4 Nonlocal Theory of Resonance Electron– Molecule Scattering

Martin Čížek and Karel Houfek

## CONTENTS

4.1 INTRODUCTION

Theoretical description of the dynamics of the molecular motion usually comprises two steps. First, quantum–chemical calculations of potential energy surfaces are performed nowadays using well-established packages of codes. The second step involves calculation of the vibrational dynamics on these potential energy surfaces within the Born–Oppenheimer approximation.

Similarly, the calculation of the *dynamics of electron–molecule collisions* involving nuclear* dynamics proceeds in two steps. The appropriate generalization of the Born–Oppenheimer approximation is called the *nonlocal resonance theory*. The term is historic; the resonances actually do not have to be involved, although they (or virtual states) appear in most of the cases, at least for some molecular geometries. The calculation of the electron dynamics for the fixed molecular geometry has to provide not only the potential energy surfaces, but also the electron-scattering quantities. A set of all quantities needed to perform the calculation of the nuclear dynamics is called the *nonlocal resonance model*. For a specific molecule, we need the potential energy surfaces for both the neutral molecule and the anion and also the transition elements for releasing the electron from the molecular anion into the continuum (at fixed molecular geometry). The last quantities complicate the definition of the nonlocal resonance model, since the transition elements (called the *coupling amplitudes*) depend on both the molecular geometry and the energy of the released electron. The same amplitude also controls the electron capture into the anionic state.

The separation of the electron and the nuclear motion is a very important assumption. Each of the two steps is already quite difficult and the problem to treat both the electronic and nuclear motion simultaneously would be immense. The success of this divide-and-conquer strategy depends on the proper separation of the electronic problem to a discrete state and the continuum. If it is successful, the full nonadiabatic nature of the exchange of energy between electrons and nuclei is properly captured.

We would also like to stress that once the nonlocal resonance model is set up, the number of processes can be treated on the equal theoretical level. The process

$$e^- + AB(v_i) \rightarrow e^- + AB(v_f) \tag{4.1}$$
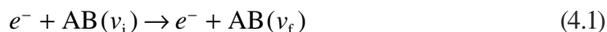
includes both *elastic scattering* (but with full account of inelastic interaction) and *vibrational excitation*. It also comprises the *collisional detachment*

$$e^- + AB(v_i) \rightarrow A + B + e^-, \tag{4.2}$$

which is nothing else but the vibrational excitation in the dissociation continuum state of the molecule. Here, A and B are two (monatomic or polyatomic) parts of the studied molecule. The proper treatment of the vibrational excitation must also include the competing process of *dissociative electron attachment*

$$e^- + AB(v_i) \rightarrow A + B^-. \tag{4.3}$$

The same calculation can, of course, provide also the full information about the reverse processes of *associative detachment* or *three-particle recombination* which is the inverse of Equation 4.2.

In this chapter, we will assume that the fixed-nuclei electron-scattering problem was solved (see Chapter 2 for a review of methods dealing with the fixed-nuclei electron scattering) and we focus on the separation of the electronic Hilbert space into the

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* We use the term nuclear dynamics when we talk about the dynamics of motion of nuclei in the molecule here. When talking about the electron–molecule collisions, we try to avoid the term "vibrational dynamics," because some processes include the dissociation of the molecule.

discrete state and the continuum and on the derivation of the equations describing the nuclear (= vibrational or dissociation) dynamics of the resonance electron–molecule collisions. We will also discuss numerical methods for solving these equations. An application of the theory to particular systems and a discussion of various structures appearing in the cross sections due to nuclear dynamics will be presented in Chapter 5.

4.1.1 Brief Overview of the Methods

Treatment of the vibrational excitation or dissociative attachment requires the inclusion of both electronic and nuclear dynamics of the system. The straightforward basis expansion of the vibrational (and rotational) degrees of freedom together with electronic wave functions leads to coupled channel expansions (see Morrison and Sun 1995 and references therein). This approach has been applied to several systems but it is not suitable for treatment of the resonant or dissociative dynamics, where the nuclear motion gets very far from the vibrations in the initial molecular state and the basis would be too large for the calculation to be feasible.

Closely related to the close coupling approach is the *R*-matrix method for electron scattering (discussed in more detail in Chapter 2, including the references) with extension to include the vibrational dynamics by Schneider et al. (1979). Although the introduction of the *R*-matrix sphere may lead to smaller basis, the method itself also falls in the class of methods using direct expansion in combined electronic and vibrational space and does not remove the necessity to use a very large basis in the case of strongly coupled electron and vibrational motions.

The simplest case of the separation of the electronic and vibrational degrees of freedom is straightforward application of the Born–Oppenheimer approximation (applicability of the adiabatic approximation for scattering processes was discussed, for example, by Chase (1956)). This is possible only in the case of elastic scattering and vibrational excitation in the absence of resonances. The fixed-nuclei electron-scattering problem is solved and sandwiched between bra-vector describing the final vibrational state and ket-vector for the initial vibrational state. The resulting *T*-matrix describes the vibrational excitation process in the adiabatic nuclei approximation. The electron–vibrational correlation is completely ignored in this approach and it is therefore also not suited for the description of the processes involving resonances.

Fortunately the strong correlation of electronic and vibrational motion can often be attributed to one or few electronic states. It is therefore feasible to separate the electronic Hilbert space in the part containing these states and the rest that can be treated within the Born–Oppenheimer approximation. The projection-operator method of Feshbach developed in nuclear physics (Feshbach 1958, 1962) is ideally suited to perform such separation. The approach is basically equivalent to Fano's theory of discrete states embedded in the continuum (Fano 1961). The projection-operator approach was introduced to describe molecular processes involving the electron continuum by Chen (1966), O'Malley (1966), Bardsley (1968), and Nakamura (1971) in the late 1960s and early 1970s. As pointed out earlier, the projection-operator approach only divides the electronic states into two subspaces for each molecular geometry. This division is useful only if it restores the conditions of validity of the Born–Oppenheimer approximation as discussed by O'Malley (1971). The new basis in the electronic Hilbert space is

thus called *diabatic basis*, in contrast to the conventional adiabatic basis that diagonalizes the electronic Hamiltonian for each molecular geometry. Recently, the performance of such generalized Born–Oppenheimer approximation was tested on a numerically solvable model containing one electronic and one nuclear coordinates (Houfek et al. 2006). It was shown (Houfek et al. 2008) that the nonlocal resonance theory can give correct results contrary to some other approximations.

The equations governing the nuclear motion in the projection-operator-based theories include the nonlocal, complex, and energy-dependent effective potential which is difficult to deal with. Therefore, the early treatments of collisions employed the *local complex potential approximation*. The nonlocality of the full theory is closely related to energy dependence of the effective potential. The local complex potential approximation is not able to describe the threshold effects properly as discussed by Bardsley (1968).

The role of the threshold effects in the full nonlocal version of the theory was studied in detail by Domcke (1991). He showed that the nonlocal theory is capable of describing correctly the various types of singularities in the fixed-nuclei electron–molecule *S*-matrix (bound and virtual states, resonances) and to include their influence on the vibrational dynamics. Cederbaum and Domcke (1981) furthermore introduced an analytic model solvable in terms of continued fractions. The numerical treatment of the full nonlocal dynamics was furthermore developed by Horáček (1995) and applied to several diatomic molecules (see Chapter 5 for the details).

The projection-operator formulation leads to a parametrization of the Hamiltonian which is then used for the calculation of the dynamics. The similar approach was developed by Fabrikant (1985) based on the single-pole approximation within the *R*-matrix theory. Although the definition of the discrete state is somewhat special in this case (and it is not clear that it gives the proper diabatic state), the resulting equations for the vibrational dynamics have been shown to be equivalent to the projection-operator formulation of the nonlocal resonance model (see Fabrikant 1990 or Hotop et al. 2003 and references therein). Similar approach is also the zero-range (or effective-range) approximation theory (Gauyacq and Herzenberg 1982), which parameterizes the electron dynamics based on the low-energy expansion formulas, with parameters depending on the molecular geometry. By tuning the parameters, the vibrational dynamics can also give similar results to full nonlocal calculations, but the zero-range expansions do not provide the accurate fixed-nuclei electron–molecule scattering data.

The validity of the projection-operator approach leading to the nonlocal resonance model is not limited to electron–molecule scattering processes. Employing the time-reversal symmetry, the description of the dissociative attachment is easily extended to reverse processes of associative detachment, that is, to ion–molecule collisions. The generalization to positive ions is also possible and the approach has also been applied to dissociative recombination and Penning and associative ionization (see, e.g., Bieniek 1978).

4.2   NONLOCAL RESONANCE THEORY

The basic assumption usually made to derive the nonlocal resonance theory of electron–molecule collisions is the formation of a metastable molecular anion M^- during the collision. The wave function of the whole system is then projected on

this state and the resulting dynamics in the nonlocal, energy-dependent, and complex potential is solved. The intermediate state M^- is usually the resonance (or virtual state), hence the term the nonlocal resonance theory.

Although this picture is essentially correct, there are some subtleties that occasionally led to misunderstanding. The typical situation is depicted in Figure 4.1. Here the case of a diatomic molecule is considered for simplicity. The picture is a schematic representation of the spectrum of the electronic Hamiltonian as it depends on the internuclear distance R in the molecule. The solid red curve is the potential energy curve $V_0(R)$ for the neutral molecule in the ground electronic state. The area above this curve is shaded to indicate that we have one additional electron in the electron–molecule collisions that can add arbitrary positive amount of energy to this potential energy. (The potential energy curve $V_0(R)$ is thus called the continuum threshold in this context.) In addition to this curve, we have the resonance state with energy marked by dotted blue curve inside the continuum. This is a metastable state and the electron can leave the system. The usual complication, present in most of the systems, is that this resonance state disappears above some critical internuclear distance and becomes the (electronically) bound anion state (solid blue line in Figure 4.1). The power of the nonlocal resonance theory is that it can correctly describe this transition. During this transition, as the internuclear distance R is varied, the metastable state can change its character from the resonance (directly or via a virtual state) to a bound state. We therefore prefer to call it the discrete state instead of the resonance.

To understand the situation a little bit deeper, we have to speak about the determination of the discrete state $|d\rangle$ with the wavefunction $\varphi_d(\mathbf{r}, \mathbf{q}; \mathbf{R})$ where $\mathbf{r}$ are the coordinates of the incoming electron and $\mathbf{q}$ and $\mathbf{R}$ denote collectively the coordinates of the target electrons and nuclei, respectively. In our case represented by Figure 4.1, it is rather straightforward to get φ_d for larger R, where it represents the bound state of one additional electron captured on the neutral molecule. For smaller distances, it is more complicated since there is no square integrable function associated with
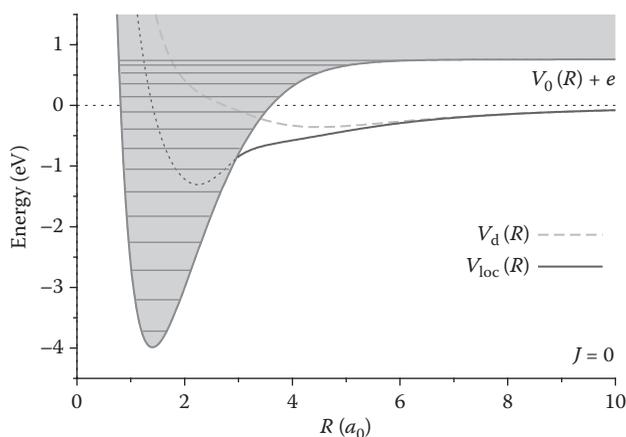

FIGURE 4.1 (**See color insert**.) Typical potential–energy curves for the electron collisions with diatomic molecules.

the resonance. The resonances (or virtual states) can still be defined as generalized eigenstates of the electronic Hamiltonian, but resulting states are not square integrable and they thus do not belong to the electronic Hilbert space. Practically, it is sufficient that the function φ_d is a square integrable function with a significant overlap with the true metastable state. This creates a large degree of arbitrariness in the theory, and we have infinitely many choices for the discrete state. This does not have to worry us, since the possible changes in the choice of the discrete state are compensated by the respective changes in the couplings to the continuum. The second criterion for the validity of the theory is the smoothness of the dependence of φ_d on the internuclear distances **R** since the diabatic approximation is used for the description of the nuclear dynamics as we will discuss later in this chapter. (See also the results of Houfek et al. (2008) on probing the nonlocal resonance model by choosing different discrete states.)

Once the discrete state φ_d is specified, the nonlocal resonance theory is developed employing the Feshbach projection-operator formalism (Feshbach 1958, 1962) with the operators Q and P chosen to project on the discrete-state and continuum parts of the electronic Hilbert space, respectively. The essence of the nonlocal resonance theory is in solving the whole dynamics in the simpler Q-part of the space. In the following, we will develop the theory in several steps. First, we define the projection operators Q and P and an appropriate basis in the electronic Hilbert space to expand these operators and the electronic Hamiltonian. The matrix elements of the electronic Hamiltonian play a central role in the construction of the nonlocal resonance models. Then, we will decompose the scattering T-matrix into the resonant and background (nonresonant) terms and give explicit formulas for them. Next, we derive the equations describing the full dynamics of the system within the Q-part of the space, which we obtain by the projection of the full wavefunction of the system on the discrete state. This quantity contains all information needed for calculation of resonance contributions to the vibrational excitation and dissociative attachment cross sections within the diabatic approximation.

The dynamics of the collision between the electron and the molecule with the fixed molecular geometry is governed by the Hamiltonian operator

$$H_{el} = T_{el} + V_{int}(\mathbf{R},\mathbf{r}), \tag{4.4}$$

where $T_{el} = -(1/2)\Delta_{\mathbf{r}}$ is the kinetic energy of the incoming electron and the second term is the effective one-electron interaction with the molecule, which is in general an energy-dependent, nonlocal in **r**, and (above the inelastic threshold) non-Hermitian operator (Domcke 1991). By introducing the optical potential V_{int}, the reference to internal electrons in the molecule (through their coordinates **q**) disappears from the description, although they are fully included through the many-body theory. It is possible to repeat the whole following derivation with explicit reference to internal molecular electrons, but in our case, below the threshold for ionization, we find it more convenient to suppress the explicit reference to other electrons. The molecular geometry is specified by a set of coordinates of all nuclei denoted here collectively by **R**. The target electrons are projected out and are implicitly included in the optical potential V_{int}. The complete dynamics of the electron–molecule collision, including the motion of the nuclei, is then described using the Hamiltonian operator

$$H = T_N + V_0(\mathbf{R}) + H_{el} \equiv H_0 + V_{int}, \tag{4.5}$$

where T_N is the kinetic energy of nuclei and $V_0(\mathbf{R})$ is the potential energy surface of the ground electronic state of the molecule of the interest. The separation of H to

$$H_0 = T_N + V_0(\mathbf{R}) + T_{el} \tag{4.6}$$

and the interaction V_{int} is a natural choice since H_0 is the channel Hamiltonian for the electron–molecule scattering (see, e.g., Taylor (1972) for use of the channel Hamiltonian in the multichannel scattering theory).

4.2.1 PROJECTION OPERATORS Q AND P

We start by defining the projection operators in the fixed-nuclei approximation.[*] All states and operators are thus understood as operating on the electronic Hilbert space H_{el}.

The operator Q projecting on the resonant part Q of H_{el} is given by

$$Q = | d \rangle \langle d |, \tag{4.7}$$

where $|d\rangle$ approximately describes the electron after being captured by the molecule. While the vector $|d\rangle$ represents the state in the electronic Hilbert space H_{el}, it can still parametrically depend on the molecular geometry, specified by the set of coordinates of all nuclei denoted here collectively as $\mathbf{R}$. We will sometimes omit the explicit reference to this dependence, but it should be kept in mind that $|d\rangle$ can depend on $\mathbf{R}$. The vector $|d\rangle$ is always given by a normalized, square-integrable, and in general complex wave function $\varphi_d(\mathbf{r}, \mathbf{R}) = \langle \mathbf{r}|d \rangle$ although (as discussed above) the state may represent a resonance (for some $\mathbf{R}$). The correct resonance wave function is not normalizable, but large overlap of this function with $|d\rangle$ is sufficient for good performance of the theory.

To simplify our derivation, we assume that there is a single isolated electronic resonance state becoming a bound state for large internuclear distances, which is true for most of the diatomic molecules. The generalization to more discrete states (or more continua) is rather straightforward.

The projector P on the complementary (nonresonant or background) part, P, of H_{el} is simply

$$P = 1 - Q. \tag{4.8}$$

It is now convenient to introduce the energy-normalized electronic states $|\mathbf{k}^{(+)}\rangle$ (*background scattering states*) that diagonalize the electronic Hamiltonian restricted on the P space, that is,

$$PH_{el}P \, | \, \mathbf{k}^{(+)} \rangle = \frac{1}{2} k^2 \, | \, \mathbf{k}^{(+)} \rangle, \tag{4.9}$$

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[*] This approximation is used for the definition of bases and projection operators but not in the final dynamical calculation where motion of nuclei is allowed (see the end of this section).

where a boundary condition for $\phi_k^{(+)}(\mathbf{r},\mathbf{R}) \equiv \langle \mathbf{r} | \mathbf{k}^{(+)} \rangle$ is determined by the incoming plane wave

$$\langle \mathbf{r} | \mathbf{k} \rangle = (2\pi)^{-\frac{3}{2}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{4.10}$$

The projector P can then be expressed in the form

$$P = \int | \mathbf{k}^{(+)} \rangle\langle \mathbf{k}^{(+)} | \, d^3\mathbf{k}. \tag{4.11}$$

The construction of the background scattering states is straightforward once the fixed-nuclei electron-scattering problem is solved. The details are discussed in Domcke (1991) and references therein. In a similar way, we define electronic states $|\mathbf{k}^{(-)}\rangle$ but with the plane wave (4.10) defining the outgoing boundary condition. The P operator expressed in these states has the same form as in Equation 4.11. It should be noted here that even though $\varphi_d(\mathbf{r}; \mathbf{R})$ can be chosen to be independent of $\mathbf{R}$ the background states $\phi_k^{(\pm)}(\mathbf{r};\mathbf{R})$ are always parametrically dependent on $\mathbf{R}$ because of explicit $\mathbf{R}$-dependence of the operator H_{el}.

Once the fixed-nuclei electron-scattering problem is solved, all the information about the electronic dynamics can be coded in the matrix elements of H_{el}. To be more specific, we introduce the notation

$$V_d(R) = V_0(R) + \langle d | H_{el} | d \rangle, \tag{4.12}$$

$$V_{dk}^{(+)}(R) = \langle d | H_{el} | \mathbf{k}^{(+)} \rangle, \tag{4.13}$$

$$V_{\mathbf{k}\mathbf{k}'} \equiv \left\{ V_0(R) + \frac{1}{2} k^2 \right\} \delta\left(\frac{1}{2} k^2 - \frac{1}{2} k'^2 \right) = \langle \mathbf{k}^{(+)} | \{ V_0(\mathbf{R}) + H_{el} \} | \mathbf{k}'^{(+)} \rangle, \tag{4.14}$$

where the last equality follows from Equation 4.9 and the energy-normalization of the continuum states. It is important to realize that $V_{\mathbf{k}\mathbf{k}'}$ is diagonal only because of the appropriate choice of $|\mathbf{k}^{(+)}\rangle$. As we will see later, this choice greatly simplifies the nuclear dynamics leading to a single equation describing the nuclear motion in the discrete state governed by the effective nonlocal potential. In addition to the matrix element $V_{dk}^{(+)}(\mathbf{R})$, we will need a matrix element

$$V_{dk}^{(-)}(\mathbf{R}) = \langle d | H_{el} | \mathbf{k}^{(-)} \rangle \tag{4.15}$$

to define the background and resonant T-matrix for vibrational excitation.

The main reason to perform the decomposition of the electronic space to the discrete state and continuum is twofold. First, the separation to the discrete state and continuum allows specifying the proper boundary condition for the dissociative attachment process. We should mention at this point that although the choice of $\mathbf{R}$-dependence of the discrete state $|d\rangle$ is to a large degree arbitrary, $|d\rangle$ should go to the proper electronic bound state describing $A + B^-$ fragments (see Equation 4.3) when $\mathbf{R}$ attains the corresponding values ($R \to \infty$ in the case of diatomics). The second reason is to restore the Born–Oppenheimer approximation. All the electron–molecule-scattering systems, where a large dissociative attachment signal is observed, feature the electronic bound states (anions) disappearing in the continuum

for some molecular geometries. The Born–Oppenheimer approximation is inherently wrong in such situations. But with a proper choice of the discrete state, we can still assume

$$\frac{\partial \phi_d(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \simeq 0, \quad \frac{\partial \phi_{\mathbf{k}}^{(+)}(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \simeq 0, \tag{4.16}$$

which allows us to use the relations

$$[T_N, P] = [T_N, Q] = 0, \tag{4.17}$$

$$T_N = PT_N P + QT_N Q, \tag{4.18}$$

$$T_N \mid d \rangle \mid \psi_{nucl} \rangle = \mid d \rangle T_N \mid \psi_{nucl} \rangle, \tag{4.19}$$

$$T_N \mid \mathbf{k}^{(+)} \rangle \mid \psi_{nucl} \rangle = \mid \mathbf{k}^{(+)} \rangle T_N \mid \psi_{nucl} \rangle. \tag{4.20}$$

These relations will be used in the subsequent sections. The expansion of the electronic Hilbert space and relations (4.16) define the *diabatic approximation*, which is the proper generalization of the Born–Oppenheimer approximation for our case.

Let us note that by introducing T_N, we started to work in the full Hilbert space of the problem and vectors like $|d\rangle |\psi_{nucl}\rangle$ are a direct product of the electronic and nuclear part. The fixed-nuclei projection operators $P(\mathbf{R})$ and $Q(\mathbf{R})$ are diagonal in the nuclear Hilbert space, that is, in combined space of electrons and nuclei, they become

$$Q = \int d\mathbf{R} \mid \mathbf{R} \rangle Q(\mathbf{R}) \langle \mathbf{R} \mid, \tag{4.21}$$

$$P = \int d\mathbf{R} \mid \mathbf{R} \rangle P(\mathbf{R}) \langle \mathbf{R} \mid. \tag{4.22}$$

4.2.2 Background and Resonant *T*-Matrices for Vibrational Excitation

We begin by writing the full Hamiltonian given by Equation 4.5 in the form

$$H = H_0 + V_1 + V_2, \tag{4.23}$$

where H_0 is given by Equation 4.6 and

$$V_1 = PH_{el}P + QH_{el}Q - T_{el}$$
$$= PH_{el}P + QH_{el}Q - H_{el} + V_{int}, \tag{4.24}$$

$$V_2 = PH_{el}Q + QH_{el}P. \tag{4.25}$$

The motivation for the choice of V_1 is to express the scattering *T*-matrix (more precisely only its *resonant* part) in terms of $|v\rangle|\mathbf{k}^{(+)}\rangle$ instead of the unperturbed initial or final state $|v\rangle|\mathbf{k}\rangle$, where $|v\rangle$ is the Born–Oppenheimer vibrational wave function $\chi_v(\mathbf{R})$ of the molecule (i.e., an eigenstate of $T_N + V_0$). We can easily see that the state $|v\rangle|\mathbf{k}^{(+)}\rangle$ is an eigenfunction of

$$H_1 \equiv H_0 + V_1 = T_N + V_0 + PH_{el}P + QH_{el}Q$$
$$= Q[T_N + V_d(\mathbf{R})]Q + P[T_N + V_0(\mathbf{R}) + H_{el}]P = QHQ + PHP \qquad (4.26)$$

within the diabatic approximation defined by Equation 4.16.

By employing the two-potential formula for the scattering T-matrix (see Goldberger and Watson (1964), p. 202), we get

$$T^{VE}_{v_i \rightarrow v_f} = \langle v_f \mid \langle \mathbf{k}_f^{(-)} \mid V_1 \mid v_i \rangle \mid \mathbf{k}_i \rangle + \langle v_f \mid \langle \mathbf{k}_f^{(-)} \mid V_2 \mid \Psi^{(+)} \rangle, \qquad (4.27)$$

where $|\Psi^{(+)}\rangle$ is the full (including both electronic and vibrational degrees of freedom) scattering wave function of the system

$$|\Psi^{(+)}\rangle = |v_i\rangle |\mathbf{k}_i^{(+)}\rangle + \frac{1}{E - H + i\varepsilon} V_2 |v_i\rangle |\mathbf{k}_i^{(+)}\rangle. \qquad (4.28)$$

The last equation shows that we can take the product $|v_i\rangle |\mathbf{k}_i^{(+)}\rangle$ as the initial state of the system to determine the wave function $|\Psi^{(+)}\rangle$ which we will use later to derive the effective equation for the nuclear dynamics.

The second term of Equation 4.27 corresponds to the resonant part of the T-matrix as defined in Domcke (1991) and is fully determined by the resonant part $Q|\Psi^{(+)}\rangle$ of the full wave function. Using Equations 4.8, 4.13, 4.25, and the orthogonality $\langle \mathbf{k}^{(-)} | d \rangle = 0$, we obtain

$$T^{res}_{v_i \rightarrow v_f} = \langle v_f \mid \langle \mathbf{k}_f^{(-)} \mid PH_{el}Q + QH_{el}P \mid \Psi^{(+)} \rangle$$
$$= \langle v_f \mid \langle \mathbf{k}_f^{(-)} \mid PH_{el}Q \mid \Psi^{(+)} \rangle. \qquad (4.29)$$

This expression can further be simplified if we define $\Psi_d(\mathbf{R}) = \langle d|\Psi^{(+)}\rangle_r$ where $\langle \cdots \rangle_r$ means an integration over the electronic coordinate r only. The resulting function is thus a state belonging to the nuclear Hilbert space. In terms of the resonant nuclear wavefunction Ψ_d, for which we will derive the effective Schrödinger equation in the following subsection, the resonant part of the T-matrix can be written as

$$T^{res}_{v_i \rightarrow v_f} = \langle v_f \mid V_{d\mathbf{k}_f}^{(-)*} \mid \Psi_d \rangle. \qquad (4.30)$$

Note that this expression differs slightly from the result of Domcke (1991). Namely, in Equation 4.14 of this work the matrix V_{dk} has no superscript, which corresponds to the matrix element $V_{dk}^{(+)}$ defined by Equation 4.13. This small difference becomes important only when the background terms defined below are added to the resonant T-matrix (which was not usually the case in previous studies of resonant electron–molecule collisions), since the coupling matrix elements $V_{dk}^{(\pm)}$ are in general complex even when the discrete state is real. The reason why we cannot use $V_{dk}^{(+)}$ instead of $V_{dk}^{(-)}$ is that in general, in spite of the fact that $\phi_k^{(-)}$ belongs to P space,

$$\langle \mathbf{k}_f^{(-)} \mid \mathbf{k}^{(+)} \rangle \neq \delta\left(\frac{1}{2} k_f^2 - \frac{1}{2} k^2 \right) \qquad (4.31)$$

(the quantity in fact equals to the background scattering matrix) and therefore

$$\langle \mathbf{k}_f^{(-)} \mid PH_{el}Q \mid d \rangle \neq \langle \mathbf{k}_f^{(+)} \mid H_{el} \mid d \rangle. \qquad (4.32)$$

Instead, if we consider a special case of the *real* discrete state and if we realize that for the radial case with a real discrete state

$$\phi_k^{(-)}(r) = (\phi_k^{(+)}(r))^*, \tag{4.33}$$

we can simplify the matrix element between electronic wave functions in Equation 4.29 as

$$\langle \mathbf{k}_f^{(-)} | PH_{el}Q | d \rangle = \langle \mathbf{k}_f^{(-)} | H_{el} | d \rangle = \langle d | H_{el} | \mathbf{k}_f^{(+)} \rangle = V_{d\mathbf{k}_f}^{(+)} \tag{4.34}$$

where we assumed that H_{el} is a Hermitian operator. Note that in this special case we can use the matrix element $V_{dk}^{(+)}$ but *without complex conjugation*. In the three-dimensional case, Equation 4.33 must be modified to

$$\phi_{\mathbf{k}}^{(-)} = (\phi_{-\mathbf{k}}^{(+)})^* \tag{4.35}$$

and thus $V_{d\mathbf{k}}^*$ in Equation 4.14 of Domcke (1991) should be replaced by $V_{d,-\mathbf{k}}$ under the assumption that φ_d is real, otherwise $V_{d\mathbf{k}}^{(-)*}$ must be used.

We now return to Equation 4.27. The first term is generally called the *background* scattering *T*-matrix and reads

$$T_{v_i \to v_f}^{bg} = \langle v_f | \langle \mathbf{k}_f^{(-)} | V_1 | \mathbf{k}_i \rangle | v_i \rangle = \langle v_f | T_{\mathbf{k}_i \to \mathbf{k}_f}^{el}(\mathbf{R}) | v_i \rangle, \tag{4.36}$$

where

$$T_{\mathbf{k}_i \to \mathbf{k}_f}^{el}(\mathbf{R}) = \langle \mathbf{k}_f^{(-)} | V_1 | \mathbf{k}_i \rangle = \langle \mathbf{k}_f | V_1 | \mathbf{k}_i^{(+)} \rangle \tag{4.37}$$

is the fixed-nuclei background scattering *T*-matrix. The resulting expression is by definition the adiabatic nuclei approximation. We obtained this expression as a consequence of the fact that we used the diabatic approximation for the projection–operator partitioned basis. Once we solve the background scattering elastic problem for each fixed $\mathbf{R}$, it is easy to calculate this quantity. All effects beyond the Born–Oppenheimer approximation are contained within the resonant contribution.

The background terms are nonzero even for inelastic vibrational excitation but generally small when compared with the resonant part of the *T*-matrix. For an example where these terms are not negligible, see the results for the F_2-like model in Houfek et al. (2008).

The wave function (4.28) contains also the information about the dissociative electron attachment. The *T*-matrix for this process reads

$$\begin{aligned} T_{v_i, \mathbf{k}_i}^{DA} &= \langle \mathbf{K}_f^{(-)} | \langle d | V_2 | \Psi^{(+)} \rangle \\ &= \langle \mathbf{K}_f^{(-)} | \langle d | QHP | \Psi^{(+)} \rangle, \end{aligned} \tag{4.38}$$

where $| \mathbf{K}_f^{(-)} \rangle | d \rangle$ is the eigenstate of H_1 representing the final state for the dissociative attachment, with $| \mathbf{K}_f^{(-)} \rangle$ standing for the dissociative eigenstate of $T_N + V_d$ ($\mathbf{R}$) with the outgoing boundary condition and $\mathbf{K}_f$ giving the wave-vector of the dissociation products. The above expression does not contain the background contribution

$$T_{v_i,\mathbf{k}_i}^{\text{bg,DA}} = \langle \mathbf{K}_f^{(-)} | \langle d | V_1 | v_i \rangle | \mathbf{k}_i \rangle$$

$$= \langle \mathbf{K}_f^{(-)} | \langle d | \{H_1 - H_0\} | v_i \rangle | \mathbf{k}_i \rangle$$

$$= \langle \mathbf{K}_f^{(-)} | v_i \rangle \langle d | \mathbf{k}_i \rangle \left\{ \frac{1}{2\mu} K_f^2 - E_{v_i} - \frac{1}{2} k_i^2 \right\},$$

which equals zero due to the energy conservation. This is consistent with the well-known fact that it is not possible to describe the dissociative attachment process within the Born–Oppenheimer approximation.

4.2.3 Integral Equation for the Nuclear Wave Function

To get the dynamical equation for the evaluation of the wave function (4.28), we write the Lippmann–Schwinger equation corresponding to separation

$$H = H_1 + V_2$$

which reads

$$| \Psi^{(+)} \rangle = | \Phi_i^{(+)} \rangle + [E - H_P + H_Q + i\varepsilon]^{-1}(H_{PQ} + H_{QP}) | \Psi^{(+)} \rangle, \qquad (4.39)$$

where ε is the usual positive infinitesimal. We also introduced the short hand notation $H_P = PHP$, $H_Q = QHQ$, $H_{PQ} = PHQ$, $H_{QP} = QHP$. The vector $| \Phi_i^{(+)} \rangle$ characterizes the initial state and must be an eigenstate of HP for electron–molecule scattering and an eigenstate of H_Q for ion–atom scattering channel. Multiplying this equation with Q and P, we obtain the system of equations

$$Q | \Psi^{(+)} \rangle = Q | \Phi_i^{(+)} \rangle + G_Q H_{QP} P | \Psi^{(+)} \rangle, \qquad (4.40)$$

$$P | \Psi^{(+)} \rangle = P | \Phi_i^{(+)} \rangle + G_P H_{PQ} Q | \Psi^{(+)} \rangle, \qquad (4.41)$$

where we have introduced Green's functions $G_Q = Q(E - H_Q + i\varepsilon)^{-1}Q$ and $GP = P(E - H_P + i\varepsilon)^{-1}P$. Substitution of Equation 4.41 into Equation 4.40 gives

$$Q | \Psi^{(+)} \rangle = Q | \Phi_i^{(+)} \rangle + G_Q H_{QP} P | \Phi_i^{(+)} \rangle + G_Q H_{QP} G_P H_{PQ} Q | \Psi^{(+)} \rangle. \qquad (4.42)$$

We thus reduced the scattering problem in the complete Hilbert space H to a scattering problem in its small subspace Q. In the next section, we will show that the Q-space part of the wave function $Q|\Psi^{(+)}\rangle$ obeys the inhomogeneous Schrödinger equation with the effective Hamiltonian (O'Malley 1966)

$$H_{\text{eff}} = H_Q + H_{QP} G_P H_{PQ}. \qquad (4.43)$$

Employing the explicit expansion of the projectors in terms of the basis $|d\rangle$, $|\mathbf{k}^{(+)}\rangle$, we find

$$H_{\text{eff}} = T_N + V_d(R) + F(E), \qquad (4.44)$$

where $F(E)$ is the operator in the nuclear space which in coordinate representation reads

$$\langle \mathbf{R} \mid F(E) \mid \mathbf{R}' \rangle = \int V_{\mathrm{dk}}(\mathbf{R}) \left(E - T_{\mathrm{N}} - V_0 - \frac{1}{2}k^2 + i\varepsilon \right)^{-1} V_{\mathrm{dk}}^*(\mathbf{R}')\, d\Omega_k\, k\, dk. \quad (4.45)$$

The integration is performed over the direction Ω_k and the length k of the electron wave-vector $\mathbf{k}$. We do not indicate the type of the coupling amplitude $V_{\mathrm{dk}}^{(\pm)}$, because both signs ($\pm$) lead to the same result since they represent the same operator $H_{QP}\, G_P H_{PQ}$ in the two different bases $|\mathbf{k}^{(\pm)}\rangle$. The operator $F(E)$ is obviously nonlocal in the coordinate representation and it can be split in the Hermitian and the anti-Hermitian parts

$$F(E, \mathbf{R}, \mathbf{R}') = \Delta(E - T_{\mathrm{N}} - V_0, \mathbf{R}, \mathbf{R}') - \frac{i}{2}\Gamma(E - T_{\mathrm{N}} - V_0, \mathbf{R}, \mathbf{R}'), \quad (4.46)$$

where

$$\Gamma(\varepsilon, \mathbf{R}, \mathbf{R}') = 2\pi \int d\Omega_k\, k\, dk\, V_{\mathrm{dk}}(\mathbf{R})\, \delta(\varepsilon - \frac{1}{2}k^2) V_{\mathrm{dk}}^*(\mathbf{R}'), \quad (4.47)$$

$$\Delta(\varepsilon, \mathbf{R}, \mathbf{R}') = \frac{1}{2\pi}\, \wp \int d\varepsilon'\, \Gamma(\varepsilon', \mathbf{R}, \mathbf{R}')/(\varepsilon - \varepsilon'). \quad (4.48)$$

We have separated the Hermitian and anti-Hermitian part of $F(E)$ using the relation $(x + i\varepsilon)^{-1} = \wp \dfrac{1}{x} - i\pi\delta(x)$. For $\mathbf{R} = \mathbf{R}'$ the functions (4.47) and (4.48) are called the width $\Gamma(\varepsilon, \mathbf{R})$ and the level shift $\Delta(\varepsilon, \mathbf{R})$ of the discrete state $|d\rangle$ due to interaction with the continuum. We would also like to point out the importance to distinguish between the functions $\Gamma(\varepsilon, \mathbf{R})$ and $\Delta(\varepsilon, \mathbf{R})$ and the Hermitian and anti-Hermitian components of the nonlocal potential (4.46). Whereas $\Gamma(\varepsilon, \mathbf{R})$ and $\Delta(\varepsilon, \mathbf{R})$ are just functions of ε and $\mathbf{R}$, the components of $F(E)$ are operators acting on the nuclear Hilbert space. The important difference is that the operator $E - T_{\mathrm{N}} - V_0$ is substituted for ε in Equations 4.47 and 4.48, which means, for example, that the ordering of terms inside integral (4.47) is important.

As we saw in Equation 4.29, the resonant part of the T-matrix for the process of vibrational excitation can be written in terms of $Q|\psi^{(+)}\rangle$, that is, in terms of $|\psi^{(+)}\rangle = \langle d|\psi^{(+)}\rangle_r$, where the integration is performed only over electronic degrees of freedom as indicated by a subscript r, that is, the result is still a state in the nuclear part of the full Hilbert space. Equation 4.42 together with the definition of the nonlocal potential $F(E)$ implies

$$| \psi^{(+)} \rangle = | \phi^{(+)} \rangle + G_Q^{(+)}(E) F(E) | \psi^{(+)} \rangle, \quad (4.49)$$

where $G_Q^{(+)}(E) = (E - V_{\mathrm{d}} - T_{\mathrm{N}} + i\varepsilon)^{-1}$ and the function

$$| \phi^{(+)} \rangle = \langle d | \Phi_{\mathrm{i}}^{(+)} \rangle_r + \langle d | G_Q H_{QP} P | \Phi_{\mathrm{i}}^{(+)} \rangle_r \quad (4.50)$$

is determined by boundary conditions for the processes of interest. Formula (4.49) is the integral version of the fundamental equation describing uniquely dynamics of

the nuclear degrees of freedom. All electronic degrees of freedom are projected out and the formula contains only operators and states in the nuclear Hilbert space of the molecule. The state $|\psi^{(+)}\rangle$ is the unique solution of this equation, but the vector $|\psi^{(+)}\rangle$ depends on the channel of interest. There are two important channels for low energies. The electron–molecule collisions $e^- + AB$ (channel I) and the ion–atom[*] collisions $A + B^-$ (channel II). For these two channels, we have

$$|\Phi_{\mathrm{I}}^{(+)}\rangle = |v_i\rangle |\mathbf{k}_i^{(+)}\rangle \Rightarrow |\phi_{\mathrm{I}}^{(+)}\rangle = G_Q^{(+)}(E)V_{\mathbf{dk}_i}^{(+)}|v_i\rangle, \tag{4.51}$$

$$|\Phi_{\mathrm{II}}^{(+)}\rangle = |d\rangle |\mathbf{K}_i^{(+)}\rangle \Rightarrow |\phi_{\mathrm{II}}^{(+)}\rangle = |\mathbf{K}_i^{(+)}\rangle, \tag{4.52}$$

where $|v_i\rangle$ is the wave function of the initial vibrational state $\chi_{v_i}(\mathbf{R})$ of the molecule AB, $\mathbf{k}_i$ is the momentum of the incoming electron and $\mathbf{K}_i$ is the center of mass relative momentum for the ion–atom collision. Solutions $|\psi_{\mathrm{I}}^{(+)}\rangle, |\psi_{\mathrm{II}}^{(+)}\rangle$ of the fundamental Equation 4.49 with incoming boundary conditions $|\phi_{\mathrm{I}}^{(+)}\rangle$ and $|\phi_{\mathrm{II}}^{(+)}\rangle$, respectively, give the full nuclear dynamics of our problem for the electron–molecule and ion–atom collisions. Similarly, we can define the solutions $|\psi_{\mathrm{I}}^{(-)}\rangle, |\psi_{\mathrm{II}}^{(-)}\rangle$, which have $e^- + AB$ and $A + B^-$ channels as outgoing asymptotes.

Finally, we write explicit formulas for the T-matrix for each of the processes (4.1) and (4.3) in terms of $|\psi^{(\pm)}\rangle$. The resonant contribution to the T-matrices for VE, DA, and AD are

$$T_{\mathrm{VE}} \equiv \langle\Phi_{\mathrm{I}}^{(-)}|PH_{PQ}Q|\Psi^{(+)}\rangle = \langle v_f|V_{\mathbf{dk}_f}^{(-)*}|\psi_{\mathrm{I}}^{(+)}\rangle, \tag{4.53}$$

$$T_{\mathrm{DA}} \equiv \langle\Psi^{(-)}|QH_{QP}P|\Phi_{\mathrm{I}}^{(+)}\rangle = \langle\psi_{\mathrm{II}}^{(-)}|V_{\mathbf{dk}_i}^{(+)}|v_i\rangle, \tag{4.54}$$

$$T_{\mathrm{AD}} \equiv \langle\Phi_{\mathrm{I}}^{(-)}|PH_{PQ}Q|\Psi^{(+)}\rangle = \langle v_f|V_{\mathbf{dk}_f}^{(-)*}|\psi_{\mathrm{II}}^{(+)}\rangle, \tag{4.55}$$

where $\langle\psi_{\mathrm{II}}^{(-)}|$ is the unique solution of

$$\langle\psi_{\mathrm{II}}^{(-)}| = \langle\mathbf{K}_f^{(-)}| + \langle\psi_{\mathrm{II}}^{(-)}|F(E)G_Q^{(+)}(E). \tag{4.56}$$

The expression for T_{DA} apparently differs from Equation 4.38. In fact, here we used the principle of microreversibility and calculated the dissociative attachment from the final state wave function. The expression (4.38) can also be written in terms of Q-projection as follows:

$$T_{\mathrm{DA}} = \langle\Phi_{\mathrm{I}}^{(-)}|QH_{QP}P|\Psi^{(+)}\rangle = \langle\mathbf{K}^{(-)}|V_{\mathbf{dk}_i}^{(+)}|v_i\rangle + \langle\mathbf{K}^{(-)}|F(E)|\psi_{\mathrm{II}}^{(+)}\rangle, \tag{4.57}$$

where we used formula (4.41) to express $P|\Psi^{(+)}\rangle$. Both expressions for T_{DA} should give identical results which can be used for cross-checking of numerical results. All the expressions for T-matrices are valid on energy shell, that is, for example, for dissociative attachment the total energy E is identical to initial and final energies

$$E = \frac{1}{2\infty}K_f^2 = E_{v_i} + \frac{1}{2}k_i^2. \tag{4.58}$$

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[*] This general formulation also applies for A being polyatomic molecular fragment.

4.2.4 DIFFERENTIAL EQUATION FOR THE NUCLEAR WAVE FUNCTION

In this section, we briefly show the derivation of the differential form of the basic equation for the nonlocal dynamics. We start with Equation 4.28 written in the form applicable for both electron–molecule and ion–atom collisions

$$|\Psi^{(+)}\rangle = |\Phi^{(+)}\rangle + \frac{1}{E - H + i\varepsilon} V_2 |\Phi^{(+)}\rangle, \tag{4.59}$$

where $|\Phi^{(+)}\rangle = |\Phi_I^{(+)}\rangle$ or $|\Phi^{(+)}\rangle = |\Phi_{II}^{(+)}\rangle$ is the appropriate solution of $H_1 = H_P + H_Q$, see Equations 4.51 and 4.52. The boundary conditions for function (4.59) are a little bit complicated. It is easier to work with

$$|\Psi_{sc}^{(+)}\rangle = |\Psi^{(+)}\rangle - |\Phi^{(+)}\rangle, \tag{4.60}$$

which is purely the outgoing wave in infinity. This type of boundary conditions can then be enforced using some variant of complex absorption potential or complex scaling methods. Equation 4.59 implies

$$(E - H)|\Psi_{sc}^{(+)}\rangle = V_2|\Phi^{(+)}\rangle = [H_{PQ} + H_{QP}]|\Phi^{(+)}\rangle. \tag{4.61}$$

We then project this equation using both projection operators P and Q

$$(E - H_Q)Q|\Psi_{sc}^{(+)}\rangle - H_{QP}P|\Psi_{sc}^{(+)}\rangle = H_{QP}P|\Phi^{(+)}\rangle, \tag{4.62}$$

$$(E - H_P)P|\Psi_{sc}^{(+)}\rangle - H_{PQ}Q|\Psi_{sc}^{(+)}\rangle = H_{PQ}Q|\Phi^{(+)}\rangle. \tag{4.63}$$

Finally, we express the P-part of $|\Psi_{sc}^{(+)}\rangle$ as

$$P|\Psi_{sc}^{(+)}\rangle = G_P(E)H_{PQ}[Q|\Psi_{sc}^{(+)}\rangle + Q|\Phi^{(+)}\rangle] \tag{4.64}$$

and substitute this in the first of the two-projected equations

$$[E - H_Q - F]Q|\Psi_{sc}^{(+)}\rangle = H_{QP}P|\Phi^{(+)}\rangle + FQ|\Phi^{(+)}\rangle. \tag{4.65}$$

To be more specific, we write this final equation in the coordinate representation for $\Psi_d^{(+)}(\mathbf{R}) = \langle d|\Psi_{sc}^{(+)}\rangle_r$ and for electron–molecule collisions, that is, for $|\Phi^{(+)}\rangle = |\Phi_I^{(+)}\rangle$,

$$(E - T_R - V_d(\mathbf{R}))\Psi_d^{(+)}(\mathbf{R}) - \int d\mathbf{R}' F(E, \mathbf{R}, \mathbf{R}')\Psi_d^{(+)}(\mathbf{R}') = V_{d\mathbf{k}_i}^{(+)}(\mathbf{R})\chi_{\nu_i}(\mathbf{R}) \tag{4.66}$$

with the nonlocal, complex, and energy-dependent potential $F(E) = H_{QP}G_P(E)H_{PQ}$ given by formula (4.45).

Once the solution $\Psi_d^{(+)}$ of Equation 4.66 is obtained, it can be used to evaluate the *resonant* part of the *T*-matrix with Equation 4.30 and the corresponding resonant contribution to the vibrational excitation cross section. The dissociative attachment can also be calculated using Equation 4.57 or from the asymptotic behavior of $\Psi_d^{(+)}$. (Note that normalization of the wave function is fixed by the right-hand side of the Schrödinger Equation 4.66.) For example, the *s*-wave contribution reads

$$\sigma_{\nu_i}^{DA}(E) = \frac{2\pi^2}{k_i^2} \frac{K_{DA}}{\mu} \lim_{R \to \infty} |\Psi_d^+(R)|^2 . \tag{4.67}$$

4.3 DETAILED TREATMENT OF ANGULAR MOMENTUM FOR DIATOMIC MOLECULES

The treatment up to now was completely general regarding the molecular vibrational degrees of freedom. The variable $\mathbf{R}$ could represent coordinates for any number of atomic nuclei in the studied molecule. The nuclear motion is then taking place in the many-dimensional space. However, for more than 1–2 degrees of freedom, the numerical effort needed to solve the corresponding integral equations would be enormous. Up to now, there are only few attempts to go beyond one degree of freedom. In this chapter, we will solve completely the dynamics for the case of diatomic molecules in terms of partial wave expansions for both the electronic and nuclear parts of the wave function. As a result, the dynamics reduces to solution of a set of coupled one-dimensional equations. The numerical methods suitable to treat such problems are then discussed in the following sections.

The partial wave expansion follows to some extent the work of Bieniek (1978), originally designed for Penning ionization. We briefly give the equivalent derivation for AD and also the formulas for DA and VE.

We start with the partial wave expansion of the discrete–continuum coupling $V_{\mathrm{dk}}(\mathbf{R})$ in the coordinate system fixed in the molecule and with the z-axis along the molecular symmetry axis. We will assume that the electronic state of the molecule AB has the Σ symmetry and the same symmetry is also assumed for the discrete state $|d\rangle$. This assumption considerably simplifies our derivation and most of the systems discussed in the next chapter are of this form. Generalization for different symmetry would be straightforward only with little longer expressions. When the Σ symmetry is assumed, the scattering problem exhibits the symmetry with respect to rotations along the internuclear axis so that the partial expansion of $|\mathbf{k}^{(+)}\rangle$ is of the form

$$\langle \mathbf{r} \mid \mathbf{k}^{(+)} \rangle = \sum_{l'lm} \phi_{l'lm}(k,r) Y_{l'm}(\hat{r}) Y_{lm}^*(\hat{k}). \tag{4.68}$$

With $\hat{k}$, we denote the unit vector in the direction of $\mathbf{k}$. Insertion of this expansion into the definition (4.13) of $V_{\mathrm{dk}}(\mathbf{R})$ yields

$$V_{\mathrm{dk}} = \sum_{l} Y_{l0}^*(\hat{k}) V_{dkl} = \sum_{l} \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) V_{dkl}, \tag{4.69}$$

where

$$V_{dkl} = \sum_{l'} \int \mathrm{d}r \mathrm{d}r' \phi_{d}^*(\mathbf{r}) H_{\mathrm{el}} \phi_{ll'm}(k,r) Y_{l'm}(\hat{r}) \Big|_{m=0}. \tag{4.70}$$

The terms with $m \neq 0$ vanish due to Σ symmetry. Expansion (4.69) was derived in the coordinate system fixed in the molecule and θ is the angle between $\hat{k}$ and $\hat{R}$. To rewrite the expansion into the center off mass system fixed in space, we employ the relation

$$\frac{2l+1}{4\pi} P_l(\hat{a} \cdot \hat{b}) = \sum_{m=-l}^{l} Y_{lm}(\hat{a}) Y_{lm}^*(\hat{b}) \tag{4.71}$$

to obtain

$$V_{d\mathbf{k}}(\mathbf{R}) = \sum_{lm} \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\hat{R}) Y_{lm}^*(\hat{k}) V_{dkl}(R). \tag{4.72}$$

This formula, unlike the previous ones, employs the spherical harmonics $Y_{lm}(\hat{n})$ in arbitrary coordinate system, that is, spherical coordinates are no longer measured from the internuclear axis $\hat{R}$.

In the second step, we expand the nonlocal part F of the effective Hamiltonian H_{eff}. This has been done in detail elsewhere (Bieniek 1978) and we will only outline the derivation briefly. The potential $V_0(R)$ is spherically symmetric, which means that the Green's function in the definition (4.45) is diagonal in the angular momentum representation

$$\langle \mathbf{R}(E - T_N - V_0 + i\varepsilon)^{-1} \mathbf{R}' \rangle = \sum_{JM} Y_{JM}(\hat{R}) \frac{1}{R} G_{0J}(E, R, R') \frac{1}{R'} Y_{JM}^*(\hat{R}'). \tag{4.73}$$

Employing this formula and expansion (4.72) in the definition (4.45) yields

$$\int d\hat{R}\, d\hat{R}'\, Y_{JM}^*(\hat{R}) F(E, \mathbf{R}, \mathbf{R}') Y_{J'M'}^*(\hat{R}') = \int dk\, d\hat{k}\, d\hat{R}\, d\hat{R}' \sum_{l_1 m_1} \sum_{J_0 M_0} \sum_{l_2 m_2}$$

$$Y_{JM}^*(\hat{R}) \sqrt{\frac{4\pi}{2l_1+1}} Y_{l_1 m_1}(\hat{R}) Y_{l_1 m_1}^*(\hat{k}) V_{dkl_1}(R)$$

$$\times Y_{J_0 M_0}(\hat{R}) \frac{1}{R} G_{0J_0}(E, R, R') \frac{1}{R'} Y_{J_0 M_0}^*(\hat{R}')$$

$$\times \sqrt{\frac{4\pi}{2l_2+1}} V_{dkl_2}(R') Y_{l_2 m_2}(\hat{k}) Y_{l_2 m_2}^*(\hat{R}') Y_{J'M'}(\hat{R}') \tag{4.74}$$

Since the spherical harmonics are orthogonal, we can perform integration over $d\hat{k}$ and then by employing the relation for complex conjugation of spherical harmonics

$$Y_{lm}^*(\hat{n}) = (-1)^m Y_{l-m}(\hat{n}), \tag{4.75}$$

and

$$\int d\hat{n}\, Y_{l_1 m_1}(\hat{n}) Y_{l_2 m_2}(\hat{n}) Y_{l_3 m_3}(\hat{n})$$

$$= \frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{4.76}$$

for integrals of products of three harmonics the integrations over $d\hat{R}$ and $d\hat{R}'$ can be performed as well. Finally, using orthogonality of Wigner 3j symbols

$$\sum_{m_1 m_2} \begin{pmatrix} l_1 & l_2 & J \\ m_1 & m_2 & M \end{pmatrix} \begin{pmatrix} l_1 & l_2 & J' \\ m_1 & m_2 & M' \end{pmatrix} = \frac{1}{2J+1} \delta_{JJ'} \delta_{MM'} \delta(l_1, l_2, J), \tag{4.77}$$

we obtain

$$\int d\hat{R}\, d\hat{R}' Y_{JM}^*(\hat{R}) F(E, \mathbf{R}, \mathbf{R}') Y_{J'M'}^*(\hat{R}') = \frac{1}{RR'} \delta_{JJ'} \delta_{MM'} f_J(E, R, R'), \qquad (4.78)$$

where

$$f_J(E, R, R') = \sum_{lJ'} (2J' + 1) \begin{pmatrix} l & J' & J \\ 0 & 0 & 0 \end{pmatrix}^2$$
$$\int dk V_{dkl}(R) G_{0J'}(E - k^2/2, R, R') V_{dkl}^*(R') \qquad (4.79)$$

or

$$F(E, \mathbf{R}, \mathbf{R}') = \sum_{JM} Y_{JM}(\hat{R}) \frac{1}{R} f_J(E, R, R') \frac{1}{R'} Y_{JM}^*(\hat{R}'). \qquad (4.80)$$

This form of expansion of the nonlocal operator F is a consequence of its spherical symmetry. It is an important property since equations for partial waves with different J are not coupled through the nonlocal potential although they are coupled with several partial waves of the molecular channel (sum over J' in Equation 4.79) accounting thus for angular momentum of the electron released in the detachment or captured in the attachment process.

A next step is to define the partial wave expansion of the wave functions. It is simpler to start with the ion–atom wave function $|\psi_{II}\rangle$. We define partial waves ψ_J and φ_J with

$$\langle \mathbf{R} | \mathbf{K}^{(+)} \rangle = N \sum_{JM} i^J \frac{1}{KR} \varphi_J^{II}(R) Y_{JM}^*(\hat{E}) Y_{JM}(\hat{R}) \qquad (4.81)$$

$$\langle \mathbf{R} | \psi_{II}^{(+)} \rangle = N \sum_{JM} i^J \frac{1}{KR} \psi_J^{II}(R) Y_{JM}^*(\hat{E}) Y_{JM}(\hat{R}) \qquad (4.82)$$

and expand the Green's function

$$\langle \mathbf{R} | G_Q^{(+)}(E) | \mathbf{R}' \rangle = \sum_{JM} Y_{JM}(\hat{R}) \frac{1}{R} G_{QJ}(E, R, R') \frac{1}{R'} Y_{JM}^*(\mathbf{R}'). \qquad (4.83)$$

The Lippmann–Schwinger equation 4.49 yields

$$\psi_J^{II}(R) = \varphi_J^{II}(R) + \int dR' dR'' G_{QJ}(E, R, R') f_J(E, R', R'') \psi_J^{II}(R''). \qquad (4.84)$$

We introduced the wave number $K = \sqrt{2 \propto E}$ in Equations 4.81 and 4.82 and the normalization coefficient $N = 4\pi \sqrt{\mu K} (2\pi)^{-3/2}$ ensures the energy normalization

$$\langle \mathbf{K}^{(+)} | \mathbf{K}'^{(+)} \rangle = \delta \left(\frac{K^2}{2\mu} - \frac{K'^2}{2\mu} \right). \qquad (4.85)$$

By employing the partial wave expansions in formula (4.55) for the associative detachment T-matrix and writing the wave functions $|\nu\rangle$ for bound states of AB in the usual separated form

$$\langle \mathbf{R} \mid \nu \rangle = \frac{1}{R} \chi_{n_f J_f}(R) Y_{J_f M_f}(\hat{R}), \tag{4.86}$$

we obtain

$$
\begin{aligned}
T_{\mathrm{AD}}(\mathbf{k}_f, \mathbf{E}) &= \langle \nu_f | V_{\mathrm{dk}_f}^{(-)*} | \psi_{\mathrm{II}}^{(+)} \rangle \\
&= \int R^2 \mathrm{d}R \mathrm{d}\hat{R} \sum_{lm} \sum_{JM} \frac{1}{R} \chi_{n_f J_f}(R) Y_{J_f M_f}^*(\hat{R}) \\
&\quad \times \sqrt{\frac{4\pi}{2l+1}} Y_{lm}^*(\hat{R}) Y_{lm}(\hat{k}\ ) V_{\mathrm{dk}_f l}^{(-)*}(R) \\
&\quad \times N i^J \frac{1}{KR} \psi_J^{\mathrm{II}}(R) Y_{JM}^*(\hat{E}) Y_{JM}(\hat{R}) \\
&= \frac{N}{K} \sum_{lmJM} t_{Jl}^{\mathrm{AD}}(\nu_f, J_f, E) Y_{lm}(\hat{k}) Y_{JM}^*(\hat{E}) \\
&\quad \times i^J \sqrt{(2J_f+1)(2J+1)} \begin{pmatrix} J_f & l & J \\ M_f & m & M \end{pmatrix} \begin{pmatrix} J_f & l & J \\ 0 & 0 & 0 \end{pmatrix}, \tag{4.87}
\end{aligned}
$$

where

$$t_{Jl}^{\mathrm{AD}}(\nu_f, J_f, E) = \int \mathrm{d}R \chi_{n_f J_f}(R) V_{\mathrm{dk}_f l}^{(-)*}(R) \psi_J^{\mathrm{II}}(R). \tag{4.88}$$

The integration formula (4.76) has been used again. The differential cross section for the associative detachment reads

$$\frac{\mathrm{d}\sigma_{\mathrm{AD}}}{\mathrm{d}\Omega}(\mathbf{k}_f, \mathbf{E}) = (2\pi)^4 \frac{g_i}{K^2} | T_{\mathrm{AD}}(\mathbf{k}_f, \mathbf{E}) |^2, \tag{4.89}$$

where g_i is the statistical factor for the discrete state potential. This factor applies only in the case that more potentials are connected to the same asymptote. The number g_i then gives the statistical probability for particles to move along the potential curve V_d. This is, for example, the case of $H + H^-$, where there are two potentials connected to the asymptote. The attractive $^2\Sigma_u$ state and the repulsive $^2\Sigma_g$ state which contributes only little to the AD cross section. The statistical factor in this example is thus $g_i = 1/2$. Some caution is also needed in the case of the homonuclear systems like that described in Bieniek and Dalgarno (1979) for H_2, where J-dependent g-factor is present as a result of different nuclear spin. Formula (4.89) can further be simplified using the orthogonality relations (4.77) if we want to know only the integral cross section (integrated over $\hat{k}_f$ and averaged over $\hat{E}$)

$$\sigma_{\mathrm{AD}}(k_f, E) = \frac{2\pi g_i}{KE} \sum_{lJ} (2J+1) \begin{pmatrix} J_f & l & J \\ 0 & 0 & 0 \end{pmatrix}^2 | t_{Jl}^{\mathrm{AD}}(\nu_f, J_f, E) |^2. \tag{4.90}$$

The total AD cross section is obtained via summation over all accessible final states ($E_{vfJf} < E$) or using the formula

$$\sigma_{tot}(E) = \frac{2\mu g_i}{KE} \sum_J (2J + 1)$$

$$+ \int dR\, dR'\, \psi_J^{II}(R)^* [f_J(E, R, R') - f_J^*(E, R', R)] \psi_J^{II}(R'), \qquad (4.91)$$

which can be derived from the total flux lost from the discrete state channel due to the non-Hermitian part of the nonlocal potential F. Comparison of the two expressions for σ_{tot} was used as a test for numerical solution of the resonant scattering problem by Bieniek (1980) and proved failure of the local complex potential approximation for associative detachment in $H^- + H$ collisions. Using the expansion of $G_{0J}(E)$ in the sum over the bound states $\chi_{vJ}(R)$ in the definition (4.79), it is possible to show that the two expressions for σ_{tot} are equivalent if no further approximation is imposed on $F(E)$.

The T-matrix and the cross section for dissociative attachment can be obtained from the principle of detailed balance since the processes AD and DA are mutually reverse. It is

$$T_{DA}(\hat{E}, \hat{k}) = T_{AD}^*(\hat{k}, \hat{E}) \qquad (4.92)$$

and the integral cross section is

$$\sigma_{DA}(E, k_i) = (2\pi)^4 \frac{g_i}{2k_i} |T_{DA}(\hat{E}, \hat{k}_i)|^2. \qquad (4.93)$$

Let us now investigate the vibrational excitation process. Employing the relation

$$G^{(+)}(E) = G_Q^{(+)}(E) + G_Q^{(+)}(E) F(E) G^{(+)}(E) \qquad (4.94)$$

for the complete Green's function $G^{(+)}(E) \equiv (E - H_{eff} + i\varepsilon)^{-1}$, Equations 4.49 and 4.51 yield

$$|\psi_I^{(+)}\rangle = G^{(+)}(E) V_{d\mathbf{k}_i}^{(+)} |\nu_i\rangle \qquad (4.95)$$

and (4.53) implies

$$T_{VE} = \langle \nu_f | V_{d\mathbf{k}_f}^{(-)*} G^{(+)}(E) V_{d\mathbf{k}_i}^{(+)} |\nu_i\rangle. \qquad (4.96)$$

Since F is spherically symmetric, it is

$$\langle \mathbf{R} | G^{(+)}(E) | \mathbf{R}'\rangle = \sum_{JM} Y_{JM}(\hat{R}) \frac{1}{R} G_J(E, R, R') \frac{1}{R'} Y_{JM}^*(\mathbf{R}'). \qquad (4.97)$$

We can thus use a similar procedure as for T_{AD} to obtain (for the resonance contribution)

$$T_{\text{VE}} = \sum_{l_1 m_1} \sum_{l_2 m_2} \sum_{JM} \int dR dR' \chi_{n_f J_f}(R) V_{dk_f l_1}^{(-)*}(R) G_J(E,R,R') V_{dk_i l_2}^{(+)}(R') \chi_{n_i J_i}(R')$$

$$\times (-1)^{M_f + m_1 + M} Y_{l_1 m_1}^*(\hat{\vec{k}}_f) Y_{l_2 m_2}^*(\hat{\vec{k}}_i)(2J+1)\sqrt{(2J_f+1)(2J_i+1)}$$

$$\times \begin{pmatrix} J_f & l_1 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_f & l_1 & J \\ -M_f & -m_1 & M \end{pmatrix} \begin{pmatrix} J & l_2 & J_i \\ -M & m_2 & M_i \end{pmatrix} \begin{pmatrix} J & l_2 & J_i \\ 0 & 0 & 0 \end{pmatrix}. \quad (4.98)$$

The formula for the vibrational excitation process is more complicated than Equation 4.87 for associative detachment since the angular momentum is transferred twice between the electron and the molecule—once during the resonant capture of an electron into the discrete state and for the second time in the autoionization. Even if we start with the molecule AB in a state v_i with a defined angular momentum, several partial waves are populated in $|\psi_I^{(+)}\rangle$ if $\Gamma_l \neq 0$ for $l > 0$. The state $|\psi_I^{(+)}\rangle$ can subsequently decay in many states v_f (with many different J_f). This complication does not apply if we introduce the following approximation.

4.3.1 Low-Energy s-Wave Approximation

Since the electron is a light particle, it feels strongly the repulsive barrier $\{l(l+1)\}/2r^2$ ($m_e = 1$ in atomic units). For large r, we can neglect the other forces and assume that the potential is spherically symmetric,[*] that is, expansion (4.68) reduces to

$$\langle \mathbf{r} | \mathbf{k}^{(+)} \rangle = \sum_{lm} \phi_{lm}(k,r) Y_{lm}(\hat{r}) Y_{lm}^*(\hat{k}). \quad (4.99)$$

If the electron energy $(1/2)k^2$ is small (near threshold energies), it is reasonable to assume that the electron cannot penetrate the repulsive barrier and $\phi_{lm}(k,r) = 0$ for r small and $l > 0$, that is,

$$V_{dkl} = 0 \quad \text{for } l > 0 \quad (4.100)$$

and

$$V_{d\mathbf{k}} = \sqrt{4\pi} Y_{00}(\hat{R}) Y_{00}(\hat{k}) V_{dk}(R), \quad (4.101)$$

where with $V_{dk}(R)$ we denoted $V_{dkl=0}(R)$. As a consequence, the sums over l can be dropped out in all previous formulas for near threshold processes, which simplifies the problem significantly. Thus, using relation

$$\begin{pmatrix} 0 & J' & J \\ 0 & 0 & 0 \end{pmatrix} = (-1)^J \delta_{JJ'} / \sqrt{2J+1}, \quad (4.102)$$

formula (4.79) yields

$$f_J(E,R,R') = \int dk V_{dk}(R) G_{0J}(E - k^2/2, R, R') V_{dk}^*(R'). \quad (4.103)$$

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[*] This is not true in the case the molecule AB possesses an electric dipole. Influence of approximation (4.100) to the cross sections then needs further investigation.

Similarly employing (4.102) and

$$\begin{pmatrix} J & J' & 0 \\ M & -M' & 0 \end{pmatrix} = (-1)^{J-M} \delta_{JJ'} \delta_{MM'} / \sqrt{2J+1} \tag{4.104}$$

the associative detachment T-matrix is found to be

$$T_{AD}(\mathbf{k}_f, \mathbf{E}) = \frac{N}{K} \frac{i^{J_f}}{\sqrt{4\pi}} Y^*_{J_f M_f}(\hat{E}) \int dR \chi_{n_f J_f}(R) V^{(-)*}_{dk_f}(R) \psi^{II}_{J_f}(R) \tag{4.105}$$

and the cross section

$$\sigma_{AD}(k_f, E) = \frac{2\pi g_i}{KE} \left| \int dR \chi_{n_f J_f}(R) V^{(-)*}_{dk_f}(R) \psi^{II}_{J_f}(R) \right|^2. \tag{4.106}$$

The description of vibrational excitation also considerably simplifies if we neglect the angular momentum of the electron. The T_{VE} thus reduces to

$$T_{VE}(\mathbf{k}_f, \mathbf{k}_i) = \frac{1}{4\pi} \delta_{J_f J_i} \delta_{M_f M_i} t^{VE}_J(n_f, k_f, n_i, k_i), \tag{4.107}$$

where

$$T^{VE}_J(n_f, k_f, n_i, k_i) = \int dR \, dR' \chi_{n_f J_f}(R) V^{(-)*}_{dk_f}(R) J(E, R, R') V^{(+)}_{dk_i}(R') \chi_{n_i J_i}(R'). \tag{4.108}$$

The presence of Kronecker delta $\delta_{J_f J_i}$ and $\delta_{M_f M_i}$ is the consequence of the angular momentum conservation for the molecule AB, when angular momentum of the electron has been neglected. We thus do not have the possibility to describe rotational excitation unless the assumption (4.100) is rejected. The formula for the partial contribution to T_{VE} can easily be transformed into the form

$$t^{VE}_J(n_f, k_f, n_i, k_i) = \int dR \chi_{n_f J}(R) V^{(-)*}_{dk_f}(R) \psi^I_J(R), \tag{4.109}$$

where $\psi^I_J(R)$ is the unique solution of

$$\psi^I_J(R) = \varphi^I_J(R) + \int dR' dR'' G_{QJ}(E, R, R') f_J(E, R', R'') \psi^I_J(R'') \tag{4.110}$$

and we have introduced the following abbreviation

$$\varphi^I_J(R) = \int dR' G_{QJ}(E, R, R') V^{(+)}_{dk_i}(R') \chi_{n_i J}(R'). \tag{4.111}$$

Equation 4.110 is the partial wave expansion of Equation 4.49 under the assumption (4.100). Finally, the angle-integrated VE cross section reads

$$\sigma_{VE}(n_f, k_f, n_i, k_i) = \frac{(2\pi)^3}{4k_i} |t^{VE}_J(n_f, k_f, n_i, k_i)|^2, \tag{4.112}$$

with J being the angular momentum of the initial state $|v_i\rangle$.

4.3.2 Parametrization of the Nonlocal Resonance Model

It is clear on the basis of the previous discussion of the theory of resonant collisions that the nuclear dynamics and the cross sections are fully determined if the functions

$$V_0(R), V_\mathrm{d}(R) \quad \text{and} \quad V_{\mathrm{d}kl}(R)$$

are known. As was shown in the last section $V_{\mathrm{d}kl}(R)$ with $l > 0$ does not contribute significantly for small energies ε and only the function $V_{\mathrm{d}k}(R)$ is important for the dynamics.[*] Further simplification can be achieved thanks to the extraction of all fast dependencies on ε and R from the background scattering due to the extraction of the resonance part of the wave function. It follows that the discrete-state-continuum coupling $V_{\mathrm{d}k}(R)$ is a slowly varying function of ε and R. The coupling $V_{\mathrm{d}k}(R)$ is a complex quantity, but the overall phase is not important, since $V_{\mathrm{d}k}(R)$ is present together with $V_{\mathrm{d}k}^*(R')$ in the nonlocal potential and only the absolute value of its matrix elements is needed for the cross sections. What is important is the relative phase between $V_{\mathrm{d}k}(R)$ and $V_{\mathrm{d}k}(R')$ in two different points R and R' but since the nonlocal resonant dynamics is restricted to a small region near the equilibrium distance R_0 of the molecule AB and since the coupling is slowly varying with R it is reasonable to assume that this relative phase can be neglected and $V_{\mathrm{d}k}(R)$ can be regarded as being a real number.[†] This assumption is unnecessary simplification if the quantities $V_{\mathrm{d}k}(R)$ are constructed directly from electron–molecule scattering calculation, but it is very helpful, when $V_{\mathrm{d}k}(R)$ is constructed from incomplete information about the electron dynamics.

Expansion of the discrete-state-continuum coupling into a sum of separable terms in energy ε and internuclear distance R is often performed

$$V_{\mathrm{d}k}(R) = \sum_i f_i(\varepsilon) g_i(R). \tag{4.113}$$

As will be discussed later, the separation of energy and distance is crucial for time demands of actual numerical calculation. It has been shown that even one term in the expansion often gives qualitatively correct results for the description of the resonant dynamics.

The nonlocal resonant dynamics described by the four functions $V_0(R)$, $V_\mathrm{d}(R)$, $f_i(\varepsilon)$, and $g_i(R)$ will be further referred to as the nonlocal resonance model of the dynamics in this work. The calculation of the function $V_0(R)$ for the particular molecule AB is a routine task of quantum chemistry and a large variety of the methods have been developed in the last few decades to treat this problem. The direct determination of $V_\mathrm{d}(R)$ and $V_{\mathrm{d}k}(R)$ is still far from routine. The calculations for the range of both ε and R are available only for the most fundamental systems like $H_2 + e^-$ (Berman et al. 1985) and $HeH^+ + e^-$ (Movre and Meyer 1997). It is therefore useful to use some analytic knowledge about the behavior of the model functions like asymptotic expansions at low energy.

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[*] There are some exceptional cases like H_2, where s-wave is forbidden by symmetry and $l = 1$ is the dominant contribution.

[†] The phase factor in $V_{\mathrm{d}k}(R)$ equals to the square root of the background scattering S-matrix $e^{\mathrm{i}\delta_{\mathrm{bg}}}$.

The threshold behavior of the discrete-state-continuum coupling $V_{dk}(R)$ for the small energies ε is determined by the long-range electron–molecule forces in accordance with the threshold law of Wigner (1948). If the molecule AB does not possess an electric dipole, the long-range electron–molecule interaction vanishes faster than r^{-2} and the threshold behavior of the coupling is (Domcke 1991)

$$\Gamma_l(\varepsilon) \equiv 2\pi \, | \, V_{dkl}(R) \, |^2 \sim \varepsilon^{(2l+1)/2}. \tag{4.114}$$

As discussed before, only the lowest l allowed by symmetry is really important, which usually is $l = 0$. In the case of polar molecules, the threshold behavior depends on the dipole moment D of the molecule. For $D < D_{\text{crit}} = 1.625$ Debye, it is (Domcke 1991)

$$\Gamma(\varepsilon) \sim E^\alpha, \tag{4.115}$$

where

$$\alpha = \sqrt{d + \frac{1}{4}} \tag{4.116}$$

and d is a dimensionless-reduced dipole moment given by the lowest eigenvalue of an infinite-dimensional tridiagonal matrix (Crawford 1967). If the molecule possesses a supercritical dipole $D > D_{\text{crit}}$ bound states exist in electron–molecule channel and the threshold behavior is more complicated. Similar situation is faced in the case of Penning ionization or dissociative recombination, where the electron is subjected to Coulomb force in the $e^- + AB^+$ channel. Nonlocal dynamics for these cases will not be investigated in this work.

The threshold law (4.114) or (4.115) fixes the form of $f_i(\varepsilon)$ near the origin $\varepsilon = 0$ and both $f_i(\varepsilon)$ and $g_i(R)$ must vanish at infinity. The value of $V_d(R)$ at infinity is fixed since $E_d = V_d - V_0$ evaluated in $R = \infty$ equals to the electron affinity of the atom A (or B).

Methods for construction of $V_d(R)$, $V_{de}(R)$ from *ab initio* fixed-R electron–molecule scattering data and other *ab initio* information will be given in the following chapter.

4.4 NUMERICAL TREATMENT OF THE NUCLEAR DYNAMICS EQUATIONS

The problem of resonant electron–molecule or ion–atom scattering has been transformed into solution of the one-dimensional Lippmann–Schwinger equation in the previous sections. The equation contains a rather complicated quantity—the nonlocal potential, resulting from a coupling of the discrete resonant state with the continuum, which has to be calculated first. As soon as the solution of the equation is known, the cross sections are easily found by evaluating the matrix elements of the discrete-state-continuum coupling V_{dk}. The general scheme for the solution of the problem can be summarized as follows:

1. To find the scattering solution $\varphi_J(R)$ and the Green's function $G_{QJ}(E)$ for the local potential V_d.
2. To calculate the nonlocal potential $f_J(E)$. As shown later, this is closely related to calculation of bound states $|v\rangle$ in the potential V_0.

3. To solve the Lippmann–Schwinger equation for the wave functions $\psi_J^I(R)$ or $\psi_J^{II}(R)$, respectively.
4. To calculate the *T*-matrix elements and cross sections (or other quantities of interest) from $\psi_{I,J}(R)$ or $\psi_J^{II}(R)$.

Step 4 is a trivial application of the formulas derived earlier. Computational procedures to perform the other three steps are outlined below.

4.4.1 Solution to the Local Problem

There have been developed large variety of methods to solve the Lippmann–Schwinger equation for a local potential in the past few decades and it is nowadays a routine task. First of all the Lippmann–Schwinger equation

$$\varphi_J(R) = u_J(R) - \frac{2\mu}{K} \int dR u_J(R_<) v_J(R_>) V_d(R') \varphi_J(R'), \qquad (4.117)$$

where $R_> = \max(R, R')$, $R_< = \min(R, R')$ and the functions u_J and v_J are given in terms of the spherical Bessel functions j_J and h_J

$$u_J(R) = KRj_J(KR), \qquad (4.118)$$

$$v_J(R) = iKRh_J(KR) \qquad (4.119)$$

are equivalent to the Schrödinger equation

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1)}{2\mu R^2} + V_d(R) \right) \varphi_J(R) = E\varphi_J(R) \qquad (4.120)$$

with corresponding boundary conditions. Standard finite-difference methods like algorithms of Numerov or Runge–Kutta can be used to solve this equation. Special methods for the case when $\varphi_J(R)$ is a fast oscillating function have also been developed (Gordon 1969, Gordon 1970). We prefer to solve the integral Equation 4.117 directly. The solution of Equation 4.117 gives the correct normalization automatically, whereas the normalization has to be found afterwards when solving the differential Schrödinger equation. As we will see later, by solving the Lippmann–Schwinger equation, we obtain also the *T*-matrix for the local problem as a byproduct. Another advantage of the integral equation formulation is the possibility of increasing the numerical precision by means of the Romberg quadrature (Horáček 1989). The long-range rotational energy term $J(J + 1)/2\mu R^2$ is treated exactly in the Lippmann–Schwinger equation method. The price for this is the occurrence of the Bessel functions in the equation, which must be calculated at many points. Nevertheless, this does not slow the calculation considerably if the solution is required for a large number of *J* since a very efficient method for calculation of large number of the Bessel functions by means of stable recurrence relations has been developed (Gillman and Fiebig 1988).

The method presented here for solving Equation 4.117 is described in detail in the article of Horáček (1989). Here, we only outline the principles and generalize the method for finding the irregular solution and the Green's function.

4.4.2 REGULAR SOLUTION

We will omit the subscripts J and d in this and the following section. The Equation 4.117 can easily be rewritten in the form

$$\varphi(R) = Au(R) - \frac{2\mu}{K} \int_0^R dR'[v(R)u(R') - u(R)v(R')]V(R')\varphi(R'), \qquad (4.121)$$

where

$$A = 1 - \frac{2\mu}{K} \int_0^\infty v(R')V(R')\varphi(R')dR'. \qquad (4.122)$$

In other words, if we introduce the function $f(R) = \phi(R)/A$, we obtain

$$f(R) = [1 - \beta(R)]u(R) + \alpha(R)v(R), \qquad (4.123)$$

where

$$\alpha(R) = -\frac{2\mu}{K} \int_0^R dR' u(R')V(R')f(R'), \qquad (4.124)$$

$$\beta(R) = -\frac{2\mu}{K} \int_0^R dR' v(R')V(R')f(R'). \qquad (4.125)$$

The constant A can be found from

$$A = (1 - \beta(\infty))^{-1} \qquad (4.126)$$

and the T-matrix for elastic scattering is given by the formula

$$t \equiv -\frac{2\mu}{K} \int_0^\infty dR\, u(R)V(R)\varphi(R) = \alpha(\infty)[1 - \beta(\infty)]^{-1}. \qquad (4.127)$$

Numerical solution of the integral Equation 4.117 on a grid $R = x_1,\ldots,x_n$ is then based on Equation 4.123. The trapezoidal rule is used for the integrals (4.124) and (4.125). We can observe that the terms with $f(R' = R)$ vanish in Equation 4.123 which can be used to calculate $f(x_{i+1})$ if $f(x_1),\ldots,f(x_i)$ are known. The use of the trapezoidal rule also facilitates the possibility to speed the convergence using the Romberg scheme.

4.4.3 IRREGULAR SOLUTION AND GREEN'S FUNCTION

The regular solution of the Schrödinger Equation 4.120 is the solution obeying the boundary condition $\varphi_{(r)}(R = 0) = 0$. Since $u(R = 0) = 0$, we can see from (4.121) that the solution of (4.117) is indeed the regular solution. The irregular solution on the other hand is the solution obeying the condition $\varphi_{(i)}(R \to \infty) \sim v(R)$. The Green's function $G_{QJ}(E, R, R')$ can be written in terms of these two solutions as

$$G_{QJ}(E, R, R') \equiv \langle R \mid \left(E + \frac{1}{2\mu} \frac{\mathrm{d}^2}{\mathrm{d}R^2} - \frac{J(J+1)}{2\mu R^2} - V(R) + i\varepsilon \right)^{-1} \mid R' \rangle \tag{4.128}$$

$$= -\frac{2\mu}{K} \varphi_{(r)}(R_<) \varphi_{(i)}(R_>).$$

It is easy to show that $\varphi_{(i)}(R)$ is the solution of

$$\varphi_{(i)}(R) = v(R) - \frac{2\mu}{K} \int\limits_0^\infty \mathrm{d}R u(R_<) v(R_>) V(R') \varphi_{(i)}(R'), \tag{4.129}$$

which can be rearranged into the form

$$\varphi_{(i)}(R) = Av(R) - \frac{2\mu}{K} \int\limits_R^\infty \mathrm{d}R' [v(R')u(R) - u(R')v(R)] V(R') \varphi_{(i)}(R'), \tag{4.130}$$

which is analogous to Equation 4.121 and it yields for $f(R) = \varphi_{(i)}(R)/A$

$$f(R) = [1 - \alpha(R)]v(R) + \beta(R)u(R) \tag{4.131}$$

with

$$\alpha(R) = -\frac{2\mu}{K} \int\limits_R^\infty \mathrm{d}R' u(R') V(R') f(R'), \tag{4.132}$$

$$\beta(R) = -\frac{2\mu}{K} \int\limits_R^\infty \mathrm{d}R' v(R') V(R') f(R'). \tag{4.133}$$

The constant A can be written in terms of α

$$A = 1 - \frac{2\mu}{K} \int\limits_0^\infty \mathrm{d}R u(R) V(R) \varphi_{(i)}(R) = 1 + A\alpha(0), \tag{4.134}$$

that is, $A = (1 - \alpha(0))^{-1}$. Equation 4.131 can be used for the numerical calculation of $f(R)$ on a grid in the same way as Equation 4.123 in the case of the regular solution. The only difference is that now the function $f(R)$ has to be calculated in the decreasing sequence of grid points starting from sufficiently large x_n, so that $f(x_n) = v(x_n)$ can be assumed. The irregular solution $\varphi_{(i)}(R)$ is then obtained by multiplication of $f(R)$ with A.

The procedure for the calculation of the regular and irregular solutions and the Green's function outlined earlier can be generalized for the coupled channel problem.

4.4.4 EVALUATION OF THE NONLOCAL POTENTIAL

The key element of evaluation of the nonlocal potential

$$F(E) = \int k \mathrm{d}k \, \mathrm{d}\hat{k} V_{\mathbf{dk}} G_0(E - \varepsilon) V_{\mathbf{dk}}^*$$

is the knowledge of the Green's function $G_0(E) \equiv (E - T_N - V_0 + i\varepsilon)^{-1}$ for the neutral molecule AB. The formula similar to Equation 4.128 is of little use here, because the regular and irregular solutions depend on energy and the integration over ε cannot easily be performed. A better idea is to expand the $G_0(E)$ in terms of bound states of molecule AB

$$\langle \mathbf{R} \mid v \rangle = \frac{1}{R} \chi_{vJ}(R) Y_{JM}(\hat{R}) \tag{4.135}$$

to obtain

$$\begin{aligned} G_0(E, \mathbf{R}, \mathbf{R}') &= \sum_v \frac{\langle \mathbf{R} \mid v \rangle \langle v \mid \mathbf{R}' \rangle}{E - E_v + i\varepsilon} \\ &= \sum_{JM} Y_{JM}(\hat{R}) \frac{1}{R} \sum_v \frac{\chi_{vJ}(R) \chi_{vJ}(R')}{E - E_v^J + i\varepsilon} \frac{1}{R'} Y_{JM}(\hat{R}'). \end{aligned} \tag{4.136}$$

Comparison of this expansion with (4.73) yields

$$\begin{aligned} G_{0J}(E, R, R') &\equiv \left(E + \frac{1}{2\mu} \frac{d^2}{dR^2} - \frac{J(J+1)}{2\mu R^2} - V_0(R) + i\varepsilon \right)^{-1} \\ &= \sum_v \frac{\chi_{vJ}(R) \chi_{vJ}(R')}{E - E_v^J + i\varepsilon}. \end{aligned} \tag{4.137}$$

This expression is convenient for the evaluation of $F(E)$ since the integration over $d\varepsilon$ can be performed analytically (see (4.47) and (4.48))

$$F(E, \mathbf{R}, \mathbf{R}') = \sum_v \langle \mathbf{R} \mid v \rangle [\Delta(E - E_v, \mathbf{R}, \mathbf{R}') - \frac{i}{2} \Gamma(E - E_v, \mathbf{R}, \mathbf{R}')] \langle v \mid \mathbf{R}' \rangle \tag{4.138}$$

or after the partial wave expansion (see formula 4.79)

$$\begin{aligned} f_J(E, R, R') = &\sum_{lJ'} (2J'+1) \begin{pmatrix} l & J' & J \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\times \sum_v \chi_{vJ'}(R) [\Delta_l(E - E_v^{J'}, R, R') - \frac{i}{2} \Gamma_l(E - E_v^{J'}, R, R')] \chi_{vJ'}(R), \end{aligned} \tag{4.139}$$

where

$$\Gamma_l(\varepsilon, R, R') = 2\pi V_{del}(R) V_{del}^*(R'), \tag{4.140}$$

$$\Delta_l(\varepsilon, R, R') = \frac{1}{2\pi} \wp \int d\varepsilon' \Gamma_l(\varepsilon', R, R') / (\varepsilon - \varepsilon'). \tag{4.141}$$

If we neglect the angular momentum of the released/captured electron (see Section 4.3.1), we get

$$f_J(E, R, R') = \sum_v \chi_{vJ}(R) [\Delta_0(E - E_v^J, R, R') - \frac{i}{2} \Gamma_0(E - E_v^J, R, R')] \chi_{vJ}(R'). \tag{4.142}$$

Minor difficulty for application of this expansion to actual numerical calculation is the presence of continuum functions in the sum over ν, which becomes important near the dissociation limit for the neutral molecule AB. This problem has been overcome by an appropriate discretization of the continuum spectrum by Horáček et al. (1996) who suggested to use the Fourier DVR method for the discretization, which is equivalent to putting the molecule AB into a box, that is, imposing the boundary condition $\chi_{\nu J}(R_c) = 0$ at a certain cutoff radius R_c. The sum over ν is then cut at a certain $\nu = \nu_{max}$. One may wonder about the role of the box boundary condition on the calculation, since the correct boundary condition should be given by prescribing the outgoing wave at some large R_c. The correct behavior is however ensured by the presence of the infinitesimal part $i\varepsilon$ in the expansion (4.137).

4.4.5 Local Approximations

A local approximation of the nonlocal dynamics is based on the replacement of the nonlocal potential $f_J(E, R, R')$ with a certain local quantity. The possibility of such a replacement is based on different timescales for electronic and nuclear dynamics. The nuclei are moving in the presence of an electron captured in the discrete resonant state $|d\rangle$. The resonant state $|d\rangle$ can decay at any point R and the electron can again be captured into $|d\rangle$ at a different point R'. If the electron released in the decay is fast, the difference between R and R' cannot be large, because otherwise the electron would be gone before nuclei succeed to travel the distance $|R-R'|$ and could not be captured again. The nonlocality of the interaction is therefore pronounced only if resonance energy $E_d = V_d - V_0$ is small, that is, if the potential curves $V_d(R)$ and $V_0(R)$ come close together or even cross each other. If they are well separated (as is often the case for the Penning ionization), it is possible to replace $V_d + f_J$ with the local approximation (Bieniek 1978, Domcke 1991, Morgner 1990)

$$V_{loc}(R) - \frac{i}{2}\Gamma_{loc}(R), \tag{4.143}$$

where

$$V_{loc}(R) = V_0(R) + E_{res}(R), \tag{4.144}$$

$$\Gamma_{loc}(R) = \Gamma(E_{res}(R), R, R), \tag{4.145}$$

and

$$E_{res}(R) = V_d(R) - V_0(R) + \Delta_J(E_{res}(R), R, R). \tag{4.146}$$

A transparent derivation of this approximation including the possibility of first-order corrections[*] has been done in the time-dependent formalism (Domcke 1991). It is also possible to show that if $E_{res}(R) < 0$ then $V_{loc}(R)$ is the bound state of H_{el} (see Equation 4.4).

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[*] In the time-dependent picture, the effective potential (after projecting out the continuum) is not only nonlocal, but contains also the memory effects. The first-order corrections depend only on the first derivative of the wave function with respect to time and R.

The local approximation (4.144) cannot give good results for the systems where the curves $V_0(R)$ and $V_d(R)$ come close together. Nevertheless, local approximations are still useful to accelerate the convergence of iteration methods for solving the nonlocal Lippmann–Schwinger equation

$$|\psi\rangle = |\varphi\rangle + G_{QJ} f_J |\varphi\rangle, \tag{4.147}$$

which corresponds to the partitioning of the potential $V_{\text{eff}} = V_d + f_J$. We can use the different partitioning $V_{\text{eff}} = V_{\text{loc}} + f_J'$ instead, with $f_J' = f_J + V_d - V_{\text{loc}}$ being a "smaller" operator than the original f_J and having a chance for faster convergence of methods for solving the corresponding Lippmann–Schwinger equation (see the next section). This subtraction of the local approximation from the full nonlocal problem is a special case of the method of *preconditioning* known in the matrix iteration methods.

Use of the approximation (4.144) is limited also by the fact that the Equation 4.146 often does not have a unique solution. A different local approximation has been proposed by Horáček et al. (1996) to accelerate the convergence (in the way suggested above). This approximation is convenient in the cases where the wave function $\psi_J(R)$ is not strongly oscillating. The first term in the Taylor expansion

$$\int f_J(E, R, R') \psi_J(R') dR' = \int f_J(E, R, R')[\psi_J(R) + (R' - R)\psi_J'(R) + \cdots] dR' \tag{4.148}$$

yields the energy-dependent local approximation

$$f_{\text{loc}}(E, R) = \int f_J(E, R, R') dR'. \tag{4.149}$$

4.4.6 Solution of Lippmann–Schwinger Equation with Nonlocal Potential

A very efficient method for computing the T-matrix elements in the presence of nonlocal interactions, the Schwinger–Lanczos algorithm, was proposed by Meyer et al. (1991). This method has been successfully used in several realistic applications (Horáček and Domcke 1996, Horáček et al. 1996, Gemperle and Horáček 1997) to calculate the cross sections for vibrational excitation, associative detachment, and dissociative attachment based on the use of the nonlocal resonance model. The essence of the method has been outlined already in Chapter 2 in connection with the solution of the fixed-nuclei electronic scattering problem. Originally, the method was designed for calculation of the diagonal T-matrix elements. In principle, it can also be used for calculation of the nondiagonal T-matrix elements resulting from multi-channel collisions, but the calculation is rather cumbersome and the incoming and outgoing states are not treated symmetrically. It is the purpose of this section to present a generalization of the Schwinger–Lanczos algorithm for the multichannel case and to establish its relation to other methods.

4.4.6.1 Short Review of the Schwinger–Lanczos Approach

According to the Schwinger variational principle (Lippmann and Schwinger 1950), the T-matrix element

$$T_{\text{fi}} \equiv \langle \phi_{\text{f}} \mid T \mid \phi_{\text{i}} \rangle = \langle \phi_{\text{f}} \mid V(V - VG_0V)^{-1}V \mid \phi_{\text{i}} \rangle \tag{4.150}$$

is given by the stationary value of the functional

$$T[\psi_-, \psi_+] = \langle \phi_{\text{f}} \mid V \mid \psi_+ \rangle + \langle \psi_- \mid V \mid \phi_{\text{i}} \rangle - \langle \psi_- \mid V - VG_0V \mid \psi_+ \rangle, \tag{4.151}$$

where V is an interaction potential and G_0 the free particle Green's function. This stationary value is achieved for $|\psi_\pm\rangle$ being solutions of the corresponding Lippmann–Schwinger equations. Considering $|\psi_\pm\rangle$ in the form

$$\mid \psi_\pm \rangle = \sum_{k=1}^{N} c_k^{(\pm)} \mid g_k \rangle, \tag{4.152}$$

with variational parameters $c_k^{(\pm)}$ we obtain an approximation to the T-matrix

$$T_{\text{fi}}^N = \sum_{k,l=1}^{N} \langle \phi_{\text{f}} \mid V \mid g_k \rangle (M^{-1})_{kl} \langle g_l \mid V \mid \phi_{\text{i}} \rangle, \tag{4.153}$$

where the matrix M is given by $M_{kl} = \langle g_k|V-VG_0V|g_l\rangle$. The set of vectors $\{|g_k\rangle\}_{k=1}^{N}$ can be chosen arbitrarily (not necessarily orthogonal) provided that M_{kl} is a regular matrix. The Schwinger–Lanczos method (SLM) was proposed for calculation of the diagonal T-matrix elements (Meyer et al. 1991), that is, $|\phi_{\text{f}}\rangle = |\phi_{\text{i}}\rangle = |\phi\rangle$, needed for evaluation of elastic cross sections. In this method, T_{fi}^N is calculated according to Equation 4.153, with $|g_1\rangle = |\phi\rangle\langle\phi|V|\phi\rangle^{-1/2}$ and the set $\{|g_k\rangle\}_{k=1}^{N}$ is taken as V-orthogonal

$$\langle g_k \mid V \mid g_l \rangle = \delta_{kl} \tag{4.154}$$

and such that the matrix VG_0V is tridiagonal

$$\langle g_{k-1} \mid VG_0V \mid g_k \rangle = \langle g_k \mid VG_0V \mid g_{k-1} \rangle = \beta_{k-1}, \tag{4.155}$$

$$\langle g_k \mid VG_0V \mid g_k \rangle = \alpha_k, \tag{4.156}$$

$$\langle g_k \mid VG_0V \mid g_l \rangle = 0 \quad \text{for} \quad |k-l| \geq 2. \tag{4.157}$$

Let us note that the complex-symmetric scalar product (i.e., without complex conjugation) is used throughout this section and not the usual (Hermitian) one, since G_0 is a symmetric but non-Hermitian operator. Only the matrix element $(M^{-1})_{11}$ is needed in Equation 4.153 and this element is for a tridiagonal matrix M easily expressible in the form of a continued fraction. The T-matrix then reads

$$T^N = \langle \phi \mid V \mid g_1 \rangle (M^{-1})_{11} \langle g_1 \mid V \mid \phi \rangle = \frac{\langle \phi \mid V \mid \phi \rangle}{1-\alpha_1-} \frac{\beta_1^2}{1-\alpha_2-} \frac{\beta_2^2}{1-\alpha_3-} \cdots \frac{\beta_{N-1}^2}{1-\alpha_N}. \tag{4.158}$$

The numbers α_k, β_k and the vectors $|g_k\rangle$ with properties (4.154) through (4.157) are constructed according to the recurrence (see Meyer et al. 1991 and references therein for more details about the Lanczos algorithm)

$$\mid r_k \rangle = G_0V \mid g_k \rangle - \beta_{k-1} \mid g_{k-1} \rangle, \tag{4.159}$$

$$\alpha_k = \langle g_k | V | r_k \rangle, \tag{4.160}$$

$$| s_k \rangle = | r_k \rangle - \alpha_k | g_k \rangle, \tag{4.161}$$

$$\beta_k = \langle g_k | V | g_k \rangle^{1/2}, \tag{4.162}$$

$$| g_{k+1} \rangle = \beta_k^{-1} | s_k \rangle, \tag{4.163}$$

with $|g_1\rangle = |\varphi\rangle \langle\varphi|V|\varphi\rangle^{-1/2}$ and $\beta_0 = 0$.

The off-diagonal matrix elements of the *T*-matrix are needed for the calculation of resonant electron–molecule and ion–atom collisions. The same Lanczos basis with the properties (4.154) through (4.157) generated by the algorithm (4.159) through (4.163) and with the starting vector $|g_1\rangle = |\varphi_i\rangle\langle\varphi_i|V|\varphi_i\rangle^{-1/2}$ can be used in such a case. The formula for the *T*-matrix element resulting from Equation 4.153 will be slightly more complicated than in the previous case

$$T_{\mathrm{fi}}^N = \sum_{k=1}^{N} \langle \phi_{\mathrm{f}} | V | g_k \rangle (M^{-1})_{k1} \langle g_1 | V | \phi_{\mathrm{i}} \rangle. \tag{4.164}$$

Note that now the first column of M^{-1} is needed instead of the single element M_{11}^{-1}. Using elementary algebra, it turns out that

$$(M^{-1})_{k\cdot 1} = \frac{\beta_1}{f_1} \frac{\beta_2}{f_2} \cdots \frac{\beta_{k-1}}{f_{k-1}} \frac{1}{f_k}, \tag{4.165}$$

where the quantities

$$f_k = 1 - \alpha_k - \beta_k^2 / f_{k+1}, \quad f_N = 1 - \alpha_N \tag{4.166}$$

are involved also in the calculation of the continued fraction (4.158). As pointed out in Meyer et al. (1991), this approach does not treat in and out states in a symmetrical manner. For this reason, the so-called band Lanczos algorithm (Meyer and Pal 1989) was proposed by Meyer et al. (1991) which leads to a banded instead of a tridiagonal matrix. Another approach preserving tridiagonality of the matrix, but using different basis sets for in- and outgoing states was proposed by Čížek et al. (2000).

It is also shown by Meyer et al. (1991) that SLM is equivalent to the method of continuous fractions of Horáček and Sasakawa (1983), see also Horáček and Sasakawa (1984, 1985).

4.4.7 Another Method of Solution of Nonlocal Dynamics

We tried to present the details of all the steps needed to solve the nonlocal nuclear dynamics in the preceding sections. Before discussing the results of the calculations for several systems in the following chapter, we would also like to mention briefly some alternative methods of solution of the equations of the nonlocal resonance theory.

The first step of the abovementioned procedure was solution of the local problem. The alternative to the direct solution of the Lippmann–Schwinger Equation

4.117 in the coordinate representation is to use the *R*-matrix basis. The advantage of this approach is that the *R*-matrix is found in one step and it can be then used for all energies (Kolorenč et al. 2002), whereas the numerical solution on the grid must be repeated for each energy.

The solution of the Lippmann–Schwinger equation for the nonlocal problem with the potential written in terms of the separable expansion (4.142) can be found directly by expansion in the vibrational basis (extended with the discretized continuum). This approach converges slower than Schwinger–Lanczos method, but it was used, for example, by Hickman (1991) for vibrational excitation of H_2. Alternative separable approximation to the nonlocal resonance potential (the Bateman approximation) was also discussed by Houfek et al. (2002).

To complete the list of the methods, we must also briefly mention the time-dependent formulation of the nonlocal resonance theory (see Domcke 1991 and references therein), the semiclassical method of Kazansky and Kalin (1990), Kalin and Kazansky (1990), the discretization of the full dynamics in the *P*-space (Kazansky 1996) or direct solution of the Schrödinger Equation 4.66 using the exterior complex scaling methods (Houfek et al. 2008).

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