (-E_b)}{\partial B} = \frac{1}{\zeta} \left| \frac{B_0 - B}{\Delta} \right|.
\]

The parameter \( \zeta \) describes the range of magnetic fields expressed as a fraction of resonance width \( \Delta \) over which the resonance exhibits universal properties and the occupation of the closed
Table 4. Parameters of Feshbach resonances shown in figure 18: resonance position $B_0$, resonance width $\Delta$, background scattering length $a_{bg}$, difference of magnetic moments between the open and closed channels $\delta \mu$, and parameter $\zeta$ characterizing the fraction of the closed channel (see equation (87)). The labels in the first column enumerate the resonances in accordance with markings in figure 18.

|    | $B_0$ (G) | $\Delta$ (G) | $a_{bg}$ ($a_0$) | $\delta \mu$ (MHz G$^{-1}$) | $\zeta$ |
|----|-----------|---------------|------------------|-----------------------------|--------|
| A  | 0.322     | $-0.000417$   | $-2019$          | 4.78                        | 0.0328 |
| B  | 5.80      | $-0.00690$    | $-1996$          | 4.76                        | 0.530  |
| C  | 29.6      | $-0.105$      | $-1919$          | 4.46                        | 7.00   |
| D  | 91.0      | $-1.38$       | $-1787$          | 3.15                        | 79.6   |
| E  | 201       | $-10.3$       | $-1803$          | 1.11                        | 151    |

channel remains small. Sufficiently close to the resonance, the binding energy is given by the universal formula $E = -\hbar^2 (2 \mu a^2)$, which leads to [60]

$$\zeta = \frac{s_{bg} |\delta \mu \Delta|}{2 E^*}.$$  (87)

For entrance-channel-dominated resonance, $\zeta \gg 1$ and $Z(B)$ remain small for detuning of the order of $\Delta$. In the opposite case $\zeta \ll 1$, the Feshbach resonance is called closed-channel dominated, and the universal regime where the energy-independent formula (84) is applicable is very narrow.

We have fitted the universal formula (84) to Feshbach resonances presented in figure 18. The results are summarized in table 4. The difference of the magnetic moments has been determined from the bound-state spectrum (lower panel of figure 18) by extracting the linear slope for the molecular states giving rise to the resonances. Finally, the parameter $\zeta$ has been calculated from equation (87). We note that only the first two Feshbach resonances, occurring at relatively small magnetic fields, are non-universal, while the remaining ones are relatively broad and entrance-channel dominated.

6.6. Magnetic Feshbach resonances at finite energies

We analyze here the dependence of elastic and inelastic rates on the magnetic field at finite collision energy, where several partial waves play, in general, an important role in collision physics. To this aim we use both our MQDT model and numerical calculations based on the CC Schrödinger equation. In order to calculate the charge-exchange rates from the CC solutions, we have generalized the approximate closure relation equation (54) to the multichannel case, including hyperfine effects and the external magnetic field. The charge-exchange process in the MQDT model has been described using the semiclassical approximation equation (60) where the MQDT function $C^{-2}(E)$ is replaced by the amplitude of the wave function in the singlet $A^1\Sigma$ channel. Details are provided in appendix B.

Figures 19–21 show the elastic and charge-transfer rates at three collision energies, $E = 1$ nK, $E = 1$ $\mu$K and $E = 1$ mK, for some typical values of singlet and triplet scattering length, $a_s = R^+ = 2081a_0$ and $a_t = -R^-$. Contributions from the lowest 2, 9 and 21 partial waves are included respectively at these three energies. At 1 nK, resonances appear mostly in the s-wave
Figure 19. Elastic (upper panel) and charge-exchange (lower panel) collision rates for collisions of Na and $^{40}\text{Ca}^+$ versus magnetic field calculated at energy $E = 1 \text{nK}$ for singlet and triplet scattering lengths $a_s = R^* = 2081 \, a_0$ and $a_t = -R^* = -2081 \, a_0$. This figure compares the CC numerical calculations (black solid) and the quantum-defect model (red dashed).

Figure 20. Same as figure 19 but for collision energy $E = 1 \mu \text{K}$. The arrow in the lower panel indicates the position of the $\ell = 3$ Feshbach resonance (see text for details).
Figure 21. Same as figure 19 but for collision energy $E = 1 \, \text{mK}$. The thick blue line represents the MQDT result averaged over a thermal distribution with temperature of 1 mK.

and are relatively broad. In addition, one can observe a few narrow resonances in the p-wave channel occurring at $B = 27$, $84.7$ and $182 \, \text{G}$. In this range of temperatures, the MQDT model is extremely accurate and agrees perfectly with the full numerical CC calculations.

At higher energy $E = 1 \, \mu\text{K}$, agreement of the analytic model with the numerical solution is still very good. At this energy, resonance peaks arise from the four lowest partial waves. The arrow in the bottom panel of figure 20 indicates the $\ell = 3$ Feshbach resonance. It is the only resonance at $E = 1 \, \mu\text{K}$ whose position is not well predicted by the analytical MQDT model. We note that the charge-transfer rates exhibit more resonance peaks than the elastic rates. This general behavior can be qualitatively understood by analyzing the number of partial waves contributing to the elastic and inelastic processes. The elastic rates are dominated by reflection from the long-range polarization potential and their contribution to the cross-section decay as $(2\ell + 1)\sin^2\xi_\ell(k) \sim 1/\ell^5$ at large $\ell$ (see equation (33)). In contrast, the charge-exchange process must involve tunneling through the centrifugal barrier, and its probability decays exponentially with $\ell$. Hence the number of partial waves contributing to the inelastic process is much smaller than for elastic scattering, and the inelastic rates are more sensitive to scattering resonances. On the other hand, the narrow resonances from high-order partial waves that appear in the elastic rates are less pronounced due to the strong background arising from reflection on the long-range potential.

Finally, at the highest energy considered ($E = 1 \, \text{mK}$), the resonances are narrower and have smaller amplitude. This effect arises due to the large number of partial waves contributing to the scattering, which have a tendency to wash out the resonance structures. We observe that at 1 mK the MQDT model basically follows the magnetic field dependence of the exact numerical rates, but it predicts accurately only resonances associated with the lowest partial waves. We note
that inclusion of the thermal averaging washes out the resonance structure for the elastic rates, while the charge-transfer rates still exhibit some resonance peaks. This is again due to the vastly different numbers of partial waves contributing to the elastic and inelastic collision processes.

7. Conclusions

Summarizing, we have developed a quantum-defect model for ultracold atom–ion collisions. The model was applied to the reference system composed of a $^{40}$Ca$^+$ ion and a $^{23}$Na atom, and its predictions were thoroughly verified by comparison with numerical CC calculations using *ab initio* potential energy curves. Our model is based on the multichannel quantum-defect formalism, where the quantum-defect parameters are defined in terms of the analytic solutions for $r^{-4}$ polarization potentials. Use of a frame transformation allows us to reduce the number of short-range parameters to essentially singlet and triplet scattering lengths only. Since for atom–ion systems of experimental interest the values of the singlet $a_s$ and triplet $a_t$ scattering lengths are not yet known, in our calculations we have assumed typical scattering lengths of the order of the characteristic length $R^*$. Once $a_s$ and $a_t$ are measured, our model can be readily applied to obtain all the basic collisional properties in the ultracold domain, including accurate positions of Feshbach and shape resonances. Application of our theory to other atom–ion systems is straightforward, amounting to a simple change of the scattering lengths and to the use of new characteristic parameters $R^*$ and $E^*$, which are determined by atomic polarizability and reduced mass.

In our studies we considered only two-body collisions in free space, ignoring the possible effects of trapping potential, which is present in realistic systems. This can be of particular importance for the ions, which acquire in the presence of a time-dependent RF potential a small-amplitude high-frequency motion known as micromotion. This effect is important for current experiments, leading on the one hand to a significant loss of atoms, and on the other hand potentially preventing sympathetic cooling of the ions to the ground state of the trapping potential [61]. Moreover, the presence of a tight ion trap with characteristic size smaller than $R^*$ modifies the long-range asymptotics of atom–ion wave functions and results, in principle, in the coupling of relative and center-of-mass motion. In addition, in the presence of a magnetic field charged ions describe cyclotron orbits, an additional confinement effect that can lead to the appearance of scattering resonances [49] and may affect the actual positions of Feshbach resonances. We are currently investigating these issues.

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Appendix A. Properties of analytical solutions for $r^{-4}$ potential

A.1. Basic derivation

We start from Mathieu’s equation of the imaginary argument (18):

$$
\frac{d^2\psi}{dz^2} - \left[a - 2q \cosh 2z\right] \psi = 0,
$$

(A.1)
where \( a = (l + \frac{1}{2})^2 \) and \( q = \sqrt{E} \). It is convenient to look for the solution of (18) in the following form:

\[
M_v(z) = \sum_{n=-\infty}^{\infty} c_n(v) e^{(2n+v)z},
\]

(A.2)

where \( v \) is the characteristic exponent. Substituting the ansatz (A.2) into (18), we obtain the following recurrence relation:

\[
[(2n + v)^2 - a]c_n + q(c_{n-1} + c_{n+1}) = 0.
\]

(A.3)

The three-term recurrence can be solved in terms of the continued fractions. In analogy to the solution of \( r^{-6} \) potentials [62], we substitute

\[
c_n = \left(-\frac{q}{4}\right)^n \frac{\Gamma \left(\frac{v+\sqrt{a}}{2} + 1\right) \Gamma \left(\frac{v+\sqrt{a}}{2} + n\right)}{\Gamma \left(\frac{v-\sqrt{a}}{2} + 1+n\right) \Gamma \left(\frac{v+\sqrt{a}}{2} + n \right)} b^+_n,
\]

(A.4)

\[
c_{-n} = \left(-\frac{q}{4}\right)^n \frac{\Gamma \left(\frac{v-\sqrt{a}}{2} - n\right) \Gamma \left(\frac{v+\sqrt{a}}{2} - n\right)}{\Gamma \left(\frac{v+\sqrt{a}}{2} \right) \Gamma \left(\frac{v-\sqrt{a}}{2} + n \right)} b^-_n
\]

(A.5)

for \( n \geq 0 \). In the case of \( n = 0 \), we have \( c_0 = b^+_0 = b^-_0 \). Now the recurrence relation (A.3) can be written as

\[
b^+_n - b^+_{n-1} = \frac{q^2 b^+_{n+1}}{[(2n+2+v)^2 - a][(2n+v)^2 - a]},
\]

(A.6)

\[
b^-_n - b^-_{n-1} = \frac{q^2 b^-_{n+1}}{[(2n+2-v)^2 - a][(2n-v)^2 - a]}.
\]

(A.7)

Finally, we substitute \( h^+_n = b^+_n/b^+_{n-1} \) and \( h^-_n = b^-_n/b^-_{n-1} \), which yields the continued fractions

\[
h^+_n = \frac{1}{1 - \frac{q^2}{[(2n+2+v)^2 - a][(2n+v)^2 - a]} h^+_{n+1}},
\]

(A.8)

\[
h^-_n = \frac{1}{1 - \frac{q^2}{[(2n+2-v)^2 - a][(2n-v)^2 - a]} h^-_{n+1}}.
\]

(A.9)

To find values of the coefficients \( c_n \), it is sufficient to set \( h^+_m = 1 \) and \( h^-_m = 1 \) for some sufficiently large \( m \) and calculate \( h^+_n \) and \( h^-_n \) up to \( n = 1 \) using (A.8) and (A.9). Then

\[
b^+_n = h^+_n h^+_1 \ldots h^+_1 c_0,
\]

(A.10)

\[
b^-_n = h^-_n h^-_1 \ldots h^-_1 c_0
\]

(A.11)

and coefficients \( c_n \) can be obtained from equations (A.4) and (A.5). Characteristic exponent \( v \) has to determined from equation (A.3) with \( n = 0 \):

\[
v^2 - a - q^2 \left( \frac{h^+_1(v)}{(v+2)^2 - a} + \frac{h^-_1(v)}{(v-2)^2 - a} \right) = 0.
\]

(A.12)
In numerical calculations, it is more convenient to find $\nu$ from [43]

$$\cos \pi \nu = 1 - \Delta(1 - \cos \pi \sqrt{a}),$$

(A.13)

where $\Delta$ is an infinite determinant (independent of $\nu$):

$$\Delta = \begin{vmatrix}
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
& & & & & & \\
1 & \gamma_{-2} & 0 & 0 & 0 & \ddots & \\
\gamma_{-1} & 1 & \gamma_{-1} & 0 & 0 & \ddots & \\
0 & \gamma_0 & 1 & \gamma_0 & 0 & \ddots & \\
0 & 0 & \gamma_1 & 1 & \gamma_1 & \ddots & \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots
\end{vmatrix},$$

(A.14)

with $\gamma_n = q/(4n^2 - a)$. Typically, determinant $\Delta$ converges very fast, and to calculate $\Delta$ it is enough to take relatively small matrices.

A.2. Asymptotic expansions for large arguments

To derive asymptotic expansion of $M_\nu(z)$ for $z \to \infty$, we observe that the leading contribution to the sum (A.2) comes from terms with large $n$. We neglect the contribution of terms with $n < 0$ and apply the following approximation for terms with $n \geq 0$:

$$c_n \approx \left(-\frac{q}{4}\right)^n \frac{\Gamma\left(\frac{\nu - \sqrt{a}}{2} + 1\right) \Gamma\left(\frac{\nu + \sqrt{a}}{2} + 1\right)}{\Gamma\left(\frac{\nu - \sqrt{a}}{2} + 1 + n\right) \Gamma\left(\frac{\nu + \sqrt{a}}{2} + 1 + n\right)} b^+_n,$$

(A.15)

where $b^+_n = \lim_{n \to \infty} b^+_n$. This yields

$$M_\nu(z) \xrightarrow{z \to \infty} b^+_n \Gamma\left(1 - \frac{\nu - \sqrt{a}}{2}\right) \Gamma\left(1 - \frac{\nu + \sqrt{a}}{2}\right) \left(\frac{2}{\sqrt{q}}\right)^\nu J_\nu(\sqrt{q} e^z),$$

(A.16)

where $J_\nu$ denotes the Bessel function. Now the asymptotic behavior for large $z$ can be easily obtained from the well-known asymptotic expansions of the Bessel functions.

In a similar way, we obtain the behavior for large and negative $z$:

$$M_\nu(z) \xrightarrow{z \to -\infty} b^-_n \Gamma\left(1 - \frac{\nu - \sqrt{a}}{2}\right) \Gamma\left(1 - \frac{\nu + \sqrt{a}}{2}\right) \left(\frac{2}{\sqrt{q}}\right)^\nu J_\nu(\sqrt{q} e^{-z}),$$

(A.17)

where $b^-_n = \lim_{n \to \infty} b^-_n$.

A.3. Two linearly independent solutions

As the two linearly independent solutions of (18), we can take $M_\nu(z)$ and $M_{-\nu}(z)$. It is convenient for our purposes, to define the following two linearly independent solutions in initial variable $r$:

$$T_\nu(r) = w(\nu) M_\nu[\ln(\sqrt{q}r)] \sqrt{r},$$

(A.18)

$$T_{-\nu}(r) = w(-\nu) M_{-\nu}[\ln(\sqrt{q}r)] \sqrt{r},$$

(A.19)

6 It is easy to observe from equation (A.3) that if $\nu$ is a characteristic exponent, then $-\nu$ must also be a characteristic exponent and $c_n(-\nu) = c_n(\nu)$.
where

\[
w(v) = \sqrt{\frac{\pi}{2}} b_\infty^+(-v) \frac{(4/q)^{v/2}}{\Gamma\left(\frac{v}{2} + \frac{3}{2}\right) \Gamma\left(\frac{5}{2} - \frac{v}{2}\right)}.
\]  

(A.20)

Using equations (A.16) and (A.17), one can easily work out the asymptotic behavior of \(T_v(r)\). For small \(r\) we obtain

\[
T_v(r) \xrightarrow{r \to 0} r \cos\left(\frac{\pi}{2} v - \frac{\pi}{4}\right),
\]

(A.21)

whereas for large \(r\) we obtain

\[
T_v(r) \xrightarrow{r \to \infty} S(v) \frac{4}{q} \cos(kr - \pi/2 - \pi/4),
\]

(A.22)

where

\[
S(v) = \frac{b_\infty^+(v) \Gamma\left(\frac{v}{2} + \frac{3}{2}\right) \Gamma\left(\frac{5}{2} - \frac{v}{2}\right)}{b_\infty^-(v) \Gamma\left(\frac{v}{2} + \frac{3}{2}\right) \Gamma\left(\frac{3}{2} - \frac{v}{2}\right)}.
\]

(A.23)

**A.4. Expansions for small \(q\)**

The small-\(q\) expansion of the characteristic exponent \(v\) can be obtained from equation (A.12):

\[
v = l + \frac{1}{2} - \frac{q^2}{4(l - \frac{1}{2})(l + \frac{1}{2})(l + \frac{3}{2})} + O(q^4).
\]

(A.24)

Utilizing this result and applying (A.8)–(A.11), we calculate the expansions of \(b_\infty^+(v)\) and \(b_\infty^-(v)\),

\[
b_\infty^+(v) = 1 + \frac{(l + \frac{1}{2}) (l + \frac{3}{2}) - (2l + 3) \left[\gamma + \psi\left(l + \frac{3}{2}\right)\right]}{(2l + 3)^2(2l - 1)(2l + 1)} q^2 + O(q^4),
\]

(A.25)

\[
b_\infty^-(v) = 1 + \frac{(l + \frac{1}{2}) (l + \frac{1}{2}) + (2l - 1) \left[\gamma + \psi\left(\frac{1}{2} - l\right)\right]}{(2l - 1)^2(2l + 3)(2l + 1)} q^2 + O(q^4),
\]

(A.26)

where \(\psi(x)\) denotes the digamma function.

Finally, the expansion of \(S(v)\) can be obtained from definition (A.23) where we substitute (A.25) and (A.26) and expand the Gamma functions. This yields

\[
S(v) = \frac{\Gamma\left(\frac{3}{2} + l\right)}{\Gamma\left(l + \frac{1}{2}\right)} \left[1 - \frac{(l - \frac{1}{2}) (l + \frac{3}{2}) \left(\psi\left(l + \frac{3}{2}\right) + \psi\left(l + \frac{1}{2}\right)\right) - (l + \frac{1}{2})^2}{4\left(l + \frac{1}{2}\right)^2 (l + \frac{3}{2})^2} q^2 + O(q^4)\right].
\]

(A.27)

**Appendix B. Multichannel calculations of radiative charge transfer**

Equation (54) based on the approximated closure relation can be easily generalized to the multichannel case including hyperfine effects and an external magnetic field. In this case, the initial state for atoms incoming in the dressed channel state \(\alpha\) of equation (46) will be labeled \(|E(\alpha)\rangle\). The reduced dipole moment becomes a matrix, with only nonvanishing diagonal elements if the total electron and nuclear spin \(\{SI\}\) representation is used.
In the presence of a magnetic field, CC scattering equations are numerically solved with a matrix perturbation \( \xi \hat{A}(r) \). The emission rate for atoms incoming at collision energy \( E \) is expressed in the DWBA in terms of the open–open scattering matrix elements \( s_{\xi\beta\alpha} = s(E \ell \beta \leftarrow E \ell \alpha; \xi) \) with and without field perturbation:

\[
\sum_{\beta} s_{\xi\beta\alpha}^a (s_{\xi\beta\alpha} - s_{0\beta\alpha}) = -2\pi i \xi \langle E \ell \alpha | \hat{A}(r) | E \ell \alpha \rangle. \tag{B.1}
\]

As in the single-channel case, right multiplication by the \( s_{0}^0 \) matrix enforces the correct boundary conditions, and symmetry of the scattering matrix \( (s_{\xi\alpha\beta} = s_{\xi\beta\alpha}) \) resulting from time-reversal invariance has been used.

Calculation of the charge-exchange rates in the MQDT approach can be done using the semiclassical formula (60), with the function \( C^{-1}(E, \ell) \) replaced by the amplitude \( A^{(fs)}_s(E, \ell) \) of the singlet component of the multichannel wave function at short range:

\[
\sigma_s(E) = \frac{2\pi}{k^2} P_{tr} \sum_{\ell} (2\ell + 1)|A^{(fs)}_s(E, \ell)|^2. \tag{B.2}
\]

In order to calculate \( A^{(fs)}_s \), we first analyze the open–open block of the multichannel wave function at large distances:

\[
F_{oo}(r) \xrightarrow{r \to \infty} [\hat{f}_{oo}(r) + \hat{g}_{oo}(r)\hat{Y}_{oo}]A_{oo}. \tag{B.3}
\]

Using relations between short-range and long-range normalized solutions, equation (B.3) can be rewritten as

\[
F_{oo}(r) \xrightarrow{r \to \infty} [f_{oo}(r) + g_{oo}(r)R(E)]C(E)[1 - \tan \lambda(E)\hat{Y}_{oo}]A_{oo}, \tag{B.4}
\]

with \( R(E) \) given by formula (11) applied for the open–open block of the renormalized quantum-defect matrix \( \hat{Y}_{oo} \). The constant matrix \( A_{oo} \) is fixed by the boundary conditions at \( r \to \infty \). With the following choice of \( A_{oo} \),

\[
A_{oo} = [1 - \tan \lambda(E)\hat{Y}_{oo}]^{-1}C(E)^{-1}[1 - iR(E)]^{-1}e^{i\hat{g}}, \tag{B.5}
\]

the wave function has a normalization corresponding to a unit flux of incoming particles:

\[
F_{oo}(r) \xrightarrow{r \to \infty} \frac{1}{2}[H^{(2)}(kr) + H^{(1)}(kr)S]. \tag{B.6}
\]

Here, \( H^{(2)}_{ij}(kr) \to \delta_{ij}e^{-i(kr-\ell)\pi/2} \sqrt{k_i} \) and \( H^{(1)}_{ij}(kr) = [H^{(2)}_{ij}(kr)]^* \) are functions exhibiting asymptotic behavior associated with the spherical Hankel functions \( h^{(2)}_{\ell}(kr) \) and \( h^{(1)}_{\ell}(kr) \), respectively.

The total wave function expressed in terms of the short-range normalized solutions reads

\[
F(r) = [f(r) + \hat{g}(r)\hat{Y}]A. \tag{B.7}
\]

with

\[
A = \begin{pmatrix}
A_{oo} \\
-[Y_{oo} + \tan \nu(E)]Y_{eo}A_{oo}
\end{pmatrix} \tag{B.8}
\]

chosen in such a way that the closed-channel wave function at large distance is proportional to the exponentially decaying solution \( \phi_0(r) \), equation (9c). Applying the frame transformation yields the multichannel amplitude of the wave function in the molecular basis,

\[
A^{(fs)} = (Z(\beta)U \cos \chi)^{-1} A, \tag{B.9}
\]

where \( \chi_{\beta\beta} = \delta_{\beta\beta} \phi_{S(\beta)} \) is the diagonal matrix containing short-range phases of the singlet \( \phi_0 \) and the triplet \( \phi_1 \) potentials, with \( S(\beta) \) denoting the total electron spin in channel \( \beta \).
References

[1] Smith W W, Makarov O P and Lin J 2005 J. Mod. Opt. 52 2253
[2] Grier A T, Cetina M, Oručević F and Vuletić V 2009 Phys. Rev. Lett. 102 223201
[3] Rellergert W G, Sullivan S T, Kotochigova S, Petrov A, Chen K, Schowalter S J and Hudson E R 2011 arXiv:1104.5478
[4] Sullivan S T, Rellergert W G, Kotochigova S, Chen K, Schowalter S J and Hudson E R 2011 arXiv:1104.3123
[5] Zipkes C, Palzer S, Sias C and Köhl M 2010 Nature 464 388
[6] Zipkes C, Palzer S, Ratschbacher L, Sias C and Köhl M 2010 Phys. Rev. Lett. 105 133201
[7] Schmid S, Härter A and Denschlag J H 2010 Phys. Rev. Lett. 105 133202
[8] Delos J B 1981 Rev. Mod. Phys. 53 287
[9] Côté R and Dalgaro A 2000 Phys. Rev. A 62 012709
[10] Bodo E, Zhang P and Dalgaro A 2008 New J. Phys. 10 033024
[11] Idziaszek Z, Calarco T, Julienne P S and Simoni A 2009 Phys. Rev. A 79 010702
[12] Gao B 2010 Phys. Rev. Lett. 104 213201
[13] Gao B, Härter A and Denschlag J H 2010 Phys. Rev. Lett. 104 213201
[14] Idziaszek Z, Calarco T and Zoller P 2007 Phys. Rev. A 76 033409
[15] Idziaszek Z, Calarco T and Zoller P 2007 Phys. Rev. A 76 033409
[16] Massignan P, Pethick C J and Smith H 2005 Phys. Rev. A 71 023606
[17] Côté R, Kharchenko V and Lukin M D 2002 Phys. Rev. Lett. 89 093001
[18] Seaton M 1981 Rep. Prog. Phys. 46 167
[19] Greene C H, Rau A R P and Fano U 1982 Phys. Rev. A 26 2441–59
[20] Mies F H 1984 J. Chem. Phys. 80 2514–25
[21] Hanna T M, Tiesinga E and Julienne P S 2009 Phys. Rev. A 79 040701
[22] Tsai C C, Freeland R S, Vogels J M, Boesten H, Verhaar B J and Heinzen D J 1997 Phys. Rev. Lett. 79 1245–8
[23] Vogels J M, Verhaar B J and Blok R H 1998 Phys. Rev. A 57 4049–52
[24] Idziaszek Z and Julienne P S 2010 Phys. Rev. Lett. 104 113202
[25] Ospelkaus S, Ni K K, Wang D, de Miranda M H G, Neyenhuis B, Quéméner G, Julienne P S, Bohn J L, Jin D S and Ye J 2010 Science 327 853–7
[26] Micheli A, Idziaszek Z, Pupillo G, Baranov M A, Zoller P and Julienne P S 2010 Phys. Rev. Lett. 105 073202
[27] Idziaszek Z, Quéméner G, Bohn J L and Julienne P S 2010 Phys. Rev. A 82 020703
[28] Julienne P S, Hanna T M and Idziaszek Z 2011 Phys. Chem. Chem. Phys. at press doi: 10.1039/C1CP21270B
[29] Makerov O P, Côté R, Michels H and Smith W W 2003 Phys. Rev. A 67 042705
[30] Watanabe S and Greene C H 1980 Phys. Rev. A 22 158–69
[31] Burke J P, Greene C H and Bohn J L 1998 Phys. Rev. Lett. 81 3355–8
[32] Gao B, Tiesinga E, Williams C J and Julienne P S 2005 Phys. Rev. A 72 042719
[33] Hanna T M, Tiesinga E and Julienne P S 2010 New J. Phys. 12 083031
[34] Vogt E and Wannier G H 1954 Phys. Rev. 95 1190–8
[35] Spector R M 1964 J. Math. Phys. 5 1185–9
[36] Idziaszek Z and Karwasz G 2006 Phys. Rev. A 73 064701
[37] Idziaszek Z and Karwasz G 2009 Eur. Phys. J. D 51 347–55
[38] Fano U 1970 Phys. Rev. A 2 353–65
[39] Rau A R P and Fano U 1971 Phys. Rev. A 4 1751–9
[40] Milne W E 1930 Phys. Rev. 35 863–7
[41] O’Malley T F, Spruch L and Rosenberg L 1961 J. Math. Phys. 2 491–8
[42] Abramowitz M and Stegun I A 1964 Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables (New York: Dover)
[43] Erdélyi A 1955 Higher Transcendental Functions vol III (New York: McGraw-Hill)
[44] Blume D and Greene C H 2002 Phys. Rev. A 65 043613
[45] Bolda E L, Tiesinga E and Julienne P S 2002 Phys. Rev. A 66 013403
[46] Landau L D and Lifshitz E M 1999 Quantum Mechanics (Oxford: Butterworth–Heinemann)
[47] Gao B 2000 Phys. Rev. A 62 050702
[48] Gao B 1996 Phys. Rev. A 54 2022–39
[49] Simoni A and Launay J-M 2011 arXiv:1106.4672
[50] Taylor J R 1972 Scattering Theory (Wiley: McGraw-Hill)
[51] Zygelman B and Dalgarno A 1988 Phys. Rev. A 38 1877–84
[52] Tellinghuisen J and Julienne P S 1984 J. Chem. Phys. 81 5779–85
[53] Julienne P S 1978 J. Chem. Phys. 68 32–41
[54] Breit G and Rabi I I 1931 Phys. Rev. 38 2082–3
[55] Tiesinga E, Williams C J and Julienne P S 1998 Phys. Rev. A 57 4257–67
[56] LeRoy R J and Bernstein R B 1970 J. Chem. Phys. 52 3869–79
[57] Mies F H, Tiesinga E and Julienne P S 2000 Phys. Rev. A 61 022721
[58] Mies F H and Julienne P S 1984 J. Chem. Phys. 80 2526–36
[59] Julienne P S and Gao B 2006 Simple Theoretical Models for Resonant Cold Atom Interactions vol 869, ed C Roos, H Häffner and R Blatt (New York: AIP) pp 261–8
[60] Chin C, Grimm R, Julienne P and Tiesinga E 2010 Rev. Mod. Phys. 82 1225–86
[61] DeVoe R G 2009 Phys. Rev. Lett. 102 063001
[62] Gao B 1998 Phys. Rev. A 58 1728–34