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Standing-wave rearrangement scattering formalism for multiarrangement quantum-defect theory

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Nonrelativistic time-independent quantum scattering theory for collisions with rearrangements is investigated for standing-wave solutions, principal-value Green's operators, and related reaction operators. The solutions corresponding to different arrangement configurations are obtained directly from the properties of the noninvertible Green's operators, without having recourse to arguments based on unitarity. By casting multichannel quantum defect theory (MQDT) as a particular case of standing-wave scattering, a formalism for multiarrangement MQDT is presented and methods for calculating the wave functions and reaction matrices are proposed. The formalism is illustrated in connection with current work on ionization and dissociation in H_2. [S1050-2947(99)07003-1]

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I. INTRODUCTION

Standard multichannel quantum-defect theory (MQDT) is concerned with the dynamics of an outer electron moving in the Coulomb field of an ionic (usually atomic or molecular) core. The short-range interactions within the ion core induce phase shifts, known as quantum defects, that modify the wave function of the electron in the long-range (Coulomb) field. MQDT is particularly well suited to the description and interpretation of Rydberg spectra and autoionizing series.

Its original formulation [1] starts from a close-coupling approach of electron ion scattering and extrapolates it for negative energies of the electron to the discrete spectrum. This formulation rests on an extensive analysis of the properties of Coulomb functions. Later, in a series of papers, Fano and co-workers connected MQDT with the more general approach to nonrelativistic quantum collisions based on the Lippmann-Schwinger equation for standing waves [2–4]. MQDT was still considered as an effective one-electron theory but was generalized to include many other types of long-range potentials (i.e., other than Coulomb). Still later, it was shown that standard quantum defect theory could be seen as a straightforward application of Wigner's *R*-matrix theory of resonance reactions to the case of an attractive Coulomb potential [5]. More recently, Rosenberg used an effective-potential formalism for electron-ion scattering to establish an extension of Levinson's theorem connecting the quantum defect and the phase shift relative to the Coulomb phase [6].

There has also been repeated interest in reactive collision types of processes, but these processes were not fully treated within MQDT: electron-ion interaction called for an MQDT treatment while other interactions where taken into account by combining the MQDT treatment with first- or second-order perturbation theory (e.g., works on dissociative recombinations [7] or on Rydberg-valence interactions [8]) or with *R*-matrix calculations [9]. On the other hand, an analysis of predissociation in diatomic molecules and inelastic atom scattering was formulated within a framework adapted from MQDT, where the outer electron is replaced by the relative particle picturing the separating atoms and close coupling refers to interatomic potentials [10,11]; but then the dynamics of the electrons was of no concern. Only recently were works published in which ionization and dissociation are treated within a unified MQDT formulation [12,13].

Apart from this, the theory of nonrelativistic rearrangement collisions has been known for quite a long time since the early papers of Lippmann [14] and Ekstein [15] and subsequent work on the three-body problem by Faddeev and Lovelace [16]. All this work relied on a formalism that uses ingoing or outgoing asymptotic travelling waves, the corresponding invertible Green's operators $\mathbb{G}^{\pm}$, and related transition $\mathbb{T}$ operators. A rearrangement collision formalism for standing waves in which standing-wave solutions are given as functions of the nonperturbed wave functions, principal value Green's operators $\mathbb{G}^{P}$, and reaction operators $\mathbb{K}$ was not, to our knowledge, fully developed (but see [17], where the particular case of identical particle scattering for standing waves was considered). This was the case in part because standing waves do not have a direct physical interpretation and also because the real operators $\mathbb{G}^{P}$ are not invertible, a fact that complicates the task of directly defining reaction operators. Nevertheless, $\mathbb{K}$ operators have been repeatedly studied because of their usefulness as a source of unitary approximations of the **S** matrix [18–20]. In this context there are many equivalent manners of defining real $\mathbb{K}$ operators, since a unitary scattering matrix is obtained via a Cayley transform.

In multichannel quantum defect theory, closed (i.e., negative energy) channels are explicitly included in the collision matrices, making the use of standing waves necessary. In their cited works on ionization and dissociation of H_2 Jungen and collaborators do not employ some rearrangement MQDT formalism. Instead, they assume certain relations between the asymptotic wave functions in each arrangement and carry out their calculations by connecting wave functions at some boundary. In this work, we present a standing-wave formalism for nonrelativistic collisions with rearrangements. Multiarrangement MQDT will appear as a particularization that can be derived from the more general formalism. To this end, we will study in Sec. II the connection between standard MQDT and the standing-wave Lippmann-Schwinger equation for single-arrangement collisions, recasting the results of Fano and co-workers in a form more suitable for multiarrangement generalizations. In Sec. III, we shall introduce our rearrangement reaction operators by explicitly considering the form of the wave functions: the solutions are thus obtained without the need for a paradigm based on unitarity, as had been previously proposed by Kouri and Levin [17]. The $\mathbb{K}$ operators will be given as functions of real Green's operators and interaction potentials. In Sec. IV, by including closed channels in the standing-wave rearrangement scattering formalism of Sec. III, we shall introduce a multiarrangement multichannel quantum-defect theory; it will be illustrated by considering ionization and dissociation in H_2 and showing the connection between this work and the assumed relations of Refs. [12] and [13]. Methods of direct calculations of the wave functions and related parameters will be suggested.

II. FROM STANDING-WAVE COLLISIONS TO MQDT

A. Lippmann-Schwinger equations

We shall consider in this section the Lippmann-Schwinger equation for the single-arrangement case (i.e., effective direct collisions). Let H be the total Hamiltonian of the system given by $H=H_0+V$. The time-independent solutions of H_0,

$$(E-H_0)|\phi_i(E)\rangle=0, \tag{2.1}$$

are supposed to be known while the solutions of H at the same energy, labeled $|\psi_i(E)\rangle$ are looked for. The outgoing and ingoing solutions $|\psi_i^+(E)\rangle$ and $|\psi_i^-(E)\rangle$ are given by the Lippmann-Schwinger (LS) equations [21,22]

$$\begin{aligned}|\psi_i^{\pm}(E)\rangle&=|\phi_i(E)\rangle+\mathbb{G}_0^{\pm}(E)V|\psi_i^{\pm}(E)\rangle\\&=|\phi_i(E)\rangle+\mathbb{G}^{\pm}(E)V|\phi_i(E)\rangle,\end{aligned} \tag{2.2}$$

where the Green's operator associated with the nonperturbed Hamiltonian is given by

$$\mathbb{G}_0^{\pm}(E)=(E-H_0\pm i\lambda)^{-1} \tag{2.3}$$

and the propagator of the full interaction by

$$\mathbb{G}^{\pm}(E)=(E-H\pm i\lambda)^{-1}, \tag{2.4}$$

The limit $\lambda\rightarrow 0$ will be implicitly understood throughout. These invertible operators fulfill the resolvent equations

$$\mathbb{G}^{\pm}=\mathbb{G}_0^{+}+\mathbb{G}_0^{\pm}V\mathbb{G}^{\pm}=\mathbb{G}_0^{+}+\mathbb{G}^{\pm}V\mathbb{G}_0^{\pm}. \tag{2.5}$$

It is then common to introduce a transition operator $\mathbb{T}$ given by

$$\mathbb{T}(E)=V+V\mathbb{G}_0^{+}(E)T(E)=V+V\mathbb{G}^{+}(E)V \tag{2.6}$$

and insert it in the LS equations. For example, for the outgoing wave this yields

$$|\psi_i^{+}(E)\rangle=|\phi_i(E)\rangle+\mathbb{G}_0^{+}(E)\mathbb{T}(E)|\phi_i(E)\rangle. \tag{2.7}$$

We have not yet stated the nature of the "free" state $|\phi_i(E)\rangle$ that is linked to the boundary conditions incorporated in the Green's operator. Henceforth we shall require $|\phi_i(E)\rangle$ to be a standing wave, unless otherwise stated. If we further demand the solution to be also a standing wave, we have the Lippmann-Schwinger equation for standing waves:

$$|\psi_i^{P}(E)\rangle=|\phi_i(E)\rangle+\mathbb{G}_0^{P}(E)V|\psi_i^{P}(E)\rangle, \tag{2.8}$$

where P stands for principal value integration, and the principal-value Green's operator $\mathbb{G}_0^P$ is related to $\mathbb{G}_0^{\pm}$ by

$$\mathbb{G}_0^{P}(E)=\mathbb{G}_0^{\pm}(E)\pm i\pi\delta(E-H_0)\equiv P(E-H_0)^{-1}. \tag{2.9}$$

As is known, $\mathbb{G}_0^P$ does not have an inverse and does not obey the resolvent equation. Thus the analog of the right-hand equalities in Eqs. (2.2) and (2.6) cannot be written for standing waves. Nevertheless, by defining

$$\mathbb{K}=V+V\mathbb{G}_0^{P}V+V\mathbb{G}_0^{P}V\mathbb{G}_0^{P}V+\cdots=(I-V\mathbb{G}_0^{P})^{-1}V, \tag{2.10}$$

which can be simply put as

$$\mathbb{K}=V+V\mathbb{G}_0^{P}\mathbb{K}, \tag{2.11}$$

direct iteration of the LS equation Eq. (2.8) yields

$$|\psi_i^{P}(E)\rangle=|\phi_i(E)\rangle+\mathbb{G}_0^{P}(E)\mathbb{K}(E)|\phi_i(E)\rangle. \tag{2.12}$$

The i index specifies the channel: an initial nonperturbed wave in channel i, $|\phi_i(E)\rangle$, gives rise to "postcollision" waves $\mathbb{G}_0^{P}(E)\mathbb{K}(E)|\phi_i(E)\rangle$, the total solution being then denoted $|\psi_i^{P}(E)\rangle$. The P superscript for principal value and the energy specification will be dropped from now on from state vectors and operators and will implicitly be understood throughout unless otherwise stated.

B. Derivation of MQDT

Multichannel quantum defect theory can be characterized by three main points.

(1) System partitioning. The system (atom or molecule) in state i is partitioned in two parts: the core, whose state is denoted $|i^+(E_i^+)\rangle$, and the effective outer electron. In the absence of the perturbing potential V, the radial states of the outer electron are given by $|f_i(\epsilon_i)\rangle$ and the orbital and spin part by $|\omega_i\rangle$, that we include with the core state in the compound notation $|i\rangle$ to account for orbital and spin couplings. Thus the solutions of H_0 are given by

$$|\phi_i(E)\rangle=|f_i(\epsilon_i)\rangle|\omega_i\rangle|i^+(E_i^+)\rangle\equiv|f_i\rangle|i\rangle, \tag{2.13}$$

where the radial degree of freedom of the outer electron (r coordinate), has been separated, and the total energy has been partitioned into the core energy E_i^+ (which is assumed to lie within the bound spectrum) and the outer electron energy ϵ_i:

$$E=E_i^{+}+\epsilon_i. \tag{2.14}$$

The core state is supposed to be an antisymmetrized product vanishing outside a core radius r_0. We will require $|\phi_i\rangle$ to be zero at $r=0$, so $|\phi_i\rangle$ is then given by a standing wave regular at the origin.

(2) Radial functions and Green's operators. ϵ_i can be positive (continuum electron corresponding to an open (O) channel, $\epsilon_i=\frac{1}{2}k_i^2$) or negative ("bound" electron, for a

closed (C) channel, $\epsilon_i = -\frac{1}{2}\kappa_i^2$); atomic units are being used. In the MQDT framework, closed channels explicitly appear in the reaction matrices (whereas in standard scattering theory the collision matrices include only the physically open channels, the discrete levels appearing as poles): open and closed channels are treated on the same footing. This is realized by defining smooth radial Green's functions, that do not present any singularities for bound states but diverge for $\epsilon_i < 0$ when $r \rightarrow \infty$. The boundary conditions at infinity are thus not included in these radial Green's functions. Greene, Fano, and Strinati have shown [3] that such radial Green's functions are defined by

$$\mathcal{G}_{\epsilon_i}(r,r') = \frac{2}{W_{\epsilon_i}[f,g]} g_i(r_>) f_i(r_<), \tag{2.15}$$

where $r_>$ ($r_<$) indicates the larger (smaller) of (r,r'). When the long-range field is simply Coulomb, $f_i(\epsilon_i,r)$ is a Coulomb function regular at $r=0$ and $g_i(\epsilon_i,r)$ is irregular and forms a radial basis with f. Both f and g are normalized to the energy. A standard choice is to set f and g as oscillating at large r with equal amplitude and 90 degrees out of phase (for $\epsilon > 0$) and with their Wronskian $W_{\epsilon_i}[f,g] = 2/\pi$. A straightforward consequence is that the Green's operators used in MQDT, which will be noted G_0 are different from the Green's operators $\mathbb{G}_0$ of Eqs. (2.8) to (2.12). It can be shown that

$$G_0(E) = \mathbb{G}_0(E) - \pi \sum_i \Theta(-\epsilon_i) |\phi_i(E)\rangle\langle\phi_i(E)| (\tan\beta_i)^{-1}, \tag{2.16}$$

where β_i is the accumulated phase function measuring the number of half-wavelengths between $r=0$ and $r=\infty$ [for a Coulomb field of charge Z, we have $\beta_i = \pi(\nu_i - l_i)$ and $\tan\beta_i = \tan\pi\nu_i$, where $\nu_i = -Z/\kappa_i$ is the effective quantum number of the outer electron). The phase function can be expressed simply in terms of the Jost functions of the long-range potential extrapolated to negative energies (see Ref. [23]). Θ is the step function: the last term thus appears only for closed channels and cancels the possible singularities of $\mathbb{G}_0$.

(3) Short-range interactions. The interaction V is short range, limited to the region inside the ion core radius r_0:

$$V|r\rangle = \Theta(r - r_0) V |r\rangle. \tag{2.17}$$

This gives rise to the following physical picture: outside the core, the outer electron only sees a long-range, centrally symmetric local field, included within H_0. Inside the core the electron has a complicated motion due to the noncentral and nonlocal interactions, but the translation of these short-range effects outside the core amounts to inducing radial phase shifts, the K operator elements, that are expected to have smooth variations with the energy of the outer electron, which is subjected far outside the core to a comparatively weak long-range force.

On the mathematical standpoint, we take the LS equation for standing waves, Eq. (2.12), choose a set of nonperturbed channels (in practice a truncated set) given by the expression (2.13) with the Green's operator G_0 given by Eq. (2.16). Because each core state has a definite energy, G_0 can be reduced, by using Eq. (2.14) and the closed-form expression of the radial Green's function (2.15) to

$$\langle r|G_0|r'\rangle = \sum_{j\in\{O+C\}} |j(E_j^+)\rangle\langle j(E_j^+)| \mathcal{G}_{\epsilon_j}(r,r'), \tag{2.18}$$

where the sum runs on open and closed channels. With the help of expressions (2.15) and (2.17) the LS equation outside the core ($r > r_0$) takes the form

$$\langle r|\psi_i\rangle \equiv \psi_i(r) = f_i(r)|i\rangle - \sum_j g_j(r)|j\rangle K_{ji}(E). \tag{2.19}$$

The K_{ji} are the on-the-energy shell elements of the K operator:

$$K_{ji}(E) = \langle f_j(\epsilon_j)| \langle j(E_j^+)|K|i(E_i^+)\rangle |f_i(\epsilon_i)\rangle, \tag{2.20}$$

where K is defined by

$$K = -\pi V + V G_0 K. \tag{2.21}$$

By projecting this last equation over a finite basis, the K_{ij} elements can be found by solving the corresponding integral equations on a coarse energy mesh (e.g., [24]) or by adapting the Schwinger variational method to equations with smooth radial Green's functions [25,26]. In practice, the K matrix, or related quantum defects $\mu_{ij} \equiv \pi^{-1} \arctan K_{ij}$ can also be determined from R-matrix calculations [27] or by fitting to experimental data or to *ab initio* computations [28].

Equation (2.19) is the generic building block of MQDT wave functions. The total standing-wave function, denoted ψ^ρ, is obtained by superposing the functions $\psi_i(r)$, each with its channel coefficient B_i^ρ:

$$\psi^\rho(r) = \sum_i |i\rangle \left[B_i^\rho f_i(r) - \sum_j B_j^\rho K_{ij} g_i(r) \right]. \tag{2.22}$$

The ρ superscript labels the eigenstates of the open-channel interaction. The B_i^ρ coefficients are found by examining asymptotic boundary conditions. For example, ionization corresponds to incoming-wave boundary conditions ([29] for the atomic case, [30] for the molecular case). If we assume that the final state corresponds to a measurement of the electron's channel i (basically its angular momentum and its coupling with the ion's angular momentum) then the final state is simply given by the solution of the LS equation,

$$|\psi_i^-\rangle = |\phi_i\rangle + \mathbb{G}_0^- \mathbb{T}^\dagger |\phi_i\rangle, \tag{2.23}$$

which can be set by Eq. (2.9) as a superposition of standing waves $|\psi_\rho\rangle$,

$$|\psi_i^-\rangle = \sum_\rho \mathbf{U}_{\rho i} e^{-i\pi\tau_\rho} \cos\pi\tau_\rho |\psi_\rho\rangle, \tag{2.24}$$

Here $\mathbf{U}$ diagonalizes $\mathbb{T}$ and $\mathbb{K}$, $e^{2i\pi\tau_\rho}$ being the eigen-phase-shifts of the (open-channel) $\mathbf{S}$ matrix, and the eigenchannel functions $|\psi_\rho\rangle$ are given by

$$|\psi_\rho\rangle=\sum_{i\in O}\mathbf{U}^\dagger_{i\rho}[|\phi_i\rangle+\mathbb{G}_0\mathbb{K}|\phi_i\rangle]. \tag{2.25}$$

Then by imposing $\psi^\rho(r)\rightarrow\langle r|\psi_\rho\rangle$ in the limit $r\rightarrow\infty$, we get by matching Eqs. (2.22) and (2.25) the following relations for closed and open channels:

$$i\in C,\quad B_i^\rho+\sum_{j\in\{O+C\}}B_j^\rho K_{ij}(\tan\beta_i)^{-}=0,$$

$$i\in O,\quad \left\{\begin{array}{l} B_i^\rho=\mathbf{U}^\dagger_{i\rho}, \\ \displaystyle\sum_{j\in\{O+C\}}B_j^\rho K_{ij}=-\pi\sum_{j\in O}\mathbf{U}^\dagger_{j\rho}\mathbb{K}_{ij}=\mathbf{U}^\dagger_{i\rho}\tan\pi\tau_\rho, \end{array}\right. \tag{2.26}$$

which is the usual MQDT system that can be solved in a standard manner [1], so as to get the values of the phase function β_i corresponding to the physical bound-state energies, as well as the eigen-phase-shifts τ_ρ and the B_i^ρ coefficients.

We have not yet included explicitly the antisymmetry requirement. Let us consider N identical particles, i.e., the outer electron of coordinate $\mathbf{r}$ colliding on an ion containing $N-1$ electrons. Then the formulas given above in this subsection hold when K is replaced by

$$K_{\mathrm{eff}}=-\pi(I-(N-1)P_{N,N-1})V+VG_0K_{\mathrm{eff}}, \tag{2.27}$$

where $P_{N,N-1}$ is a permutation operator exchanging the Nth with the $(N-1)$th electron. The derivation of Eq. (2.27) follows closely from the standard approach employed in scattering theory: N different arrangements have to be considered, each one corresponding to a different outer electron. Since standing waves and related operators replace the more usual traveling waves, the demonstration follows from our results of Sec. III and is briefly outlined in Appendix A. We will not explicitly deal with antisymmetrization in the rest of the paper since the form of the equations are not modified. But obviously, antisymmetrization has to be taken into account when calculating the reaction matrix.

III. REARRANGEMENT COLLISION FORMALISM FOR STANDING WAVES

When we consider rearrangement collisions, the total Hamiltonian of the system is partitioned in several ways, each of them corresponding to a given arrangement of the system:

$$H=H_\alpha+V^\alpha=H_\beta+V^\beta=\cdots. \tag{3.1}$$

$|\phi_{\alpha_i}(E)\rangle$ is an eigenstate of H_α; $|\psi_{\alpha_i}(E)\rangle$ is the solution of H corresponding to an ''initial'' nonperturbed i state (channel) in arrangement α. The ingoing and outgoing wave LS equations are well known,

$$|\psi^\pm_{\alpha_i}(E)\rangle=|\phi_{\alpha_i}(E)\rangle+\mathbb{G}^\pm_\alpha(E)V^\alpha|\psi^\pm_{\alpha_i}(E)\rangle, \tag{3.2}$$

where the Green's operators $\mathbb{G}^\pm_\alpha=(E-H_\alpha\pm i\lambda)^{-1}$ obey the resolvent equations (2.5) that can be set here as

$$\mathbb{G}^{\pm-1}(E)=\mathbb{G}^{\pm-1}_\alpha-V^\alpha=\mathbb{G}^{\pm-1}_\beta-V^\beta=\cdots. \tag{3.3}$$

By introducing a set of $\mathbb{T}$ operators, the LS equations are formally solved. For example, with

$$\mathbb{T}^{\alpha\alpha}=V^\alpha+V^\alpha\mathbb{G}^+_\alpha\mathbb{T}^{\alpha\alpha}=V^\alpha+V^\alpha\mathbb{G}^+V^\alpha \tag{3.4}$$

the outgoing LS equation (3.2) takes the form

$$|\psi^+_{\alpha_i}\rangle=|\phi_{\alpha_i}\rangle+\mathbb{G}^+_\alpha\mathbb{T}^{\alpha\alpha}|\phi_{\alpha_i}\rangle. \tag{3.5}$$

It is straightforward to get cross-arrangement transition operators such that $\mathbb{G}^+_\beta\mathbb{T}^{\beta\alpha}=\mathbb{G}^+_\alpha\mathbb{T}^{\alpha\alpha}$ by simply using Eq. (3.3). The well-known result is

$$\mathbb{T}^{\beta\alpha}=V^\alpha+V^\beta\mathbb{G}^+V^\alpha. \tag{3.6}$$

It is also recognized that $\mathbb{T}^{\beta\alpha}$ and

$$\overline{\mathbb{T}}^{\beta\alpha}=V^\beta+V^\beta\mathbb{G}^+V^\alpha \tag{3.7}$$

have the same on-the-energy shell elements but do not obey the same LS equation, since

$$|\psi^+_{\alpha_i}\rangle=i\lambda\mathbb{G}^+_\beta|\phi_{\alpha_i}\rangle+\mathbb{G}^+_\beta\overline{\mathbb{T}}^{\beta\alpha}|\phi_{\alpha_i}\rangle. \tag{3.8}$$

The standing-wave analog of Eq. (3.2) is

$$|\psi_{\alpha_i}\rangle=|\phi_{\alpha_i}\rangle+\mathbb{G}_\alpha V^\alpha|\psi_{\alpha_i}\rangle. \tag{3.9}$$

Then direct iteration leads to

$$|\psi_{\alpha_i}\rangle=|\phi_{\alpha_i}\rangle+\mathbb{G}_\alpha\mathbb{K}^{\alpha\alpha}|\phi_{\alpha_i}\rangle \tag{3.10}$$

with

$$\mathbb{K}^{\alpha\alpha}=V^\alpha+V^\alpha\mathbb{G}_\alpha\mathbb{K}^{\alpha\alpha}=V^\alpha(I-\mathbb{G}_\alpha V^\alpha)^{-1}=(I-V^\alpha\mathbb{G}_\alpha)^{-1}V^\alpha \tag{3.11}$$

but there is no analog for standing-wave reaction operators to the last equality (the formal solution for the $\mathbb{T}$ operators) of Eq. (3.4). Yet it can easily be established that the principal-value Green's operator of the full interaction, $\mathbb{G}$, is related to the α arrangement Green's operator $\mathbb{G}_\alpha$ by

$$\mathbb{G}=(I-\mathbb{G}_\alpha V^\alpha)^{-1}(\mathbb{G}_\alpha+\mathbb{R}_\alpha)=(\mathbb{G}_\alpha+\overline{\mathbb{R}}_\alpha)(I-V^\alpha\mathbb{G}_\alpha)^{-1}, \tag{3.12}$$

where $\mathbb{R}_\alpha$ and $\overline{\mathbb{R}}_\alpha$ are ''rest'' terms, which are not present in Eq. (3.3), and are found to be given by

$$\mathbb{R}_\alpha=-\pi^2\delta(E-H_\alpha)V^\alpha\delta(E-H)\equiv-\pi^2\delta_\alpha V^\alpha\delta, \tag{3.13}$$

$$\overline{\mathbb{R}}_\alpha=-\pi^2\delta(E-H)V^\alpha\delta(E-H_\alpha)\equiv-\pi^2\delta V^\alpha\delta_\alpha. \tag{3.14}$$

We are now looking for a cross-arrangement reaction operator $\mathbb{K}^{\beta\alpha}$ such that

$$\mathbb{G}_\alpha\mathbb{K}^{\alpha\alpha}=\mathbb{G}_\beta\mathbb{K}^{\beta\alpha}. \tag{3.15}$$

This useful relation allows to write the LS equation (3.10) for an initial nonperturbed wave in arrangement α in terms of the Green's operator in arrangement β and of the cross-arrangement reaction operator $\mathbb{K}^{\beta\alpha}$ whose expression we now derive by taking the right-hand equality of Eq. (3.11) and the relations (3.12) successively, we get

$$\mathbb{G}_\alpha \mathbb{K}^{\alpha\alpha} = \mathbb{G}_\beta (I - V^\beta \mathbb{G}_\beta)^{-1} V^\alpha + \{[(I - \mathbb{G}_\beta V^\beta)^{-1} \mathbb{R}_\beta - \overline{\mathbb{R}}_\alpha (I - V^\alpha \mathbb{G}_\alpha)^{-1}] V^\alpha\}. \tag{3.16}$$

Now from Eqs. (3.3) and (3.12) we deduce

$$\delta_\alpha = (I + \mathbb{G} V^\alpha)^{-1} \delta (I - V^\alpha \mathbb{G}_\alpha) = (I - \mathbb{G}_\alpha V^\alpha) \delta (I + V^\alpha \mathbb{G})^{-1} \tag{3.17}$$

and use this relation to show that the terms between brackets in Eq. (3.16) can be set as

$$-\pi^2 (I - \mathbb{G}_\beta V^\beta)^{-1} \{\delta_\beta (V^\beta - V^\alpha) \delta_\alpha\} \mathbb{K}^{\alpha\alpha}, \tag{3.18}$$

which vanishes because $V^\beta - V^\alpha = H_\alpha - H_\beta$ is projected onto states corresponding to different arrangements but having the same energy. We have then found an operator $\mathbb{K}^{\beta\alpha}$ that can be set, following Eq. (3.16) and iterating once as

$$\mathbb{K}^{\beta\alpha} = (I - V^\beta \mathbb{G}_\beta)^{-1} V^\alpha = V^\alpha + V^\beta \mathbb{G}_\beta \mathbb{K}^{\beta\alpha}. \tag{3.19}$$

Notice that $\mathbb{T}^{\beta\alpha}$ can also be written in a similar form, but $\mathbb{K}^{\beta\alpha}$ cannot be formulated like Eq. (3.6). In fact, from Eqs. (3.19) and (3.12) we see that

$$\mathbb{K}^{\beta\alpha} = V^\alpha + V^\beta \mathbb{G} V^\alpha - V^\beta (I - \mathbb{G}_\beta V^\beta)^{-1} \mathbb{R}_\beta V^\alpha. \tag{3.20}$$

We can also display an operator $\overline{\mathbb{K}}^{\beta\alpha}$ having the same on-shell elements as $\mathbb{K}^{\beta\alpha}$ and related to $\mathbb{K}^{\beta\alpha}$, as in the case of the $\mathbb{T}$ operators by $\overline{\mathbb{K}}^{\beta\alpha} = \mathbb{K}^{\beta\alpha} + V^\beta - V^\alpha$. Then it may be shown that

$$\overline{\mathbb{K}}^{\beta\alpha} = V^\beta (I - \mathbb{G}_\alpha V^\beta)^{-1} = V^\beta + \overline{\mathbb{K}}^{\beta\alpha} \mathbb{G}_\alpha V^\alpha. \tag{3.21}$$

It is interesting to note that the LS equation with $\overline{\mathbb{K}}^{\beta\alpha}$, given since $\mathbb{G}_\beta (V^\beta - V^\alpha) |\phi_{\alpha_i}\rangle = |\phi_{\alpha_i}\rangle$ by

$$|\psi_{\alpha_i}\rangle = \mathbb{G}_\beta \overline{\mathbb{K}}^{\beta\alpha} |\phi_{\alpha_i}\rangle \tag{3.22}$$

has only a homogeneous term. The infinitesimal term appearing in the LS equations for traveling waves [see Eq. (3.8)] that was in question ever since the early works on rearrangement collisions theory [31] does not appear for standing waves. There does not seem to be any inconsistency in this latter case, precisely because the principal-value Green's operators are not invertible.

Half-on-shell integral equations are readily derived from the expressions (3.19) or (3.21), thus avoiding recourse to the damping equation and related unitarity arguments, as had been done previously in the case of the scattering of two identical particles [17,32] (identical particle scattering is considered in Appendix A). As usual in rearrangement scattering, $\mathbb{K}$ is the matrix of the whole set of same-arrangement and cross-arrangement operators. It can be checked that $\mathbb{K}^{\alpha\alpha}$ is Hermitian, and that relations of the type $\mathbb{K}^{\alpha\beta\dagger} = \overline{\mathbb{K}}^{\beta\alpha}$ lead to a symmetric on-shell $\mathbb{K}$ matrix for real potentials. Moreover, these results can be extended in a straightforward manner when more than two arrangements are considered.

IV. MULTIARRANGEMENT MQDT

A. General remarks

We have derived in the last section a formalism for collisions with rearrangement for the standing-wave type of wave functions. We have seen in Sec. II B how multichannel quantum defect theory follows from the general formulation of standing-wave scattering. We then expect multiarrangement MQDT to follow in a straightforward manner from the results of Sec. III. This is done so by setting the multiarrangement MQDT Green's operator in arrangement α as

$$G_\alpha = \mathbb{G}_\alpha - P_\alpha, \tag{4.1}$$

where

$$P_\alpha(E) = \pi \sum_i \Theta(-\epsilon_i)(\tan \beta_{\alpha_i})^{-1} |\phi_{\alpha_i}(E)\rangle\langle\phi_{\alpha_i}(E)| \tag{4.2}$$

''projects'' on the closed channels in arrangement α and acts in a similar way to the $\delta(E - H_\alpha)$ type of operators. It is not to be confused with the principal value symbol, although addition of this term to $\mathbb{G}_\alpha$ cancels the closed-channel singularities and thus acts similarly to the principal value symbol in the open-channel Green's operator. Here β_{α_i} is the accumulated phase function, introduced in Eq. (2.16) above, for the arrangement α. Note that P_α vanishes in the absence of closed channels.

The next step is to replace, in Eq. (3.11), the operators $\mathbb{G}_\alpha$, $\mathbb{R}_\alpha$, and $\overline{\mathbb{R}}_\alpha$ by G_α, R_α, and $\overline{R}_\alpha$, given, respectively, by Eq. (4.1) and

$$R_\alpha = P_\alpha (I + V^\alpha \mathbb{G}) - \pi^2 \delta_\alpha V^\alpha \delta, \tag{4.3}$$

$$\overline{R}_\alpha = (I + \mathbb{G} V^\alpha) P_\alpha - \pi^2 \delta V^\alpha \delta_\alpha. \tag{4.4}$$

Then by defining

$$K^{\alpha\alpha} = -\pi^{-1} V^\alpha + V^\alpha G_\alpha K^{\alpha\alpha} = -\pi (I - V^\alpha G_\alpha)^{-1} V^\alpha \tag{4.5}$$

we are led to the analog of Eq. (3.16):

$$G_\alpha K^{\alpha\alpha} = -\pi G_\beta (I - V^\beta G_\beta)^{-1} V^\alpha - \pi \{[(I - G_\beta V^\beta)^{-1} R_\beta - \overline{R}_\alpha (I - V^\alpha G_\alpha)^{-1}] V^\alpha\}. \tag{4.6}$$

Now by using Eq. (3.17) and further demonstrating that

$$G_\beta (V^\beta - V^\alpha) P_\alpha = \mathbb{G}_\beta (V^\beta - V^\alpha) P_\alpha = P_\alpha \tag{4.7}$$

the braces in Eq. (4.6) are seen to vanish, so that the results of Sec. III hold (with the conventional $-\pi$ factor added in the definition of the reaction operators).

We then conclude that the reaction matrices are obtained by solving the operator equation

$$K^{\beta\alpha} = -\pi V^\alpha + V^\beta \mathbb{G}_\beta K^{\beta\alpha} - V^\beta P_\beta K^{\beta\alpha}, \tag{4.8}$$

where α and β label different or identical arrangements. The solution of the total Hamiltonian corresponding to a nonperturbed wave in arrangement α and channel $i, |\phi_\alpha,\rangle$, is given by one of the equivalent expressions

$$|\psi_{\alpha_i}(E)\rangle = |\phi_{\alpha_i}(E)\rangle - \pi^{-1} G_\alpha(E) K^{\alpha\alpha}(E) |\phi_{\alpha_i}(E)\rangle, \tag{4.9}$$

$$|\psi_{\alpha_i}(E)\rangle = -\pi^{-1} G_\beta(E) \overline{K}^{\beta\alpha}(E) |\phi_{\alpha_i}(E)\rangle, \tag{4.10}$$

and the solution of H corresponding to a nonperturbed wave in arrangement β and channel j is given in terms of $|\phi_{\beta_j}\rangle$ by

$$|\psi_{\beta_j}(E)\rangle = |\phi_{\beta_j}(E)\rangle - \pi^{-1} G_\beta(E) K^{\beta\beta}(E) |\phi_{\beta_j}(E)\rangle \tag{4.11}$$

or

$$|\psi_{\beta_j}(E)\rangle = -\pi^{-1} G_\alpha(E) \overline{K}^{\alpha\beta}(E) |\phi_{\beta_j}(E)\rangle. \tag{4.12}$$

For simplicity we consider here only two arrangements. The total wave function is then the superposition

$$|\psi^\rho\rangle = \sum_i B_i^\rho |\psi_{\alpha_i}\rangle + \sum_j B_j^\rho |\psi_{\beta_j}\rangle, \tag{4.13}$$

which can be seen as a consequence of the orthogonality of the Hilbert spaces spanned by the states that develop from different initial channels.

The reaction matrices can be calculated by coupled integral equations from their definitions in terms of the interaction potentials and the principal value Green's operators. The coefficients are determined by matching $|\psi^\rho\rangle$ to asymptotic open-channel functions. As in Sec. II above, the ρ superscript has been introduced to anticipate the manifold of standing waves corresponding to a given physical process.

For definiteness, this will be illustrated below on a specific example. Since in most problems approximate Hamiltonians are used, we don't expect the equality between Eqs. (4.9) and (4.10) to hold exactly. Rather Eqs. (4.9) and (4.10) will alternatively be used in different domains where the approximations introduced in the Hamiltonians have a sense.

B. Ionization and dissociation in H_2

H_2 has always been the prototype of the application of MQDT to molecular problems. Although dissociation related effects were studied by combining MQDT with a perturbative or R-matrix approach [8,9], only recently was a work published in which a unified quantum defect theory treatment is carried out [12]. This treatment was then used as a base for the study of wave packets [13]. Notwithstanding, Jungen and co-workers do not explicitly use some equivalent of multi-arrangement MQDT. They determine an effective total reaction matrix by assuming the form of the asymptotic wave functions [see their Eq. (1) in both articles] while considering two types of wave functions, inner (for small internuclear distance R) and outer (large R) dissociative functions, the parameters being found by matching these functions at some boundary. Our aim in the following is not to conduct practical calculations of a definite process involving both ionization and dissociation—the problem will be tackled elsewhere [33]—but rather to give an illustration of the standing-wave formalism, i.e., how a multiarrangement quantum defect theory may, in principle, be used to treat processes involving different arrangements, that are here the two possible fragmentation ways of H_2.

As in Ref. [12], we will suppose that the molecular energy is below the threshold for dissociative ionization, and that dissociation is correctly described by the sole covalent configuration $\mathrm{H}(1s)+\mathrm{H}(nl)$. Then the particles may gather in two different arrangements: I for ionization, describing $e^- - \mathrm{H}_2^+$ asymptotic states (r radial coordinate) as well as scattering of negative energy electrons giving rise to the bound states of H_2; and D for dissociation, that is, $\mathrm{H}(1s)$-$\mathrm{H}(nl)$ scattering (R coordinate). The Hamiltonian is consequently partitioned as $H = H_I + V^I = H_D + V^D$.

The Hamiltonians and the coupled and uncoupled wave functions in the I arrangement have been repeatedly used [34,28,35] and will not be given here. Since $|\phi_{I_i}\rangle \equiv |f_i\rangle |i\rangle$ only include bound states of the ion, we shall require the vibrational functions to be bounded (i.e., $\langle R|\phi_{I_i}\rangle = 0$ for large R).

For the D arrangement, we will take the Born-Oppenheimer (BO) approximated Hamiltonian. H_D then contains the electronic and rotational Hamiltonians, as well as the kinetic term of the vibrational Hamiltonian, while V^D includes the internuclear interaction R^{-1}, the electronic energy and the constant term $-V^D(R \to \infty) = \frac{1}{2}(1+n^{-2})$. The eigenstates of H_D are set as

$$\langle R|\phi_{D_d}\rangle = \mathcal{F}_d(R) |\phi_d^{el}\rangle |\phi_d^{\mathrm{rot}}\rangle \equiv \mathcal{F}_d(R) |d\rangle, \tag{4.14}$$

where $\mathcal{F}_d(R)$ is a (standing) free function regular at the origin (sine type) and $\mathcal{G}_d(R)$ is the irregular companion.

As stated, the reaction matrices may, in principle, be obtained from coupled integral equations. There are different manners of setting up the numerical problem, depending on which technique is used (these are described, for example, in the review papers [36,37] and references therein). Employing a formulation with half-on-shell integral equations drastically reduces the dimension of the linear system to be solved, the disadvantage is then that a new system has to be set up for different energies. Briefly, to calculate the on-shell elements $K^{\beta\alpha}_{\beta_i\alpha_j}(E,E) = \langle \phi_{\beta_i}(E) | K^{\beta\alpha} | \phi_{\alpha_j}(E)\rangle$ where the greek letters α and β stand for I or D and the lowercase latin letters i and j label the channels, Eq. (4.8) is taken half-on-shell between $\langle \phi_{\beta_i}(E_{n_i})|$ and $|\phi_{\alpha_j}(E)\rangle$. The Green's operator $\mathbb{G}_\beta$ is replaced by its eigenfunction expansion over a truncated set of channels; thus half-on-shell reaction matrix elements appear. The $P_\beta(E)$ operator, as given by Eq. (4.2), gives rise to on-shell matrix elements. The following equation between matrix elements is obtained:

$$\begin{aligned} K^{\beta\alpha}_{\beta_i\alpha_j}(E_{n_i},E) = {} & V^{\alpha}_{\beta_i\alpha_j}(E_{n_i},E) \\ & + \sum_k \int_{n_k} \frac{V^{\beta}_{\beta_i\beta_k}(E_{n_i},E_{n_k})}{\epsilon_k - \epsilon_{n_k}} K^{\beta\alpha}_{\beta_k\alpha_j}(E_{n_k},E) \\ & - \sum_k \Theta(-\epsilon_k)[\tan \beta_{\beta_k}(E)]^{-1} \\ & \times V^{\beta}_{\beta_i\beta_k}(E_{n_i},E) K^{\beta\alpha}_{\beta_k\alpha_j}(E,E). \end{aligned} \tag{4.15}$$

A quadrature, symbolized by $\int_{n_k}$, has been imposed on this equation: the principal part integration over positive energies and the formal sum running over all the discrete negative energies for each channel k in the arrangement β are replaced by the sum over the quadrature points E_{n_k} [or equivalently ϵ_{n_k} by a suitable generalization of Eq. (2.14)]. E_{n_i} is thus one of the quadrature points, corresponding to a given energy in channel i. By matching the energy E to one of the quadrature points, Eq. (4.15) leads to the following matrix equation:

$$\overrightarrow{K_j^{\beta\alpha}}(E)=\overrightarrow{V_j^{\alpha}}(E)+\underline{V_1}\overrightarrow{K_j^{\beta\alpha}}(E)+\underline{V_2}\overrightarrow{K_j^{\beta\alpha}}(E), \qquad (4.16)$$

where $\underline{V_1}$ ($\underline{V_2}$) is the matrix corresponding to the second (third) term of the right-hand side of Eq. (4.15). As denoted by the arrow, $\overrightarrow{K_j^{\beta\alpha}}$ is a vector containing the jth column of the half-on-shell reaction matrix $K^{\beta\alpha}_{\beta_i\alpha_j}$; if q_i is the total number of quadrature points for channel i and the total number of channels is labeled by N, then $\overrightarrow{K_j^{\beta\alpha}}$ contains $\Sigma_{k=1}^{N}q_k$ elements. Equation (4.16) may be set as

$$[\underline{I}-\underline{V}]\overrightarrow{K_j^{\beta\alpha}}(E)=\overrightarrow{V_j^{\alpha}}(E). \qquad (4.17)$$

To solve the system, the matrix $\underline{V}$ is first calculated at the selected energy E (although only $\underline{V_2}$ and a small submatrix of $\underline{V_1}$ explicitly depend on E). The inhomogeneous term $\overrightarrow{V_j^{\alpha}}(E)$ is then determined, and the system is solved for the jth column of $K^{\beta\alpha}_{\beta_i\alpha_j}$ by an appropriate method. For example, the linear algebraic method developed by Collins and Schneider [38,39] combines an iteration process with a variational scheme and is well suited to solve a large system of linear equations; moreover, it has successfully been applied, within a different theoretical framework, to electron scattering from H_2^+. The other columns of $K^{\beta\alpha}_{\beta_i\alpha_j}$ are solved by calculating the corresponding inhomogeneous vector and by using the same potential matrix $\underline{V}$. In a final step, the on-shell elements of the reaction matrix are recovered. Note that in all cases the $\underline{V}$ matrix only contains same-arrangement potential elements, and thus $\underline{V}$ enters in the computations of both same-arrangement and cross-arrangement reaction matrices: the cross-arrangement interaction is only explicitly calculated to the first order (this is a direct consequence of the propagator property of the Green's operators).

Details of the calculations and different methods of approximation will be discussed in a future paper. Here, three remarks are in order. First, when the outer electron is within the reaction zone, the Born-Oppenheimer approximation holds also in the I arrangement, and the free channel functions $|\phi_{I_i}\rangle$ may accordingly be expanded as BO functions via a rotational and vibrational transformation [28]. The same holds for the Green's operator G_I. Second, working with reaction matrices that include closed channels and "smooth" Green's functions, and with energy-normalized radial functions is expected to reduce the size of the energy mesh. Finally, we have not explicitly included the antisymmetry requirements in the potential matrix elements of Eqs. (4.15)–(4.17); as advanced at the end of Sec. II, doing so does not change the form of the equations nor the structure of the linear system, although it does complicate the calculation of the potential matrix elements.

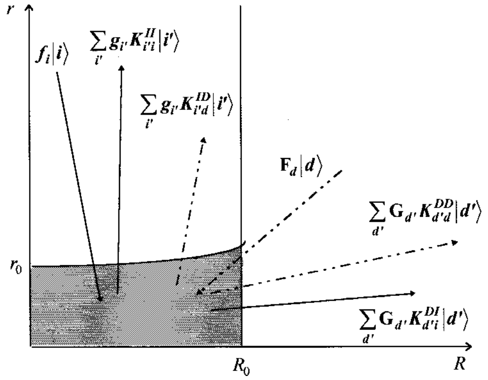

FIG. 1. The arrows picture the different terms of the wave function in the radial coordinate (R for the nuclei, r for the electron) plane, that are valid outside the core (in gray). The solid lines represent $|\psi_{I_i}\rangle$ and the dotted lines represent $|\psi_{D_d}\rangle$.

Now, taking Eqs. (4.9) and (4.11) with $\alpha=I$ and $\beta=D$ and reducing the Green's operators to on shell radial (r or R) Green's functions as in Sec. II leads to

$$\langle r|\psi_{I_i}\rangle=f_i(r)|i\rangle-\sum_{i'} g_{i'}(r)|i'\rangle K^{II}_{ii'}, \quad r>r_0, \qquad (4.18)$$

$$\langle R|\psi_{D_d}\rangle=\mathcal{F}_d(R)|d\rangle-\sum_{d'} \mathcal{G}_{d'}(R)|d'\rangle K^{DD}_{dd'}, \quad R>R_0. \qquad (4.19)$$

where $K^{II}_{ii'}$ and $K^{DD}_{dd'}$ are the on-the-energy shell matrix elements of the same-arrangement reaction operators [for example $K^{II}_{ii'}(E)=\langle\phi_{I_i}(E)|K^{II}(E)|\phi_{I_{i'}}(E)\rangle$]. From Eqs. (4.10) and (4.12) we get expressions with the cross-arrangement reaction operators

$$\begin{aligned}\langle R|\psi_{I_i}\rangle&=-\pi^{-1}\langle R|G_D\overline{K}^{DI}|\phi_{I_i}\rangle\\&=-\sum_{d'}\mathcal{G}_{d'}(R)|d'\rangle\overline{K}^{DI}_{d'i}, \quad R>R_0, \qquad (4.20)\end{aligned}$$

and

$$\begin{aligned}\langle r|\psi_{D_d}\rangle&=-\pi^{-1}\langle r|G_I\overline{K}^{ID}|\phi_{D_d}\rangle\\&=-\sum_{i'} g_{i'}(r)|i'\rangle\overline{K}^{ID}_{i'd}, \quad r>r_0. \qquad (4.21)\end{aligned}$$

Notice that because the reduction of the Green's operators takes the simple MQDT form only when the perturbation potentials vanish ($r>r_0$ or $R>R_0$) the expressions (4.18) to (4.21) are only valid in definite regions of the (R,r) plane represented in Fig. 1. As usual, within MQDT the wave function inside the core is not known; the physical core defined by both $r<r_0$ and $R<R_0$ is gray dashed on the figure. The solid lines represent Eqs. (4.18) and (4.20), that we can think of as the scattered waves from an initial nonperturbed state $|f_i\rangle|i\rangle$, including exponentially diverging functions for

closed channels. The dotted lines represent an initially nonperturbed state $|F_d\rangle|d\rangle$ in the D arrangement scattering into other dissociation waves, Eq. (4.19), or into I arrangement waves, Eq. (4.21).

The total wave function is accordingly given by Eq. (4.13). For $r \gg r_0$ it is convenient to use Eqs. (4.18) and (4.21) since $\langle r|G_I$ is known (and for $R \gg R_0$ the other two pairs). The following expressions are obtained (with the on-shell equalities $K^{ID}_{id'} = \overline{K}^{ID}_{id'}$ and $K^{DI}_{di'} = \overline{K}^{DI}_{di'}$):

$$\langle r|\psi^\rho\rangle = \sum_{i\in\{I_O+I_P\}} |i\rangle \Bigg\{ B^\rho_i f_i(r) - \Bigg[\sum_{i'} B^\rho_{i'} K^{II}_{i'i} + \sum_{d'} B^\rho_{d'} K^{ID}_{id'} \Bigg] g_i(r) \Bigg\}, \quad r > r_0, \tag{4.22}$$

$$\langle R|\psi^\rho\rangle = \sum_d |d\rangle \Bigg\{ B^\rho_d \mathcal{F}_d(R) - \Bigg[\sum_{d'} B^\rho_{d'} K^{DD}_{d'd} + \sum_{i'} B^\rho_{i'} K^{DI}_{di'} \Bigg] \mathcal{G}_d(R) \Bigg\}, \quad R > R_0. \tag{4.23}$$

In a final step, these two equations are matched to the standing-wave decompositions of ingoing ionization and ingoing dissociation functions. The basic idea is the same as in the single arrangement problem of Sec. II [see Eqs. (2.23)–(2.26)] although the calculations are a bit more involved: for each ρ, there are now not one, but two eigenchannel functions (one per arrangement) that have both the same phase shift (see Appendix B). Since we are considering both closed (I_C) and open (I_O) channels in the I arrangement and only open channels in the D arrangement, the result is

$$\begin{aligned}
&i \in I_C, \quad \sum_{i'\in\{I_O+I_C\}} B^\rho_i K^{II}_{ii'} + \sum_{d'\in D} B^\rho_{d'} K^{ID}_{id'} + B^\rho_i \tan\beta_i = 0,\\
&i \in I_O, \quad \begin{cases} B^\rho_i = \mathbf{U}^\dagger_{i\rho}, \\ \displaystyle\sum_{i'\in\{I_O+I_C\}} B^\rho_{i'} K^{II}_{ii'} + \sum_{d'\in D} B^\rho_{d'} K^{ID}_{id'} = -\pi \sum_{j\in\{I_O+D\}} \mathbb{K}_{ij} \mathbf{U}^\dagger_{j\rho} = \mathbf{U}^\dagger_{i\rho} \tan\pi\tau_\rho, \end{cases}\\
&d \in D, \quad \begin{cases} B^\rho_d = \mathbf{U}^\dagger_{d\rho}, \\ \displaystyle\sum_{d'\in D} B^\rho_{d'} K^{DD}_{dd'} + \sum_{i'\in\{I_O+I_C\}} B^\rho_{i'} K^{DI}_{di'} = -\pi \sum_{j\in\{I_O+D\}} \mathbb{K}_{dj} \mathbf{U}^\dagger_{j\rho} = \mathbf{U}^\dagger_{d\rho} \tan\pi\tau_\rho, \end{cases}
\end{aligned} \tag{4.24}$$

where $\mathbb{K}_{ij}$ are the elements of the open channels physical full reaction matrix with eigenvalues $-\pi^{-1}\tan\pi\tau_\rho$, composed with the blocks $\mathbb{K}^{II}$, $\mathbb{K}^{ID}$, $\mathbb{K}^{DI}$, and $\mathbb{K}^{DD}$; $-\pi\mathbb{K}$ is related to the total $\mathbf{S}$ matrix by a Cayley transform. Here $\mathbf{U}$ diagonalizes $\mathbf{S}$. We are thus led to solving a system similar in form to the well-known typical MQDT system. The bound-state energies as well as the eigenphaseshifts τ_ρ of the (ionization and dissociation) open-channel interactions are found first; then, for each ρ, the B^ρ_i coefficients are determined at the energy E of interest. As expected, the values taken by the phase function in the I arrangement, β_i, now also depend on the waves scattered from the D arrangement.

V. CONCLUSION

In this article, we have first developed a standing-wave rearrangement scattering formalism in which the wave functions are given in terms of same-arrangement and cross-arrangement reaction operators. A few works using standing waves in reactive collisions have been done in the past (e.g., [40]), but the specific characteristics of standing-wave operators were not taken into account: the expressions valid for traveling waves were employed in the standing-wave context, although it has been known for quite a long time [41,32] that such a direct transposition for infinite-order expressions may lead to errors (as seen in Sec. III, the relations for travelling wave equations and collision operators do not always hold for standing waves).

By examining the relation between MQDT and the Lippmann-Schwinger approach, we have then derived a formalism for standing-wave rearrangement scattering with the explicit inclusion of closed channels. The methods of MQDT have by now far outpassed their original domain of atomic quantum defects, and since the formalism of Sec. IV extends these methods to rearrangement scattering, the theory may be seen as a multiarrangement MQDT. Besides giving a formal basis for ongoing research, the development of a multiarrangement quantum-defect theory concurs with current works concerned by the connection of different theoretical approaches to treat problems involving simultaneous motions of the nuclei and of an outer electron in diatomic systems.

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APPENDIX A: ANTISYMMETRIZED REACTION OPERATOR

We consider an electron colliding on a target containing $N-1$ electrons. The Hamiltonian is partitioned following

$$H=H_1+V_1=H_2+V_2=\cdots=H_N+V_N, \tag{A1}$$

where the index indicates which electron is initially colliding. Suppose that the Nth electron, in state i collides on the core represented by the antisymmetrized product $i^+(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1})$. Then in the notation of Sec. IV A the solution is given by

$$|\psi_{N_i}\rangle=|\phi_{N_i}\rangle-\pi^{-1}G_N K^{NN}|\phi_{N_i}\rangle, \tag{A2}$$

where N labels the arrangement and we shall set $\langle r|\phi_{N_i}\rangle \equiv f_i(r_N)|i_N\rangle$.

As known, when antisymmetrizing, we only need to consider the $N-1$ permutations $P_{N,\gamma}$ ($\gamma\in\{1,\ldots,N-1\}$) that do not leave the core unchanged. The antisymmetrizer is then given up to a normalizing constant by

$$\mathcal{A}=I-\sum_{\gamma=1}^{N-1} P_{N,\gamma} \tag{A3}$$

and the antisymmetrized solution is $\mathcal{A}|\psi_{N_i}\rangle$. With the help of the key Eq. (3.15) and by reducing G_N, we get for $r_N>r_0$

$$\langle r_N|\mathcal{A}G_N K^{NN}|\phi_{N_i}\rangle=\pi\sum_j g_j(r_N)|j_N\rangle \times\langle\phi_{N_j}|\left[K^{NN}-\sum_{\gamma=1}^{N-1}P_{N,\gamma}K^{\gamma N}\right]|\phi_{N_i}\rangle. \tag{A4}$$

We further take into account the finite spatial extent of the core, so that for $r_N>r_0$ we have $\langle r_N|\mathcal{A}|\phi_{N_i}\rangle=f_i(r_N)|i_N\rangle$, and finally

$$\langle r_N|\mathcal{A}|\psi_{N_i}\rangle=f_i(r_N)|i_N\rangle-\sum_j g_j(r_N)|j_N\rangle\langle\phi_{N_j}|K_{\text{eff}}|\phi_{N_i}\rangle \tag{A5}$$

where K_{eff} is given by the expression between brackets [ ] in Eq. (A4). It can easily be shown that, when calculating matrix elements, K_{eff} can be set as

$$K_{\text{eff}}=K^{NN}-(N-1)P_{N-1,N}K^{N-1N} \tag{A6}$$

$$=-\pi(I-(N-1)P_{N-1,N})V_N+V_N G_N K_{\text{eff}}. \tag{A7}$$

In fact, since we may consider the $f_i(r_N)$ to be orthogonal to any core function, the expressions can be further simplified when calculating the matrix elements of the reaction operator.

APPENDIX B: MULTIARRANGEMENT MQDT BOUNDARY CONDITIONS IN $I+D$ SCATTERING

The state vector of an ionized electron in channel i is given by the ingoing wave,

$$|\psi_{I_i}^-\rangle=|\phi_{I_i}\rangle+\mathbb{G}_I^-\mathbb{T}^{\dagger II}|\phi_{I_i}\rangle. \tag{B1}$$

Although the operators here are initially defined on the asymptotic I arrangement Hilbert space, we can envisage them as defined on the super Hilbert space, which is the direct sum of the asymptotic spaces, on which the total collision matrices $\mathbf{S}$ or $\mathbf{T}$ are defined. Then there is a unitary matrix $\mathbf{U}$ that diagonalizes $\mathbf{T}$, so that $\mathbb{T}^{\dagger II}$ can be expressed with the eigen-phase-shifts of $\mathbf{S}$, allowing for the introduction of the different $\mathbb{K}$ operators. After some algebraic manipulations and with the help of Eq. (2.9), Eq. (B1) is set as a superposition of standing waves:

$$|\psi_{I_i}^-\rangle=\sum_\rho \mathbf{U}_{\rho i}e^{-i\pi\tau_\rho}\cos\pi\tau_\rho|\psi_{I_\rho}\rangle \tag{B2}$$

with

$$|\psi_{I_\rho}\rangle=\sum_{i\in I_O}\mathbf{U}_{i\rho}^\dagger|\phi_{I_i}\rangle+\sum_{i\in I_O}\mathbf{U}_{i\rho}^\dagger\mathbb{G}_I\mathbb{K}^{II}|\phi_{I_i}\rangle + \sum_{d\in D}\mathbf{U}_{d\rho}^\dagger\mathbb{G}_I\mathbb{K}^{ID}|\phi_{D_d}\rangle. \tag{B3}$$

Then by reducing the Green's operator, and since $\mathbf{U}$ also diagonalizes the total reaction matrix $\mathbb{K}$ with diagonal elements $-\pi^{-1}\tan\pi\tau_\rho$, we obtain

$$\langle r|\psi_{I_\rho}\rangle=\sum_{i\in I_O}|i\rangle\mathbf{U}_{i\rho}^\dagger[f_i(r)-\tan\pi\tau_\rho g_i(r)]. \tag{B4}$$

The same reasoning gives the decomposition of the state vector of the dissociated fragments in channel d,

$$|\psi_{D_d}^-\rangle=|\phi_{D_d}\rangle+\mathbb{G}_D^-\mathbb{T}^{\dagger DD}|\phi_{D_d}\rangle, \tag{B5}$$

into standing waves

$$|\psi_{D_\rho}\rangle=\sum_d\mathbf{U}_{d\rho}^\dagger|\phi_{D_d}\rangle+\sum_d\mathbf{U}_{d\rho}^\dagger\mathbb{G}_D\mathbb{K}^{DD}|\phi_{D_d}\rangle + \sum_{i\in I_O}\mathbf{U}_{i\rho}^\dagger\mathbb{G}_D\mathbb{K}^{DI}|\phi_{I_i}\rangle \tag{B6}$$

and by reducing $\mathbb{G}_D$

$$\langle R|\psi_{D_\rho}\rangle=\sum_d|d\rangle\mathbf{U}_{d\rho}^\dagger[\mathcal{F}_d(R)-\tan\pi\tau_\rho\mathcal{G}_d(R)]. \tag{B7}$$

Notice that unlike the case of direct (single-arrangement) scattering, there are now two distinct eigenchannel functions, $|\psi_{I_\rho}\rangle$ and $|\psi_{D_\rho}\rangle$, but they both have a common phase shift [compare Eqs. (B4) and (B7) with Eq. (1) of Ref. [12]].

Now the total wave function, Eq. (4.13), is easily matched to Eq. (B4) when $r\to\infty$ *and* to Eq. (B7) when $R\to\infty$ by establishing the following relations:

$$\langle r|G_I K^L \xrightarrow[r\to\infty]{} \langle r|\mathbb{G}_I\mathbb{K}^L-\pi \times\sum_{i\in\{I_O+I_P\}}\Theta(-\epsilon_i)(\tan\beta_i)^{-1}f_i(r)|i\rangle\langle\phi_{I_i}|K^L, \tag{B8}$$

where L stands for II or ID, and the trivial equality

$$\langle R|G_D=\langle R|\mathbb{G}_D. \tag{B9}$$

This yields the system given in Eq. (4.24).

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