Correspondence between the surface integral and linear combination of atomic orbitals methods for ionic-covalent interactions in mutual neutralization processes involving H⁻/D⁻

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The surface integral method for estimating ionic-covalent interactions in diatomic systems been successful in producing cross sections for mutual neutralization (MN) in reasonable agreement with experimental results for branching fractions between final states in systems such as O^+/O^- and N^+/O^-. However, for simpler cases of MN involving H^- or D^-, such as Li^+/D^- and Na^+/D^-, it has not produced results that are in agreement with experiments and other theoretical calculations; in particular, for Li^+/D^- calculations predict the wrong ordering of importance of final channels, including the incorrect most populated channel. The reason for this anomaly is investigated, and a leading constant to the asymptotic H^- wave function is found that is different by roughly a factor of $1/\sqrt{2}$ from that which has been used in previous calculations with the surface integral method involving H^- or D^-. With this correction, far better agreement with both experimental results and calculations with full quantum and linear combination of atomic orbitals (LCAO) methods is obtained. Further, it is shown that the surface integral method and LCAO methods have the same asymptotic behavior, in contrast to previous claims. This result suggests the surface integral method, which is comparatively easy to calculate, has greater potential for estimating MN processes than earlier comparisons had suggested.

I. INTRODUCTION

Charge transfer, in which an electron moves from one atom or ion to another during a collision, is a fundamental atomic process. Mutual neutralization (MN), with the corresponding reverse process ion-pair production

$$A^+ + B^- \rightleftharpoons A^* + B, \qquad (1)$$
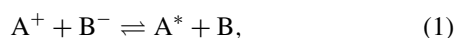
is an important special case, and methods for estimating cross sections are important for interpreting experimental results and testing our understanding of the physical mechanisms involved [1–3], as well as modeling various plasma environments such as planetary and planetary-satellite atmospheres [4], including earth's ionosphere [5] and stellar atmospheres [6,7], and being important for diagnostics of and fusion plasma applications and high-energy physics experiments employing negative-ion sources [8]. The transferred electron is captured into specific excited states A^*, and thus affects the distribution of populations of states of atom A and its observed spectrum. These processes occur predominantly through interactions between ionic ($A^+ + B^-$) and covalent ($A^* + B$) configurations at avoided crossings in the adiabatic potential-energy curves (e.g., [9,10]). Any method for estimating MN

cross sections thus hinges on the ability to calculate the ionic-covalent interactions.

A promising approach is the surface integral method. The general technique was independently developed roughly simultaneously by a number of workers and thus is known by various names, including the Holstein-Herring method (e.g., [11]), the Firsov-Landau-Herring method (e.g., [12]), and the Landau-Herring method (e.g., [13–15]). The original papers on the idea include those by Firsov [16], Holstein [17], and Herring [18], and the method was used to solve problems in Landau and Lifshitz's text *Quantum Mechanics* [19], published in Russian in the 1950s; the asymptotic (large internuclear distance R) splitting between gerade and ungerade states for H_2^+ is solved in Sec. 81 of Ref. [19], building on problem 3 in Sec. 50. The basic idea is that the interaction energy can be calculated from the electronic current flowing across a surface between the two nuclei, obtained by manipulating Schrödinger equations corresponding to cases where the electron is localized on either nucleus. On the assumption that the wave functions are close to zero at the surface, i.e., in the limit of large internuclear separations, the method allows the interaction to be derived in terms of the atomic electronic wave functions at the surface.

A key point in the use of the method is the choice of the integration surface to ensure that wave functions are small. Smirnov [20] derived expressions for the interaction in the $A^+ + e + B$ system, assuming the interaction between e and B to be zero and taking the integration surface as the midplane, halfway between the two nuclei. Janev and Salin [14,15] instead account for the potential due to B and chose the integration surface to be a sphere around B where the potential becomes suitably small; see also Ref. [13] for an earlier application in resonant charge transfer.

Janev and Salin's expressions for the couplings from the surface integral method, which for consistency with previous work [21,22] we will call the Landau-Herring-Janev (LHJ) method, have been used in various studies of MN involving H^-, coupled with Landau-Zener dynamics, including MN of alkalis with H^- [23], H_3^+ with H^- [24], Si^+ with H^- [25], and H^+ and Be^+ with H^- [26]. In Refs. [21,22] the method was compared with full quantum and linear combination of atomic orbitals (LCAO) calculation results for MN of Li^+, Na^+, and Mg^+ with H^-, and the results were found to differ significantly. Recent experimental results for branching fractions in Li^+/D^- [1,2] and Na^+/D^- [3] have allowed calculations to be tested, and full quantum and LCAO results [7] have shown good agreement, implying the LHJ method is in disagreement with these experiments. This is puzzling, given that the LHJ method has been shown to produce estimates in reasonable agreement with experiment for MN of N^+/O^- and O^+/O^- [27,28].

Asymptotic methods such as LHJ and LCAO are of significant importance for many applications, as estimates can be made rather inexpensively compared to full quantum calculation (quantum chemistry potentials and couplings with quantum scattering), and thus, it is valuable to resolve the origin of this discrepancy. The fact that the LHJ method appears to work well for MN involving O^- and less well for the simpler H^- would seem to suggest the following possible explanations: (1) there is a problem with the H^- wave function used, (2) the agreement for O^- is fortuitous, or (3) the full quantum, LCAO, and experimental results are in error. In this paper it will be shown that an error appears to have been made in deriving the asymptotic H^- wave function used in all applications to MN involving H^-, and correcting this error brings the LHJ method into reasonable agreement with other theories and experiments. Previous claims that the discrepancy between the LHJ and LCAO methods is due to fundamental problems in the LCAO method are reexamined in light of this.

II. THEORY

Mutual neutralization occurs predominantly at avoided crossings between adiabatic molecular potential curves, corresponding to real crossings in a diabatic representation (e.g., [9,10]). In a diabatic representation the states of the system can be described in terms of ionic and covalent configurations. The ionic configuration is the case where the active electron is located on core B, that is, $A^+ + (e + B)$, labeled i with the corresponding diabatic electronic wave function Φ_i, and the covalent configuration is the case where the active electron is located on core A^+, that is, $(A^+ + e) + B$, labeled c with wave function Φ_c; see Fig. 1 for a sketch of the system. These two configurations have corresponding diabatic states with potentials that cross, $H_{ii} = \langle \Phi_i | H | \Phi_i \rangle$ and $H_{cc} = \langle \Phi_c | H | \Phi_c \rangle$, where H is the Hamiltonian, and have an off-diagonal interaction (coupling) $H_{ic} = \langle \Phi_i | H | \Phi_c \rangle$. In the adiabatic representation, the potentials avoid crossing, and a key quantity is the splitting between the adiabatic potential curves ΔU, as it enters the Landau-Zener formula for the transition probability [9,29,30]. The transition probability between adiabatic states is (in atomic units, which are used
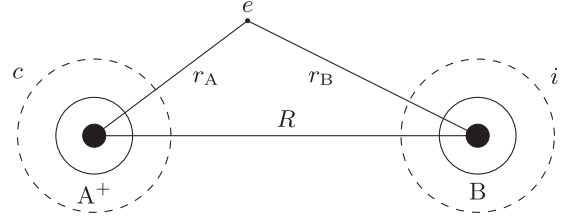

FIG. 1. Sketch of the $A^+ + e + B$ system, where A^+ is the singly charged core, e is the active electron, and B is a neutral atom. In the MN process [Eq. (1)], the electron moves from being localized on center B, the ionic configuration i, to being localized on A, the covalent configuration c.

throughout)

$$P = \exp \left(-\frac{\pi \Delta U^2}{2 v_R |d(H_{ii} - H_{cc})/dR|_{R=R_x}} \right), \quad (2)$$

where v_R is the radial component of the velocity of the relative motion of the nuclei, R is the internuclear distance, and R_x is the distance at which the diabatic potentials H_{ii} and H_{cc} cross. The splitting ΔU is related to the interaction $H_{ic} = \langle \Phi_i | H | \Phi_c \rangle$ in the (nonorthogonal) diabatic basis (e.g., [31,32]),

$$\Delta U(R_x) = \frac{|\Delta(R_x)|}{1 - S_{ic}^2}, \quad \Delta(R_x) = 2(H_{ii} S_{ic} - H_{ic})\big|_{R=R_x}, \quad (3)$$

where $S_{ic} = \langle \Phi_i | \Phi_c \rangle$ is the overlap between states i and c. Note that if the diabatic basis is orthogonal,

$$\Delta U(R_x) = \Delta(R_x) = 2 H_{ic}(R_x). \quad (4)$$

The references mentioned above, as well as Refs. [10,21,33], can be consulted for more details on the Landau-Zener model and the relationship between adiabatic and diabatic representations, including orthogonal and nonorthogonal representations.

A. Surface integral method

The surface integral method can be used to estimate the quantity Δ via

$$\Delta(R_x) = \int_s (\Phi_i^* \nabla \Phi_c - \Phi_c^* \nabla \Phi_i) d\vec{s}, \quad (5)$$

where s is the surface of integration; see Refs. [12,14,15,31] for more details. Note that here, the wave functions Φ are only the spatial components.

The LHJ theory, which chooses the surface s to be a sphere centered on B, derives an analytic expression for $\Delta(R_x)$ written in terms of the asymptotic forms of the spatial atomic wave function φ of the active electron. That is,

$$\Phi(\vec{r}, \vec{R}) \xrightarrow{R \to \infty} \varphi(\vec{r}) = \mathcal{R}_{nl}(r) Y_{lm}(\theta, \phi), \quad (6)$$

such that $\mathcal{R}_{nl}(r)$ is the radial part of the wave function, Y_{lm} is the spherical harmonic function, and $\vec{r}$ is the active electron coordinate with respect to the relevant nucleus ($\vec{r_A}$ or $\vec{r_B}$). When the active electron is on core A^+, i.e., the system is in the covalent configuration c, the asymptotic behavior of the Coulomb wave function (i.e., the leading term of the

asymptotic expansion) is used:

$$\mathcal{R}_c(r) = N_c r^{1/\gamma_c - 1} \exp\left(-\gamma_c r\right), \tag{7}$$

where $-\gamma_c^2/2$ is the binding energy of the electron and the quantum numbers nl are now dropped from the radial function $\mathcal{R}$ for simplicity. When the electron is on core B, thus forming a negative ion, and the system is in the ionic configuration i, the appropriate asymptotic form is used:

$$\mathcal{R}_i(r) = N_i \frac{2\gamma_i}{\pi} k_{l_i}(\gamma_i r), \tag{8}$$

where $-\gamma_i^2/2$ is the binding energy of the electron, and thus, $E_{\mathrm{B}}^- = \gamma_i^2/2$ is the electron affinity of the negative ion, $k_l(x)$ is the modified spherical Bessel function (e.g., [34]), and l_i is the orbital angular momentum quantum number. For the specific case of $l_i = 0$,

$$\mathcal{R}_i(r) = N_i \exp\left(-\gamma_i r\right)/r. \tag{9}$$

Both wave functions contain leading constants, N_c and N_i, that must be determined. In the case of N_c, it can be estimated from the Coulomb wave-function normalization constant from quantum defect theory [35–37] (see, e.g., Eq. (19) of Ref. [14]), which can be expected to give accurate results for sufficiently excited states with diffuse wave functions well described by quantum defect theory. The leading-constant factor for the negative-ion function is, however, more problematic to determine. Due to the $1/r$ factor, the normalization is dominated by contributions at short distances where the asymptotic form is not valid and overestimates the wave function, and the value given by normalization $N_i = \sqrt{2\gamma_i}$ (see Ref. [38]) cannot be expected to give an accurate representation of the asymptotic behavior. N_i should therefore be determined by comparison with detailed atomic structure calculations. One expects $N_i > \sqrt{2\gamma_i}$, and this has sometimes led to the use of a cutoff value r_0, below which the wave function is zero and can be chosen to give correct normalization (e.g., Refs. [21,38]).

Using these wave functions, Refs. [15,39] give the expression for $\Delta(R_x)$ as

$$\Delta(R_x) = \frac{\delta_{m_i m_c} N_i \mathcal{R}_c(R_x)}{(2\gamma_i R_x)^{|m_c|} |m_c|!}$$
$$\times \left[\frac{(2l_c + 1)(2l_i + 1)(l_c + |m_c|)!(l_i + |m_i|)!}{(l_c - |m_c|)!(l_i - |m_i|)!} \right]^{1/2}, \tag{10}$$

which for $l_i = 0$, as in the case of H$^-$ (^1S), reduces to the rather simple expression

$$\Delta(R_x) = N_i \mathcal{R}_c(R_x) \times (2l_c + 1)^{1/2}. \tag{11}$$

The modification due to angular momentum coupling to core electrons in complex systems, including those with equivalent electrons, is given in Refs. [12,15,39]. The major advantage of this approach is that, as can be seen, it reduces to an analytic expression and does not require the evaluation of any matrix elements of the Hamiltonian.

B. LCAO method

The LCAO approach can be used to calculate $\Delta(R_x)$ through the calculation of the matrix elements of the

Hamiltonian using the same or similar atomic wave functions for the active electron. This was done in Refs. [21,32,40,41] for the case involving H$^-$, considering two electrons. The main differences between these different descriptions are the treatment of the two-electron wave functions, leading to slightly different expressions, but they are equivalent asymptotically (at large separations R). For the purposes of our discussion, a much simpler one-electron version is preferable, again equivalent to the above formulations at large R.

Considering the model and coordinate system given in Fig. 1, ignoring any interactions with the neutral atom B, the Hamiltonian is $H = -1/r_A$, and we have the rather simple expression in terms of atomic wave functions

$$H_{ii} = \langle \varphi_i | -\frac{1}{r_A} | \varphi_i \rangle, \tag{12}$$

where for large R we have

$$\langle \varphi_i | \frac{1}{r_A} | \varphi_i \rangle \approx \frac{1}{R}, \tag{13}$$

and similarly,

$$H_{ic} = \langle \varphi_i | -\frac{1}{r_A} | \varphi_c \rangle. \tag{14}$$

Using these results in Eq. (3), we obtain

$$\Delta(R_x) \approx 2\left(-\frac{1}{R} \langle \varphi_i | \varphi_c \rangle - \langle \varphi_i | -\frac{1}{r_A} | \varphi_c \rangle \right) \Big|_{R=R_x}$$
$$\approx 2 \langle \varphi_i | \frac{1}{r_A} - \frac{1}{R} | \varphi_c \rangle \Big|_{R=R_x}, \tag{15}$$

where we now define

$$T_{ic}(R) \equiv 2 \langle \varphi_i | \frac{1}{r_A} - \frac{1}{R} | \varphi_c \rangle, \tag{16}$$

the "postinteraction operator" T of charge-transfer theory also found in Refs. [32,40]. The same result is found through a different derivation in Sec. 10.3 of Ref. [42].

Analytic expressions for $T_{ic}(R)$ can be obtained by adopting the asymptotic forms of the atomic wave functions given above, although for any given l_c and l_i, they are significantly more complex than those arising from the surface integral method for $\Delta(R_x)$ given above. Expressions for both $T_{ic}(R)$ and $S_{ic}(R)$ for the $l_c = l_i = 0$ case are given in the Appendix.

C. H$^-$ asymptotic wave function

The general theory of asymptotic wave functions has been well expounded, for example, in Sec. 2.1 of Ref. [43], as well as Ref. [44]. The derivation of the asymptotic wave function for H$^-$ is particularly simple, and so it is instructive for the following discussion to present the basic equations (see, e.g., Refs. [41,42,44] for details). The two-electron nonrelativistic Hamiltonian, in atomic units, is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}, \tag{17}$$

where r_1 and r_2 are distances of electrons with labels 1 and 2 to the proton and r_{12} is the distance between electrons. Taking the asymptotic case $r_1 \gg r_2$, then $r_{12} \approx r_1$, the asymptotic form then allows separation into terms related to each

electron,

$$H \approx \left(-\frac{1}{2}\nabla_1^2\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_2}\right) \equiv H_1 + H_2, \quad (18)$$

such that H_1 is the Hamiltonian for the loosely bound distant electron and H_2 is the Hamiltonian for the tightly bound electron close to the proton. Then the time-independent Schrödinger equation becomes

$$(H_1 + H_2)\psi = \left(-E_{H^-} + E_H^{1s}\right)\psi, \quad (19)$$

where ψ is the electronic wave function, E_H^{1s} is the energy of the hydrogen ground state (-0.5 a.u.), and E_{H^-} is the electron affinity of H (a positive value; see below). Separating the total wave function ψ into spatial and spin functions $\psi = \varphi(\vec{r}_1, \vec{r}_2)\chi_{S=0}$, where $\chi_{S=0}$ is the singlet spin function, the asymptotic spatial wave function becomes

$$\varphi^{asymp}(\vec{r}_1, \vec{r}_2) = \varphi_{LR}(\vec{r}_1)\varphi_{1s}^H(\vec{r}_2), \quad (20)$$

where $H_2\varphi_{1s}^H(\vec{r}_2) = E_H^{1s}\varphi_{1s}^H(\vec{r}_2)$ and thus $\varphi_{1s}^H(\vec{r}) = \exp(-r)/\sqrt{\pi}$ is the hydrogen ground-state function, and the long-range (LR) electron function is the solution of

$$H_1\varphi_{LR}(\vec{r}_1) = \left(-\frac{1}{2}\nabla_1^2\right)\varphi_{LR}(\vec{r}_1) = -E_{H^-}\varphi_{LR}(\vec{r}_1). \quad (21)$$

The spherically symmetric ($l = 0$) solution is

$$\varphi_{LR}(\vec{r}) = A\exp(-\gamma r)/r \quad \gamma r \gg 1, \quad (22)$$

where $\gamma = \sqrt{2E_{H^-}}$ and A is an arbitrary constant related to N_i in Eq. (9), which we need to determine. The electron affinity of H from modern measurements is $E_{H^-} = 0.754195(19)$ eV or 0.0277162 a.u. [45], which gives $\gamma = 0.235441$ in atomic units. The validity condition $\gamma r \gg 1$ thus requires $r \gg 1/\gamma = 4.26$ a.u. As will be shown below, $A = N_i\frac{1}{\sqrt{4\pi}}$, and correct normalization would imply $N_i = \sqrt{2\gamma} \approx 0.686$ and $A \approx 0.194$.

Unfortunately, a range of different definitions and notations for the asymptotic function and the leading constant have been used in various sources. Part of this difference often arises from separation into radial and angular components, for this case ($l = 0$)

$$\varphi_{LR}(\vec{r}) = \mathcal{R}(r)Y_{00}(\theta, \phi) = \mathcal{R}(r)\frac{1}{\sqrt{4\pi}}. \quad (23)$$

In early papers by Smirnov [20], the following definition was used:

$$\mathcal{R}(r) = A_{S65}\sqrt{2\gamma}\exp(-\gamma r)/r, \quad (24)$$

where $\sqrt{2\gamma}$ arises because the function is correctly normalized if $A_{S65} = 1$ (see Sec. II A). In Ref. [20], the value $A_{S65}^2 = 2.65$ was derived, which means $A_{S65} = 1.63$. This implies $A = A_{S65}\sqrt{2\gamma}\frac{1}{\sqrt{4\pi}} = 0.316$. Later work by Smirnov and others [14,23,38,42,46] adopted the definition

$$\mathcal{R}(r) = A_S\exp(-\gamma r)/r = B_S\sqrt{2\gamma}\exp(-\gamma r)/r, \quad (25)$$

such that B in Ref. [42], here denoted B_S, is equal to A_{S65}. Note that $A_S = N_i$ and is thus the value required for use in the equations of Janev and Salin [14,15], that is, Eqs. (10) and (11). Smirnov [38,42,46] derived A_S from the simple Chandrasekhar two- and three-parameter wave functions [47], finding a value of $A_S = 1.13 \pm 0.06$, and thus, $B_S = A_{S65} = 1.64 \pm 0.08$. A value of A_S in this range has been used in

all applications of the LHJ method to processes involving H$^-$ [21–26]. This gives $A = A_S\frac{1}{\sqrt{4\pi}} = 0.319$.

In LCAO applications [40,41] the value $A = 0.223106$ has been used, determined from the 203-parameter variational wave function of Pekeris [48], with asymptotic values of the wave function being presented in Ref. [49]. This derivation will be discussed in Sec. II C 1. In Ref. [22] the LCAO method was applied, and the same value is essentially used, but a factor of $\sqrt{2}$ must be applied to adjust for the antisymmetrized version of the asymptotic wave function that was employed.

Clearly, there is a discrepancy between the leading constant of the asymptotic wave function derived by Smirnov and used in all LHJ theory applications, $A \approx 0.319$, and the value that has been applied in LCAO calculations, i.e., $A \approx 0.223$. The two values of A differ by a factor of roughly $\sqrt{2}$. In the following we repeat both derivations in detail to show the source of the problem.

1. Direct matching of the asymptotic wave function

The most straightforward approach to determining the appropriate constant in the asymptotic wave function is through direct matching to a calculated wave function for H$^-$. This is the approach that has been used in the LCAO case, and the method stems from Ref. [49]. They defined a function equal to the two-electron spatial wave function where either $r_1 = 0$ or $r_2 = 0$, $\psi(r)$ in their notation. Here, we denote this same function:

$$\varphi_0(r) \equiv \varphi(\vec{r}_1 = 0, |\vec{r}_2| = r) = \varphi(|\vec{r}_1| = r, \vec{r}_2 = 0)$$
$$= C(r)\exp(-\gamma r)/r, \quad (26)$$

such that $C(r)$ is the same as in Ref. [49] and converges to a constant value $C(\infty)$ at large r [50]. Equating to the asymptotic wave function from above, Eq. (20), taking $r_2 = 0$, we obtain

$$\varphi_0^{asymp}(r) = \varphi_{LR}(|\vec{r}_1| = r)\varphi_{1s}^H(\vec{r}_2 = 0)$$
$$= \varphi_{LR}(r)\frac{1}{\sqrt{\pi}}$$
$$= A\exp(-\gamma r)/r\frac{1}{\sqrt{\pi}}, \quad (27)$$

which means $A = C(\infty)\sqrt{\pi}$. In Ref. [49], $C(\infty) = 0.125874$, and thus, $A = 0.223106$ was found by matching points at $r = 14$–16 a.u. from the calculated values of $\varphi_0(r)$ extracted from the 203-parameter wave function of Ref. [48] given in their Table 1. This is the value used in LCAO calculations.

Figure 2 compares $\varphi_0(r)$ extracted from various detailed calculations of the wave function $\varphi(\vec{r}_1, \vec{r}_2)$ with asymptotic forms of the wave function $\varphi_0^{asymp}(r)$ for the two different values of A discussed above. It is clearly seen that $A \sim 0.223$ matches all the functions better than the higher value of $A \sim 0.319$. Note that among detailed calculations, only the Pekeris wave function has the expected asymptotic form even at very long range since the variational form of the wave function used ensures correct asymptotic behavior. The two- and three-parameter wave functions derived by Chandrasekhar [47] are of particular interest as they were used by Smirnov and also because they are so simple that they can be used to exemplify
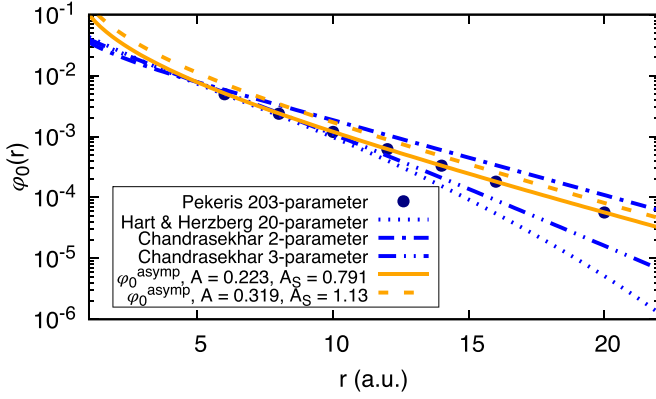
FIG. 2. The asymptotic H$^-$ wave function $\varphi_0(r)$ as defined in Eq. (26), extracted from various detailed calculations of the wave function $\varphi(\vec{r}_1, \vec{r}_2)$: the 203-parameter function from Pekeris [48] calculated in Ref. [49], the 19-parameter function of Hart and Herzberg [51], and the 2- and 3-parameter functions of Chandrasekhar [47]. Asymptotic forms [Eq. (27)] with the two values of A discussed in the text are also shown.
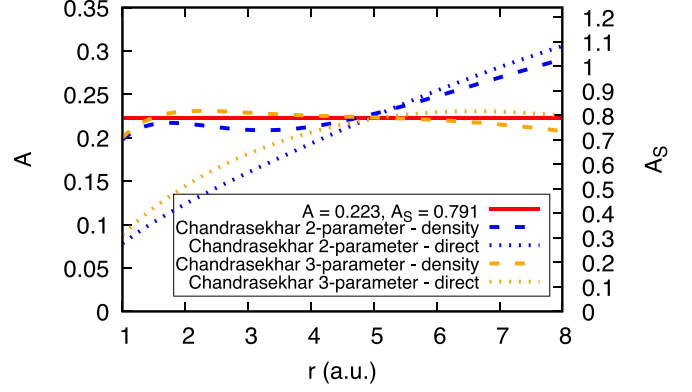

FIG. 3. Derived values for A as a function of r. Corresponding values for A_S are shown on the right axis. The blue (dark gray) lines show the values derived from Chandrasekhar's two-parameter wave function, and the orange (light gray) lines are from the three-parameter wave function. In each case, dashed lines are from the electronic density matching method, and dotted lines are from the direct matching method. The horizontal solid red line shows the value derived from direct matching to the accurate wave function due to Pekeris [48]; see Fig. 2 and Sec. II C 1.

various issues. The Chandrasekhar wave function is

$$\varphi(\vec{r}_1, \vec{r}_2) = N[\exp{(-ar_1 - br_2)} + \exp{(-ar_2 - br_1)}]$$
$$\times (1 + cr_{12}), \tag{28}$$

where for the two-parameter function ($c = 0$) he found through variational calculations $a = 1.03925$ and $b = 0.28309$ and it can be found from the normalization condition that $N = 0.031443$ and for the three-parameter function introducing correlation he found $a = 1.07478$, $b = 0.47758$, $c = 0.31214$ and it can be found that $N = 0.031226$. That $a \approx 1$ in both cases shows the expected result of an unscreened hydrogen $1s$-like function for the electron close to the proton, with a more distant long-range electron. Having said that, it is clear that the functions do not have the correct asymptotic behavior when the distant electron is very far from the nucleus. The Chandrasekhar 2-parameter function does not have asymptotic behavior at any distance, and the 3-parameter and Hart and Herzberg 20-parameter functions [51] have only roughly asymptotic behavior in the region $r \approx 4$–10 a.u. This is due to the fact that the asymptotic region has little influence on the state energies and thus the wave function determined by variational methods.

2. Electronic-density-matching method

An alternative approach, which has been used by Smirnov [38,42,46], is to match the electron density function. Generally, for an N-electron system, ignoring spin, the electronic density is

$$\rho(\vec{r}) = N \int d\vec{r}_2 \cdots \int d\vec{r}_N |\varphi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)|^2, \tag{29}$$

and thus, for H$^-$ and two electrons

$$\rho(\vec{r}) = 2 \int d\vec{r}_2 |\varphi(\vec{r}, \vec{r}_2)|^2. \tag{30}$$

For the asymptotic form this gives

$$\rho^{\text{asymp}}(\vec{r}) = 2 \int d\vec{r}_2 \left| \varphi_{\text{LR}}(\vec{r}) \varphi_{1s}^H(\vec{r}_2) \right|^2$$
$$= 2 |\varphi_{\text{LR}}(\vec{r})|^2$$
$$= 2A^2 \exp{(-2\gamma r)}/r. \tag{31}$$

As done by Smirnov, one can derive analytical expressions for the asymptotic constant A or some related version of it, e.g., A_S or A_{S65}, as a function of r by equating the asymptotic form with the electronic density calculated from Chandrasekhar's wave functions, and the expressions found by Smirnov are given in Refs. [38,42]. Using *Mathematica*, this analysis was repeated here, making use of Hylleraas coordinates for the three-parameter case [52,53], and the results are plotted in Fig. 3.

From Fig. 3 it can be seen that the values of A and A_S as a function of r from electronic density matching of both the two- and three-parameter Chandrasekhar wave functions are roughly constant and in agreement around $r = 2$–5 a.u., the region used by Smirnov to derive A_S. Figure 3 clearly favors a low value, $A \approx 0.22$ ($A_S \approx 0.79$), rather than a high value, $A \approx 0.32$ ($A_S \approx 1.13$). Thus, the analysis presented here from electron density matching is roughly in agreement with the value from direct matching, $A = 0.223$ ($A_S = 0.791$), which is roughly a factor of $1/\sqrt{2}$ lower than that found by Smirnov, $A \approx 0.32$ ($A_S = 1.13$). The difference is not precisely a factor of $1/\sqrt{2}$ since different wave functions are used, the direct method permitting the easy use of the accurate 203-parameter function of Pekeris.

Note that the criterion for validity of the asymptotic wave function, $r \gg 1/\gamma = 4.26$ a.u., is not satisfied across this entire region $r = 2$–5 a.u. Further, it is clear that the Chandrasekhar wave functions do not have correct asymptotic behavior, as is seen from application of the direct method, which gives rapidly varying values of A (see also Fig. 3). That

the density-matching method using these simple wave functions gives values that agree reasonably with the values from direct matching of the accurate and asymptotically correct wave function of Pekeris is thus perhaps somewhat surprising. It may reflect that the density method, by accounting for contributions from both electrons at intermediate distances, reaches asymptotic behavior at smaller internuclear distances than the direct method, in which the second electron is fixed at the nucleus. Contributions from both electrons to the wave function are equal, $\varphi_{LR}(\vec{r}) = \varphi_{1s}^H(\vec{r})$, at roughly $r = 2.3$ a.u.

III. COMPARISON OF THEORETICAL CALCULATIONS AND EXPERIMENTS

Experiments were recently performed in Louvain on MN of Li^+/D^- [1] and at the Double ElectroStatic Ion Ring ExpEriment (DESIREE) facility in Stockholm on Li^+/D^- [2] and Na^+/D^- [3], resolving final states and thus measuring branching fractions for the neutral products. D^- is preferred over H^- in the experiments for practical reasons but is basically identical to H^- in terms of binding energy (electron affinity) and thus electronic structure. The different mass leads to trajectory (Coulomb-focusing) effects but is easily accounted for in the dynamical calculations. In a recent paper [7], existing full quantum calculations [54–56] and (two-electron) LCAO method calculations [21,22] were compared with experiment, generally finding good agreement, with the full quantum calculations performing best, in line with expectations. The reader is referred to Ref. [7] for a discussion regarding these comparisons, including the discussion of Coulomb-focusing effects caused by H^- versus D^-.

Here, these comparisons are supplemented with calculations from the LHJ theory using the two A values discussed, and these calculations use the same code as the LCAO calculations, described in Refs. [21,22]. The results are shown for Li^+/D^- in Fig. 4 and for Na^+/D^- in Fig. 5. To aid comparison (see Ref. [7]), the plots are presented on the reduced energy scale, which is defined as $E_R = E_{CM}/\mu = \frac{1}{2}v^2$, where E_{CM} is the collision energy in the center-of-mass frame, μ is the reduced mass of the system, and v is the relative velocity. It is clear that the comparisons with experiment are significantly improved for both Li^+/D^- and Na^+/D^- if the low value of $A = 0.223$ is adopted, compared to the high value of $A = 0.319$. In particular we note that for Li^+/D^- (Fig. 4), the high value leads to the prediction of $3p$ being the dominant channel at low energy, rather than $3s$, as clearly seen to a high degree of certainty in experiments. This discrepancy is resolved for the LHJ theory with the lower value of A. Further, the low value of A leads to much better consistency between full quantum, LCAO, and LHJ predictions in both cases. Note also that LHJ with the high value of A leads to variation of the branching fractions at lower collision energies.

Janev and Radulovic [23] also performed calculations with the LHJ method for Li^+/H^- and Na^+/H^-, although state-resolved results were shown for only Na^+/H^- (their Fig. 1). Our results for Na^+/H^- partial cross sections are significantly different from theirs; in particular at low energy they found $3p$ to be the second most populated channel, only an order of magnitude lower than $4s$. This is in strong disagreement with experiment, where the $3p$ channel is not observed, and
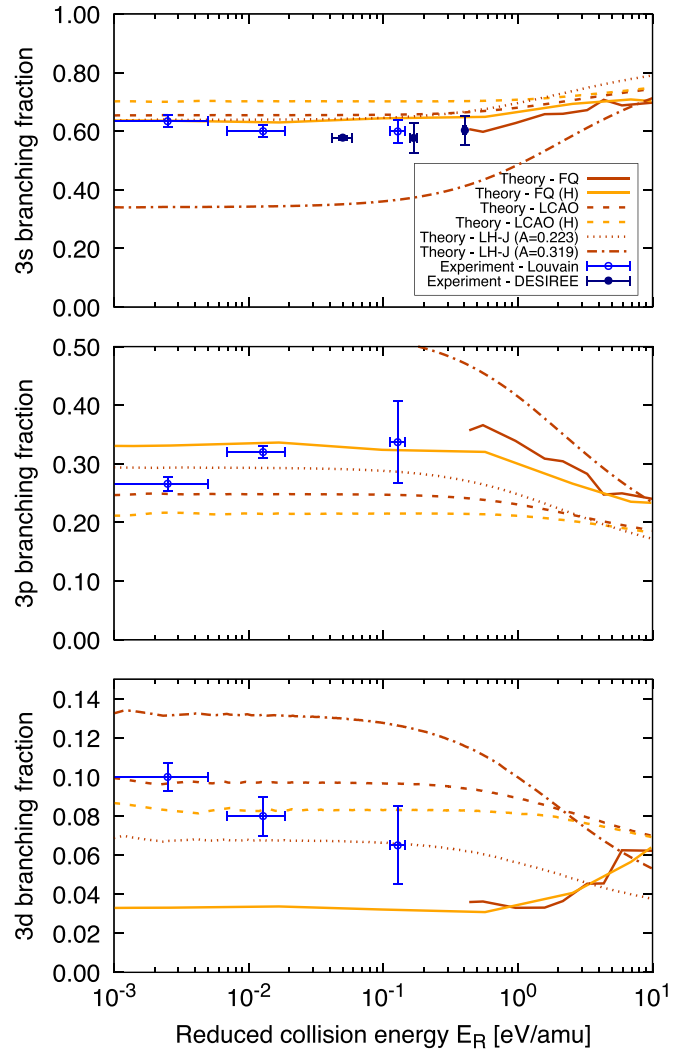

FIG. 4. Branching fractions for the MN reaction $Li^+ + D^- \rightarrow Li(nl) + D$ as a function of reduced collision energy. The $3s$, $3p$, and $3d$ channels are shown in separate panels. Experimental results from Louvain [1] and from DESIREE [2] are shown, with estimated errors (1σ). Theoretical results are shown from full quantum (FQ) calculations and LCAO and LHJ asymptotic methods with the old (high) value for A and the new (low) value for A; see text for further details. Theoretical results are also shown for the case where D^- is replaced by H^-, marked by (H) in the legend.

with all other calculations, including our LHJ calculations with the old, high value of A, for which we find the cross section for $3p$ to be more than five orders of magnitude lower than $4s$; this may suggest a labeling error. In Ref. [56] substantial differences were also noted compared to full quantum calculations. This was investigated further by comparing our LHJ theory avoided-crossing parameters with those in Table 1 of Ref. [23], in particular $\Delta(R_x)$. However, for both Li and Na we were unable to reproduce all of their results using the equations and numbers in the paper. Using their equations, their value for the leading constant in the negative-ion radial wave function, and their values for R_x, we obtain $\Delta(R_x)$ in agreement (within 10%) for a few crossings (Li $2s$ and $2p$, Na $3p$), but for the majority there are significant differences
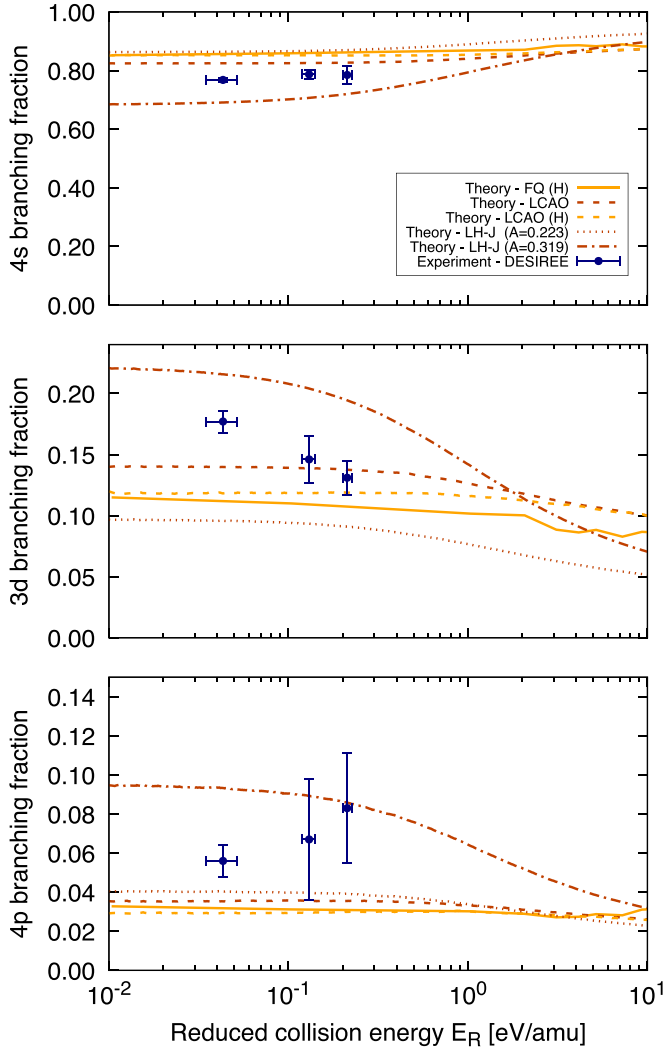
FIG. 5. Branching fractions for the MN reaction $Na^+ + D^- \rightarrow Na(nl) + D$ as a function of reduced collision energy. The $4s$, $3d$, and $4p$ channels are shown in separate panels. Experimental results from DESIREE [3] are shown, with estimated errors (1σ). Theoretical results are shown from full quantum (FQ) calculations and LCAO and LHJ asymptotic methods with the old (high) value for A and the new (low) value for A; see text for further details. Theoretical results are also shown for the case where D^- is replaced by H^-, marked by (H) in the legend.

(up to a factor of 2.5 for Na $4p$), with our result usually being larger (only for Li $3d$ do we obtain a roughly 20% smaller value). Our LHJ theory values using $A = 0.319$ agree well with what we calculate from the equations in Ref. [23], which are just simpler versions of the more general theory. As such, detailed comparison of the avoided-crossing parameters is not particularly enlightening for the more general problem of interest here, namely, the relationship between LHJ theory, LCAO theory, and experiment.

Dochain and Urban [57] semiempirically found a similar need for a factor of $1/\sqrt{2}$ correction to the couplings in LHJ theory and in doing so obtained good matches to experimental results for MN of D^- with He^+, Li^+, Na^+, C^+, and N^+, although with some discrepancies for O^+.

Finally, it is worth noting that calculations with the Smirnov formulation of the surface integral method [20], taking the surface of integration as the midplane between the two atoms, while improving with the lower value of A, still perform substantially worse than the Janev and Salin formulation (see also Ref. [26]).

IV. DISCUSSION

It was claimed in Ref. [39] that the LCAO method is "essentially incorrect for the problem of calculation of $\Delta(R)$," with reference to the work of Herring [18]. It is, however, unclear that the criticisms of the LCAO method for the cases discussed by Herring, the exchange interaction [58] in H_2^+ and H_2, apply also to ionic-covalent interactions. First, the problem of the $1/r_{12}$ term described for the exchange interaction in H_2 is not relevant, as it does not enter the one-electron LCAO method (see Sec. II B) and in the two-electron methods enters only empirically via the H^- electron affinity and wave function (e.g., Eq. (10) of Ref. [21]). Second, in both cases, a basis with a single tightly bound $1s$ wave function is used in the LCAO description. In the case studied in detail by Herring for the exchange splitting in H_2^+, the surface integral approach permits a modification factor which increases the value of the wave function between the two nuclei, capturing departures of the molecular wave function from the atomic ones, which cannot be modeled in a LCAO basis with a single fixed orbital. In contrast, the LCAO method for ionic-covalent interactions employs two wave functions that capture the main components of the molecular wave function at internuclear distances corresponding to the crossing.

More quantitatively, Ref. [39] claimed that there is a discrepancy between the asymptotic behavior of the interactions in the LHJ and LCAO formulations. For LHJ the interaction has the asymptotic behavior

$$\Delta_{LHJ}(R_x) \propto \exp(-\gamma_c R_x) \tag{32}$$

at large R_x [see Eqs. (10) and (7)], while for LCAO at large R, Ref. [39] claimed the asymptotic behavior is

$$\Delta_{LCAO}(R_x) \propto \exp[-(\gamma_i + \gamma_c)R_x]; \tag{33}$$

however, this relationship is asserted without proof and misses the important fact that γ_i and γ_c are related at the crossing point R_x. Assuming a pure Coulomb interaction for the ionic potential and a null potential for the covalent state, the crossing point is given by

$$\frac{1}{R_x} = \frac{\gamma_c^2}{2} - \frac{\gamma_i^2}{2}. \tag{34}$$

Using the one-electron LCAO expression for $T_{ic}(R)$ for $l_c = l_i = 0$ given in the Appendix and making the substitution $\gamma_i \rightarrow \sqrt{\gamma_c^2/2 - 2/R_x}$, an analytic expression for $\Delta_{LCAO}(R_x) = T_{ic}(R = R_x)$ can be obtained. This results in a complicated expression which is no longer dependent on γ_i and which can be shown to have the same behavior as the LHJ theory for large R_x; i.e., for $l_c = 0$

$$\Delta_{LHJ}(R_x) = N_i \mathcal{R}_c(R_x). \tag{35}$$

This agreement is most convincingly shown by numerical results for the ratio $\Delta_{LCAO}/\Delta_{LHJ}$, which is dependent only on

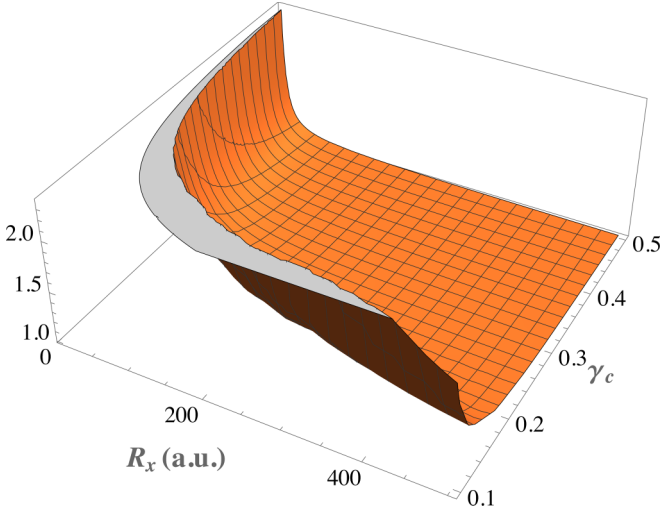FIG. 6. Three-dimensional mesh plot of the ratio $\Delta_{\mathrm{LCAO}}/\Delta_{\mathrm{LHJ}}$ as a function of γ_c and R_x for $l_c = l_i = 0$ analytic expressions obtained as described in the text. The ratio tends to 1 for $R_x \gg \gamma_c^{-2}$ (see text). The plot ranges from $n^* = 2$ ($\gamma_c = 0.5$) to $n^* = 10$ ($\gamma_c = 0.1$).

γ_c and R_x, as shown in Fig. 6. The condition for validity of the LHJ method is $R_x \gg \gamma_i^{-2}$ (Ref. [14]), which, noting that for large R_x we have $\gamma_i \approx \gamma_c - 1/(\gamma_c R_x)$, is roughly equivalent to $R_x \gg \gamma_c^{-2}$. The ratio is seen to be exactly 1 in the region of validity of the LHJ theory. Note the effective principle quantum number of the neutral state on A is $n^* = 1/\gamma_c$; thus, the validity criterion can also be written $R_x \gg n^{*2}$. Outside the region of validity for the LHJ theory, at crossings at shorter internuclear distances, the LCAO theory gives larger interactions, and the disagreement increases very rapidly.

In summary, previous claims that LCAO theory is incorrect for ionic-covalent interactions at large internuclear distance seem to be unfounded, and correction of the leading constant for the H$^-$ asymptotic wave function in the LHJ theory brings the two theories into reasonable quantitative agreement for the two cases of MN of Li$^+$ and Na$^+$ with H$^-$ and D$^-$. It has also been shown that the LCAO and LHJ theories have the same behavior for large R_x. The LCAO theory has been developed only for cases involving H$^-$ and D$^-$, treating two electrons to varying degrees of complexity. The surface integral method, LHJ, is, however, easily applied to any given situation if the asymptotic wave function for the negative ion is known. The results shown here suggest that if correct wave functions for the active electron on the negative ion can be obtained, LHJ theory can be used to obtain reasonable estimates for MN processes occurring at a large internuclear distance in practically any system, perhaps even those involving molecules, and thus is of potentially great utility for situations such as astrophysical modeling, where often a large number of rate estimates are needed and completeness can be more important than accuracy. It would be useful also to further develop and investigate the utility of the one-electron LCAO method as outlined in this paper, enabling application to complex atoms beyond H$^-$ and D$^-$.

APPENDIX: ONE-ELECTRON LCAO INTEGRALS FOR $l_c = l_i = 0$

The matrix element $T_{ic}(R)$ can be derived analytically using the asymptotic atomic wave functions, Eqs. (7) and (9), for the radial parts $\mathcal{R}_c$ and $\mathcal{R}_i$ of the asymptotic spatial atomic wave functions φ_c and φ_i, respectively. The simplest possible case is taken, where both φ_c and φ_i are spherically symmetric and $l_c = l_i = 0$. It is instructive to first consider the overlap, which can be shown to be

$$S_{ic}(R) = \langle \varphi_c | \varphi_i \rangle = \frac{N_i}{\gamma_i R} \int_0^R dr \, r \, \mathcal{R}_c(r) e^{-\gamma_i R} \sinh(\gamma_i r) + \int_R^\infty dr \, r \, \mathcal{R}_c(r) e^{-\gamma_i r} \sinh(\gamma_i R), \tag{A1}$$

where $r = r_A$ (see Fig. 1). Performing these integrals with the aid of *Mathematica*, we obtain in its most compact form

$$
\begin{aligned}
S_{ic}(R) = -\frac{N_c N_i}{2\gamma_i R} [(\gamma_c - \gamma_i)(\gamma_c + \gamma_i)]^{-\frac{\gamma_c+1}{\gamma_c}} e^{-\gamma_i R} \Bigg\{ &(\gamma_c - \gamma_i)^{\frac{1}{\gamma_c}+1} \left[e^{2\gamma_i R} \Gamma\left(1 + \frac{1}{\gamma_c}, (\gamma_c + \gamma_i)R\right) - \Gamma\left(1 + \frac{1}{\gamma_c}\right) \right] \\
&+ (\gamma_c + \gamma_i)^{\frac{1}{\gamma_c}+1} \left[\Gamma\left(1 + \frac{1}{\gamma_c}\right) - \Gamma\left(1 + \frac{1}{\gamma_c}, (\gamma_c - \gamma_i)R\right) \right] \Bigg\},
\end{aligned}
\tag{A2}
$$

where $\Gamma(z)$ is the Euler gamma function and $\Gamma(a, z)$ is the incomplete gamma function (see, e.g., Ref. [34]). Similarly, $T_{ic}(R)$ can be evaluated simply by adding the operator $T = 2(\frac{1}{r_A} - \frac{1}{R})$ into Eq. (A1). Evaluating these integrals gives, in its most compact

form,

$$T_{ic}(R) = -\frac{N_c N_i}{\gamma_c \gamma_i R^2}[(\gamma_c - \gamma_i)(\gamma_c + \gamma_i)]^{-\frac{\gamma_c+1}{\gamma_c}} e^{-\gamma_i R} \Bigg(2\gamma_c \gamma_i e^{R(\gamma_i - \gamma_c)}[R(\gamma_c - \gamma_i)(\gamma_c + \gamma_i)]^{\frac{1}{\gamma_c}}$$

$$-\left\{ (\gamma_c - \gamma_i)^{\frac{1}{\gamma_c}+1}[\gamma_c R(\gamma_c + \gamma_i) - 1]\left[\Gamma\left(\frac{1}{\gamma_c}\right) - e^{2\gamma_i R}\Gamma\left(\frac{1}{\gamma_c}, (\gamma_c + \gamma_i)R\right) \right] \right\}$$

$$+ (\gamma_c + \gamma_i)^{\frac{1}{\gamma_c}+1}[\gamma_c R(\gamma_c - \gamma_i) - 1]\left[\Gamma\left(\frac{1}{\gamma_c}\right) - \Gamma\left(\frac{1}{\gamma_c}, (\gamma_c - \gamma_i)R\right) \right] \Bigg). \tag{A3}$$

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