

Generalized diatomics-in-molecules method for polyatomic anions

A. K. Belyaev,¹ A. S. Tiukanov,¹ and W. Domcke²

¹*Department of Theoretical Physics, A. I. Herzen University of Russia, St. Petersburg 191186, Russia*

²*Institute of Physical and Theoretical Chemistry, Technical University of Munich, D-85747 Garching, Germany*

(Received 21 May 2001; published 14 December 2001)

The diatomics-in-molecules (DIM) method for the construction of polyatomic potential-energy functions from the potential energies of atomic and diatomic fragments is generalized to obtain a description of potential-energy functions of both quasistationary and bound states of polyatomic anions. The formulation is based on the combination of the DIM method with the projection-operator approach of scattering theory. The proposed theory allows the construction of diabatic discrete states, electron-molecule scattering continua, and discrete-continuum coupling elements from the corresponding data of the fragments. The polyatomic projection-operator description obtained in this way provides the basis for a rigorous treatment of the nuclear dynamics in short-lived electron-molecule collision complexes and ion-molecule collisions in terms of energy-dependent, complex, and nonlocal effective potentials. More approximate local complex potential-energy surfaces of quasistationary states of polyatomic anions also can be obtained with the generalized DIM method via the determination of the poles of the multichannel electron-molecule scattering matrix in the fixed-nuclei limit. Although the focus of the present work is on anions, the proposed theory is also applicable to quasistationary states of neutral and positively charged polyatomic systems including clusters. To illustrate the concepts, the generalized DIM method is applied to obtain the potential-energy functions of the ground and first excited states of the H_3^- anion, making use of information that is available for the bound and resonance states of H^- and H_2^- .

DOI: 10.1103/PhysRevA.65.012508

PACS number(s): 31.50.-x, 31.10.+z, 33.35.+r, 34.20.-b

I. INTRODUCTION

Remarkable progress has been achieved in the quantum-mechanical theory of elementary reactions, see, for example, [1,2] and references therein. Many detailed and accurate experimental and theoretical studies of the reaction dynamics of triatomic systems have been reported in recent years, and impressive agreement between theory and experiment has been obtained. The theoretical studies require two essential prerequisites: an accurate Born-Oppenheimer potential-energy surface (PES) as well as appropriate numerical techniques for treating the quantum-scattering problem with proper inclusion of rearrangement channels.

The simplest chemically reactive systems are $\text{H} + \text{H}_2$ and its isotopic variants. For $\text{H} + \text{H}_2$ an accurate ground-state PES has been available for some time [3,4]. For this prototypical system, a great variety of methods for the treatment of the collision dynamics, based on time-independent scattering theory or on time-dependent wave-packet propagation, have been successfully applied. At least at low collision energies, the $\text{H} + \text{H}_2$ collision system appears to be understood in considerable detail [1,5].

Another fundamental collision system is $\text{H}^- + \text{H}_2$, as well as isotopic variants thereof, e.g., $\text{H}^- + \text{D}_2$ and $\text{D}^- + \text{H}_2$. The $\text{H}^- + \text{H}_2$ complex represents the prototype of chemical reactions involving negative ions, which are of both fundamental and applied importance. Under certain conditions, H^- ions can be abundant in low-temperature hydrogen plasmas. The development of efficient H^- sources [6] is of considerable applied interest, in particular, for neutral-beam heating in fusion research. In this context a detailed understanding of the collision behavior of negative ions interacting with neutral molecules is of particular interest.

Recently, a wealth of new experimental data on low-energy $\text{H}^- + \text{H}_2$ and $\text{H}^- + \text{D}_2$ collisions has been obtained [7–11]. These precise and detailed data represent a challenge for the theory of elementary chemical-reaction dynamics involving negative ions. A particularly interesting aspect, which is absent in the $\text{H} + \text{H}_2$ system, is the existence of the electron detachment channel, i.e., $\text{H}^- + \text{H}_2 \rightarrow \text{H} + \text{H}_2 + e^-$, which also has been experimentally observed [12]. The reaction dynamics of the H_3^- system is thus considerably more involved than the dynamics of the H_3 system, and a significant extension of the theoretical framework is required.

Electron detachment processes usually occur via quasistationary states, which are known to be difficult to calculate with standard quantum-chemical variational methods. The calculations of the ground state and the first excited state PESs of the H_3^- system for collinear geometry, carried out by the molecular-orbital (MO) configuration-interaction (CI) method, give a clear example of these difficulties [13]; while for the PES of the ground state, different *ab initio* calculations agree reasonably with each other [13–16], the PES of the first excited state obtained with the MO CI method [13] actually corresponds to the surface of the neutral H_3 molecule with an additional electron in a diffuse molecular orbital, but not to a PES of a quasistationary state. This fact has the following explanation: the ground state is bound and thus properly described by the variational approach, whereas the first excited state is mainly quasistationary [17,18] and hence corresponds to an electronic state embedded in the $e^- + \text{H}_3$ scattering continuum. Another example is the N_2H^- complex. It has been shown [19] that PESs of quasistationary states obtained by the *ab initio* variational method exhibit unstable behavior with respect to a change of the size of the basis set.

In principle, scattering theory provides the proper framework for the description of quasistationary electronic states of molecules. Both bound states as well as nonstationary states (resonances) are given as poles of the analytically continued scattering matrix [20,21]. A variety of computational schemes have been developed for the *ab initio* implementation of the electron-molecule scattering theory and the determination of resonances. Examples are the Kohn variational principle [22], the separable potential method [23], the *R*-matrix method [24], as well as complex-rotation and complex-basis-function methods [25–27]. An alternative is variational calculations employing complex absorbing potentials [28]. With respect to the inclusion of electron-correlation effects, which is required, e.g., for the description of target polarization effects and the description of bond breaking, these calculations for resonance states have not yet reached the same level of sophistication as the established variational calculations for bound states. The technical difficulties encountered in the implementation of the methods based on scattering theory have prevented their application for the calculation of complex PESs, in particular, for polyatomic anions. In fact only few *ab initio* calculations of complete potential-energy functions of nonstationary states of diatomic anions have been reported (see, e.g., [23,26]) and no complete energy surfaces of nonstationary states of triatomic anions or larger systems have so far been obtained with *ab initio* methods.

The present stage of development of calculations for the PESs of triatomic anions appears comparable to the situation for neutral triatomics a couple of decades ago. Under these circumstances, the diatomics-in-molecules (DIM) method [29] appears to represent an attractive compromise between accuracy and feasibility. The idea of the DIM method is based on the fragmentation of the electronic Hamiltonian of a polyatomic molecule, which allows one to construct the Hamiltonian matrix from atomic and diatomic fragment energies. Diagonalization of the Hamiltonian matrix constructed in this way provides PESs for a polyatomic molecule. The DIM method has been widely used for the construction of the PESs of triatomic and larger molecules in the past [29–31] as well as recently [32–36]. It has been employed to obtain potential-energy functions for liquids [37,38], solids [39,40] and clusters [41–43].

If so-called local complex potentials (LCP) [44,45] of quasistationary states of diatomics are used as fragment potentials, one may construct a complex Hamiltonian matrix and then get local complex PESs for a polyatomic system. This approach is called the LCP DIM method. Indeed, the LCP DIM method has been applied to obtain the real parts of PESs of polyatomic anions [17,18,46–48], as well as of quasistationary states of neutral molecules [49–51]. As shown below, the straightforward application of the LCP DIM procedure to quasistationary states of polyatomics can lead to artifacts such as a complex potential for a bound state. The DIM method therefore needs to be generalized for the treatment of quasistationary states.

The LCP approximation, which basically corresponds to the Breit-Wigner pole approximation [21], has its limitations, moreover, for short-lived resonances and for resonances near

continuum thresholds. If the lifetime of the electron-molecule collision complex is short, or threshold effects are important, the LCP approximation breaks down and a more general complex effective potential has to be introduced, which is energy-dependent and nonlocal [52,53]. This so-called nonlocal theory allows for an accurate treatment of the nuclear dynamics also for very short-lived collision complexes [53]. To the best of our knowledge, the nonlocal complex-potential formalism has been applied to diatomic systems only. In view of the existence of such an essentially rigorous treatment of the nuclear dynamics in quasistationary states, it appears attractive to extend the DIM method to obtain a generalized approach that allows one to calculate both local and nonlocal complex PESs of polyatomic anions. This is the goal of the present paper.

It is worth mentioning that calculations of PESs [16–18] as well as of nonadiabatic couplings [54] for the H_3^- collisional system have opened the possibility of dynamical treatments of different processes in $\text{H}^- + \text{H}_2$ collisions [17,55–66]. These dynamical treatments are mostly based on the single PES of the ground state of H_3^- . Nonadiabatic effects have been treated only in Refs. [62,65]. Obtaining more reliable information about the potentials of this system, even within the LCP approximation, which is sometimes sufficient for the dynamical treatment (see, for example, [67]), will allow one to perform more rigorous dynamical studies of all processes in collisions of H^- with H_2 .

The article is organized as follows. Section II gives a short description of the projection-operator (PO) approach for diatomic systems, which forms the basis of the description of resonances. Section III gives a new description of the DIM method. In Sec. IV the PO formalism is combined with the DIM method to obtain a description of nonstationary PESs of polyatomic anions beyond the LCP approximation. An illustrative example is given in Sec. V.

II. THE PROJECTION-OPERATOR APPROACH FOR DIATOMICS

Let \hat{H}_e denote the electronic Hamiltonian of a molecular anion. For the sake of simplicity, the case of only one discrete state and one continuum is treated in this section. It is straightforward to extend the formalism to the case of several discrete states and several continua (see Sec. IV). Assume that a state $|\psi_d\rangle$ with a localized (square-integrable) wave function is given, which approximately describes a resonance in the scattering of an electron from a neutral molecule. This so-called discrete state with the energy expectation value

$$V_d = \langle \psi_d | \hat{H}_e | \psi_d \rangle \quad (1)$$

is not an eigenstate of \hat{H}_e , but is coupled with a scattering continuum $|\phi_{nk}\rangle = |\psi_n\rangle |k\rangle$ via matrix elements

$$V_{d,nk} = \langle \psi_d | \hat{H}_e | \phi_{nk} \rangle. \quad (2)$$

Here $|\psi_n\rangle$ denotes the ground eigenstate of the target molecule with energy V_n (the subscript n stands for “neutral”)

and $|k\rangle$ is a single-electron continuum state. For a diatomic target, both V_n and V_d depend only on the internuclear separation R , while $V_{d,nk}$ depends both on R as well as the energy and angular momentum quantum numbers of the continuum electron. The $|\phi_{nk}\rangle$ are so-called background-scattering states, constructed to be orthogonal to $|\psi_d\rangle$. An explicit prescription for the construction of the $|\psi_d\rangle$ and $|\phi_{nk}\rangle$ can be found in Ref. [53].

Given these electronic states, we can define mutually orthogonal projection operators [53,68,69]

$$\hat{Q} = |\psi_d\rangle\langle\psi_d|, \quad (3)$$

$$\hat{P} = 1 - \hat{Q} = \sum_k |\phi_{nk}\rangle\langle\phi_{nk}|. \quad (4)$$

By solving the background-scattering problem [53], the representation of \hat{H}_e can be made diagonal in the P space [53,68,69].

We thus have the following representation of the fixed-nuclei Hamiltonian in the complete electronic space $\{|\psi_d\rangle, |\phi_{nk}\rangle\}$,

$$\begin{aligned} \hat{H}_e &= \hat{H}_{QQ} + \hat{H}_{PP} + \hat{H}_{PQ} + \hat{H}_{QP} \\ &= |\psi_d\rangle V_d \langle\psi_d| + \int k dk d\Omega_k |\phi_{nk}\rangle (V_n + E_k) \langle\phi_{nk}| \\ &\quad + \int k dk d\Omega_k (|\psi_d\rangle V_{d,nk} \langle\phi_{nk}| + |\phi_{nk}\rangle V_{nk,d} \langle\psi_d|), \end{aligned} \quad (5)$$

where $E_k = k^2/2$ is the kinetic energy of the continuum electron.

For the manipulations to be described in the following sections, it is convenient to define the infinite-dimensional matrix representation \underline{H} of \hat{H}_e ,

$$\underline{H} = \begin{pmatrix} V_d & V_{d,nk} & V_{d,nk'} & \dots \\ V_{nk,d} & V_n + E_k & 0 & \dots \\ V_{nk',d} & 0 & V_n + E_{k'} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (6)$$

where k, k', \dots have continuous values. Throughout the article a double underlined symbol denotes a matrix, while a single underlined symbol stands for a basis set (a column vector). \underline{H} has the structure of an ‘‘arrow’’ matrix.

If the fixed-nuclei Hamiltonian is given in the form Eq. (5), algebraic expressions can be derived for the S and T matrices [53,68–70]. The fixed-nuclei T matrix for the transition from an initial state nk to a final state nk' , for example, is given by

$$\begin{aligned} T_{nk',nk}(R) &= V_{nk',d}(R) [E_k + V_n(R) - V_d(R) - F(k,R)]^{-1} \\ &\quad \times V_{d,nk}(R), \end{aligned} \quad (7)$$

where

$$F(k,R) = \int_0^\infty dE' \frac{|V_{d,nk'}(R)|^2}{E_k - E'} = \Delta(E_k, R) - \frac{i}{2} \Gamma(E_k, R) \quad (8)$$

is the so-called level-shift function.

Resonances, bound states and virtual states of an anion, defined as the poles of the T matrix, are thus given by the complex solutions of the following equation in the complex k plane [53,71,72]:

$$\frac{k^2}{2} + V_n(R) - V_d(R) - F(k,R) = 0. \quad (9)$$

Here $F(k,R)$ is the analytic continuation of the level-shift function (8) into the complex k plane. The real part of the solution $k^2/2$ of Eq. (9) defines the position of the resonance with respect to the potential of the neutral molecule ground state, while the imaginary part gives the decay width [21].

Alternatively, the position of the resonance may be obtained from the solution of the following equation for real positive E_k ,

$$E_k + V_n(R) - V_d(R) - \Delta(E_k, R) = 0, \quad (10)$$

which defines the pole of the K matrix. Obviously Eq. (10) is the real analog of the complex equation (9). When the decay width of the resonance is sufficiently small, the solution of Eq. (10) is approximately equal to the real part of the solution of Eq. (9), whereas for broad resonances the two solutions may differ significantly [73]. The width of the resonance has to be found by evaluating $\Gamma(E_k, R)$ at the resonance energy

$$\Gamma(R) = \Gamma(E_{res}(R), R) = 2\pi |V_{d,nk_{res}}(R)|^2. \quad (11)$$

Either Eq. (9) or Eqs. (10) and (11) define a local complex potential-energy function of the resonance,

$$V_{res}(R) = U_{res}(R) - \frac{i}{2} \Gamma(R), \quad (12)$$

$$U_{res}(R) = V_n(R) + E_{res}(R). \quad (13)$$

When the LCP (12),(13) is used, together with the nuclear kinetic-energy operator \hat{T}_N , to evaluate the resolvent in the T matrix [cf. Eq. (7)], one obtains the so-called LCP approximation for resonant electron-molecule scattering [44,45,52,53]. This approximation has been shown to fail for broad resonances as well as in the presence of threshold effects [53]. The main reason of this failure is the breakdown of the Breit-Wigner pole approximation in such situations.

It is the essence of the projection-operator formalism that it defines a more general energy-dependent nonlocal complex effective potential, which governs the nuclear motion in the collision complex. It is defined as [52,53]

$$V^{eff}(R, R'; E) = V_d(R) \delta(R - R') + F(R, R'; E), \quad (14)$$

$$F(R, R'; E) = \int k dk d\Omega_k V_{d, nk}(R) \times \tilde{G}_n^{(+)}(R, R'; E - k^2/2) V_{nk, d}(R'). \quad (15)$$

Here E is the total (conserved) energy of the collision complex and

$$\tilde{G}_n^{(+)}(R, R'; E) = \langle R | (E - \hat{T}_N - V_n + i\eta)^{-1} | R' \rangle \quad (16)$$

denotes the Green's function for nuclear motion in the target state $|\psi_n\rangle$. η is the usual positive infinitesimal.

It should be emphasized that the nonlocal complex potential is completely determined by the functions $V_n(R)$, $V_d(R)$, and $V_{d, nk}(R)$.¹ The explicit construction of $V^{eff}(R, R'; E)$ by *ab initio* methods has been achieved for a few diatomic molecules, e.g., H₂ and HCl [74,75], for the case of electronically elastic scattering. Recently, discrete electronic potentials $V_d(R)$ and discrete-continuum coupling elements also have been obtained for a few polyatomic molecules, but only as a function of a single selected nuclear coordinate [76].

III. THE DIATOMICS-IN-MOLECULES METHOD

Let us briefly describe the DIM method for the construction of potential-energy surfaces and nonadiabatic coupling matrix elements for electronically bound states of polyatomic molecules. Within the DIM method, the potential-energy surfaces are obtained by the diagonalization of the Hamiltonian matrix calculated with a chosen basis set. The construction of the Hamiltonian matrix is based on the representation of a polyatomic Hamiltonian via atomic and diatomic Hamiltonians. Detailed descriptions of the standard DIM approach can be found, for example, in [18,29–31]. As has been shown by numerous examples, this approach provides reliable potential-energy surfaces and nonadiabatic couplings for neutral molecules and positive ions. In order to derive in the following section the generalized DIM method applicable for a description of both bound and quasistationary states of polyatomic anions, as well as for treating quasistationary states of neutral and positively charged polyatomic systems, let us derive in this section a new formulation of the DIM method.

In the framework of the DIM method, the basis many-electron functions $|\Psi_m^{anti}\rangle$ of an N -atomic molecule $AB \cdots Z$ are taken as superpositions of antisymmetrized products of atomic wave functions²

¹Note that as mentioned above the discrete-continuum couplings also depend on the electron energy via the continuous index k .

²In general, basis functions can be taken as simple products of atomic wave functions, but in practice it is more convenient to choose basis functions as linear combinations of such products in order to describe spin-adopted states.

$$\underline{|\Psi^{anti}\rangle} = \left\{ \begin{array}{c} |\Psi_1^{anti}\rangle \\ |\Psi_2^{anti}\rangle \\ \vdots \\ |\Psi_m^{anti}\rangle \\ \vdots \end{array} \right\}, \quad |\Psi_m^{anti}\rangle = \hat{A} |\Psi_m\rangle,$$

$$|\Psi_m\rangle = \hat{s} |\chi_m^a\rangle |\chi_m^b\rangle \cdots |\chi_m^z\rangle, \quad (17)$$

where \hat{A} is the operator of antisymmetrization, m is the generalized index of a molecular basis function, $|\chi_m^\alpha\rangle$ denotes an electronic wave function of a monoatomic particle α , and the operator \hat{s} makes a linear combination of wave functions to obtain spin-adopted states. It should be pointed out that within the DIM method the basis sets are restricted to wave functions of electronically bound states only.

The essence of the DIM method is the fragmentational representation of the N -atomic ($N \geq 3$) Hamiltonian via diatomic ($\hat{H}^{\alpha\beta}$) and atomic (\hat{H}^α) Hamiltonians [29],

$$\hat{H}_e = \sum_{\alpha\beta} \hat{H}^{\alpha\beta} - (N-2) \sum_{\alpha} \hat{H}^{\alpha}, \quad (18)$$

where the summation is carried out over all possible fragmentations. Note that the atomic wave functions $|\chi_m^\alpha\rangle$ are eigenfunctions of the corresponding atomic Hamiltonian \hat{H}^α .

The construction of the Hamiltonian matrix can be performed via the operation of the Hamiltonian \hat{H}_e on the basis set $\underline{|\Psi^{anti}\rangle}$. According to Eq. (18) this can be expressed via the operations of the diatomic $\hat{H}^{\alpha\beta}$ and the atomic \hat{H}^α Hamiltonians on the same set. These Hamiltonians can be written via adiabatic potentials and adiabatic wave functions of both bound and continuum states. For example, for a diatomic fragment $\alpha\beta$, the Hamiltonian has the form

$$\hat{H}^{\alpha\beta} = \sum_j |\psi_j^{\alpha\beta}\rangle V_j^{\alpha\beta} \langle \psi_j^{\alpha\beta}| + \sum_n \int k dk d\Omega_k |\phi_{nk}^{\alpha\beta}\rangle (V_n^{\alpha\beta} + E_k) \langle \phi_{nk}^{\alpha\beta}|, \quad (19)$$

where $|\psi_j^{\alpha\beta}\rangle$ denotes a diatomic adiabatic wave function (eigenfunction) of a bound state j with a corresponding adiabatic potential-energy function $V_j^{\alpha\beta}(R_{\alpha\beta})$, $|\phi_{nk}^{\alpha\beta}\rangle$ is a continuum state associated with the target state $|\psi_n^{\alpha\beta}\rangle$ with a corresponding potential $V_n^{\alpha\beta}(R_{\alpha\beta})$, and $R_{\alpha\beta}$ is an internuclear separation of the fragments α and β . Taking into account Eq. (19), the commutation of the electronic Hamiltonian with the operator of antisymmetrization, the fact that the basis set is constructed from wave functions of bound states only, and the mutual orthogonality of the adiabatic wave functions, the operation of the diatomic Hamiltonian $\hat{H}^{\alpha\beta}$ on a basis wave function $|\Psi_m^{anti}\rangle$ can be written as follows:

$$\begin{aligned}\hat{H}^{\alpha\beta}|\Psi_m^{anti}\rangle &= \hat{A}\hat{H}^{\alpha\beta}|\Psi_m\rangle \\ &= \hat{A}\sum_j |\Psi_j^{\alpha\beta}\rangle V_j^{\alpha\beta} \langle \Psi_j^{\alpha\beta} | \Psi_m \rangle.\end{aligned}\quad (20)$$

Here the wave functions $|\Psi_j^{\alpha\beta}\rangle$ of the whole polyatomic anion are constructed from products of the diatomic wave functions $|\psi_j^{\alpha\beta}\rangle$ multiplied by wave functions of electrons that are not included in $\hat{H}^{\alpha\beta}$,

$$|\Psi_j^{\alpha\beta}\rangle = \hat{s} |\psi_j^{\alpha\beta}\rangle |\chi_j^\gamma\rangle \cdots |\chi_j^\omega\rangle. \quad (21)$$

The overlap integrals in the Eq. (20) represent matrix elements of a transformation operator $\hat{B}^{\alpha\beta}$ for the construction of the functions $|\Psi_j^{\alpha\beta}\rangle$ from the basis set $|\Psi\rangle$. The corresponding matrix representation $\underline{B}^{\alpha\beta}$ links these two sets

$$\underline{|\Psi^{\alpha\beta}\rangle} = \underline{B}^{\alpha\beta} \underline{|\Psi\rangle}. \quad (22)$$

In practice, the elements of the matrix $\underline{B}^{\alpha\beta}$ are obtained as overlap integrals calculated with the wave functions of the electrons that are included in the diatomic fragment $\alpha\beta$, that is, as overlap integrals between the eigenfunctions $|\psi_j^{\alpha\beta}\rangle$ and the parts of the basis functions $|\Psi_m\rangle$, which depend on the electrons treated. Taking this into account, the operation of the diatomic Hamiltonian $\hat{H}^{\alpha\beta}$ on the whole basis set $\underline{|\Psi^{anti}\rangle}$ can be written in matrix form

$$\hat{H}^{\alpha\beta} \underline{|\Psi^{anti}\rangle} = \hat{A} \underline{B}^{\alpha\beta\dagger} \underline{V}^{\alpha\beta} \underline{|\Psi^{\alpha\beta}\rangle} = \underline{B}^{\alpha\beta\dagger} \underline{V}^{\alpha\beta} \underline{B}^{\alpha\beta} \underline{|\Psi^{anti}\rangle}. \quad (23)$$

Here $\underline{V}^{\alpha\beta}$ is a diagonal matrix, whose elements are the diatomic adiabatic potentials $V_j^{\alpha\beta}$ of the fragment $\alpha\beta$.

The operation of other fragment Hamiltonians in Eq. (18) on the basis set $\underline{|\Psi^{anti}\rangle}$ can be written in a way similar to Eq. (23), and finally the operation of the total electronic Hamiltonian \hat{H}_e on the whole basis set $\underline{|\Psi^{anti}\rangle}$ can be described by means of the following Hamiltonian matrix \underline{H}^{DIM} :

$$\hat{H}_e \underline{|\Psi^{anti}\rangle} = \underline{H}^{DIM} \underline{|\Psi^{anti}\rangle}, \quad (24)$$

where

$$\underline{H}^{DIM} = \sum_{\alpha\beta} \underline{B}^{\alpha\beta\dagger} \underline{V}^{\alpha\beta} \underline{B}^{\alpha\beta} - (N-2) \sum_{\alpha} \underline{V}^{\alpha}. \quad (25)$$

As continuum wave functions are not included and the basis set of bound-state wave functions in practice is truncated to a finite number, the matrix \underline{H}^{DIM} is finite, and, hence, its diagonalization provides both the potential-energy surfaces and eigenfunctions of the polyatomic molecule under consideration. The Hamiltonian matrix (25) coincides with the Hamiltonian matrix obtained by using another approach [18].

Thus, within the framework of the DIM approach, the input data required are the diatomic adiabatic potentials, the atomic energies, and the matrices $\underline{B}^{\alpha\beta}$ for the construction of diatomic eigenfunctions from products of single-atomic

wave functions. These data can be calculated separately for each atomic and diatomic fragment. Couplings of monoatomic bound states with continua are not considered within the conventional DIM method.

IV. COMBINATION OF THE PROJECTION-OPERATOR APPROACH AND THE DIATOMICS-IN-MOLECULES METHOD

Let us consider an N -atomic anion ($N \geq 3$). The basis set of the antisymmetrized many-electron functions $|\Psi_m^{anti}\rangle$ of the anion is taken in the form of Eq. (17), but includes continuum wave functions as well. In the spirit of the PO approach, the basis set of nonantisymmetrized basis functions $|\Psi_m\rangle$ consists of two subsets: (i) a set of discrete-state wave functions $|\Psi_{d_i}\rangle$ (all electrons are bound) and (ii) a set of continuum-state functions $|\Phi_{n,\tau,k}\rangle = |\Psi_{n,\tau}\rangle |k\rangle$ (one electron is unbound),

$$\underline{|\Psi\rangle} = \left\{ \begin{array}{l} \underline{|\Psi_d\rangle} \\ \underline{|\Phi_{nk}\rangle} \end{array} \right\}. \quad (26)$$

$|\Psi_{n,\tau}\rangle$ denotes an electronic state of the target molecule. From here on, the Latin indices i, j stand for discrete states with corresponding potentials V_{d_j} , while the Greek indices τ, λ stand for electronic ground and excited states of the neutral molecule with the potentials $V_{n,\tau}$, $V_{n,\lambda}$, respectively; the Greek superscripts α, β, γ label nuclei. The generalized index m runs over: (i) an index i (or j) of discrete states of an anion, (ii) an index τ (or λ) of electronic states of a neutral molecule, and (iii) an electronic continuum variable k ,

$$\{m\} = \{\{i\}; \{\tau k\}\}. \quad (27)$$

In the spirit of DIM, the basis functions $|\Psi_{d_i}\rangle$ and $|\Psi_{n,\tau}\rangle$ are chosen as superpositions of corresponding products of atomic wave functions [see Eq. (17)].

The electronic Hamiltonian \hat{H}_e of a polyatomic anion is represented in terms of diatomic $\hat{H}^{\alpha\beta}$ and atomic \hat{H}^α Hamiltonians by Eq. (18). Each of the fragment Hamiltonians $\hat{H}^{\alpha\beta}$ or \hat{H}^α can be written in the PO form as the generalization of Eq. (5). For the case of several discrete states of an anion interacting with several electron-scattering continua one has, for example,

$$\begin{aligned}\hat{H}^{\alpha\beta} &= \sum_j |\psi_{d_j}^{\alpha\beta}\rangle V_{d_j}^{\alpha\beta} \langle \psi_{d_j}^{\alpha\beta} | \\ &+ \sum_\lambda \int k^{\alpha\beta} dk^{\alpha\beta} d\Omega_{k^{\alpha\beta}} |\psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle \\ &\times (V_{n_\lambda}^{\alpha\beta} + E_{k^{\alpha\beta}}) \langle k^{\alpha\beta} | \langle \psi_{n_\lambda}^{\alpha\beta} | + \sum_{j,\lambda} \int k^{\alpha\beta} dk^{\alpha\beta} d\Omega_{k^{\alpha\beta}} \\ &\times (|\psi_{d_j}^{\alpha\beta}\rangle V_{d_j}^{\alpha\beta} V_{n_\lambda k}^{\alpha\beta} \langle k^{\alpha\beta} | \langle \psi_{n_\lambda}^{\alpha\beta} | \\ &+ |\psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle V_{n_\lambda k, d_j}^{\alpha\beta} \langle \psi_{d_j}^{\alpha\beta} |).\end{aligned}\quad (28)$$

Note that the small letters ψ and ϕ stand for diatomic wave functions, while the capital letters Ψ and Φ are used for polyatomic wave functions. The superscript $\alpha\beta$ determines a specified diatomic fragment with an internuclear distance $R_{\alpha\beta}$. For example, $|\psi_{d_j}^{\alpha\beta}\rangle$ stands for the wave function of a discrete state j of a diatomic fragment $\alpha\beta$ with a corresponding potential $V_{d_j}^{\alpha\beta}(R_{\alpha\beta})$, and so on.

According to the DIM philosophy one needs to construct the Hamiltonian matrix. This can be done by the operation of

the Hamiltonian \hat{H}_e on the basis set via the operation of the atomic and diatomic fragment Hamiltonians on a basis function. Of course, in the present case the Hamiltonian matrix is infinite dimensional. Taking into account that the operators $\hat{H}^{\alpha\beta}$ and \hat{A} commute with each other, and adding the unit operator $\sum_{m'} |\Psi_{m'}\rangle\langle\Psi_{m'}|$ in each term in Eq. (28), the operation of $\hat{H}^{\alpha\beta}$ on the basis wave function $|\Psi_m^{anti}\rangle$ [similar to the operation on a single term in Eq. (20)] can be written in the following form:

$$\begin{aligned} \hat{H}^{\alpha\beta}|\Psi_m^{anti}\rangle &= \hat{A}\hat{H}^{\alpha\beta}|\Psi_m\rangle \\ &= \hat{A}\left\{ \sum_{j,m'} |\Psi_{m'}\rangle\langle\Psi_{m'}|\Psi_{d_j}^{\alpha\beta}\rangle V_{d_j}^{\alpha\beta}\langle\Psi_{d_j}^{\alpha\beta}|\Psi_m\rangle \right. \\ &\quad + \sum_{\lambda,m'} \int k^{\alpha\beta} dk^{\alpha\beta} d\Omega_{k^{\alpha\beta}} |\Psi_{m'}\rangle\langle\Psi_{m'}|\Psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle (V_{n_\lambda}^{\alpha\beta} + E_{k^{\alpha\beta}}) \langle k^{\alpha\beta} | \langle\Psi_{n_\lambda}^{\alpha\beta}|\Psi_m\rangle \\ &\quad + \sum_{j,\lambda,m'} \left(\int k^{\alpha\beta} dk^{\alpha\beta} d\Omega_{k^{\alpha\beta}} |\Psi_{m'}\rangle\langle\Psi_{m'}|\Psi_{d_j}^{\alpha\beta}\rangle V_{d_j,n_\lambda}^{\alpha\beta} \langle k^{\alpha\beta} | \langle\Psi_{n_\lambda}^{\alpha\beta}|\Psi_m\rangle \right. \\ &\quad \left. \left. + \int k^{\alpha\beta} dk^{\alpha\beta} d\Omega_{k^{\alpha\beta}} |\Psi_{m'}\rangle\langle\Psi_{m'}|\Psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle V_{n_\lambda,k,d_j}^{\alpha\beta} \langle\Psi_{d_j}^{\alpha\beta}|\Psi_m\rangle \right) \right\}. \end{aligned} \quad (29)$$

Here, as well as in the preceding section, the transformation from the diatomic functions $|\psi_{d_j}^{\alpha\beta}\rangle$ and $|\psi_{n_\lambda}^{\alpha\beta}\rangle$ to the polyatomic functions $|\Psi_{d_j}^{\alpha\beta}\rangle$ and $|\Psi_{n_\lambda}^{\alpha\beta}\rangle$ was performed. The generalized index m' runs over both discrete and continuous values, and, hence, the summation over m' in the last equation means the summation over the integer indices i' and τ' of the anion discrete states and continuum states, respectively, and the integration over \vec{k}' ($k' dk' d\Omega_{k'}$). Taking into account the orthogonality of discrete and continuum states, the summation over m' in the first and the third terms in the right-hand side of the last equation results in the summation over the discrete state index i' only, while in the second and in the fourth terms it results in both the summation over the index τ' and the integration over $k' dk' d\Omega_{k'}$.

As the wave functions $|\Psi_{d_j}^{\alpha\beta}\rangle$ are constructed from the electronically bound wave functions, the overlap integrals between $|\Psi_{d_j}^{\alpha\beta}\rangle$ and the wave functions $|\Psi_m\rangle$ from the Q subspace represent matrix elements of a unitary-transformation operator $\hat{D}^{\alpha\beta}$ ($|\Psi_{d_j}^{\alpha\beta}\rangle = \hat{D}^{\alpha\beta}|\Psi_{d_j}\rangle$), operating in Q ,

$$\langle\Psi_m|\Psi_{d_j}^{\alpha\beta}\rangle = \langle\Psi_{d_i}|\Psi_{d_j}^{\alpha\beta}\rangle \delta_{m\{i\}} = D_{ji}^{\alpha\beta} \delta_{m\{i\}}. \quad (30)$$

Here the Kronecker symbol $\delta_{m\{i\}}$ is nonzero only if the index m corresponds to a function from the Q subspace. In a similar way in the P subspace one has

$$\begin{aligned} \langle\Psi_m|\Psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle &= \langle k | \langle\Psi_{n_\tau}|\Psi_{n_\lambda}^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle \delta_{m\{\tau k\}} \\ &= C_{\lambda k^{\alpha\beta}, \tau k}^{\alpha\beta} \delta_{kk^{\alpha\beta}} \delta_{m\{\tau k\}}. \end{aligned} \quad (31)$$

The unitary operator $\hat{C}^{\alpha\beta}$ determines the construction of the wave functions of a neutral diatomic fragment from the basis functions $|\Psi_{n_\tau}\rangle$, and the construction of the continuum wave functions of an electron scattered on a diatomic fragment $\alpha\beta$ from the wave functions $|k\rangle$ of the electron scattered on the whole anion ($|\Psi_n^{\alpha\beta}\rangle |k^{\alpha\beta}\rangle = \hat{C}^{\alpha\beta}|\Psi_n\rangle |k\rangle$). As a result, the operator $\hat{C}^{\alpha\beta}$ is a product of two commuting operators: ${}^n\hat{C}^{\alpha\beta}$ operating on the wave functions of bound states of the neutral molecule (the target states) and ${}^c\hat{C}^{\alpha\beta}$ operating on the continuum wave functions of a scattered electron.

The Kronecker symbol $\delta_{kk^{\alpha\beta}}$, being equal to

$$\delta_{kk^{\alpha\beta}} = \delta_{E_k E_{k^{\alpha\beta}}} \delta(\Omega_k - \Omega_{k^{\alpha\beta}}), \quad (32)$$

selects continuum states of equal energy

$$E_k = E_{k^{\alpha\beta}}, \quad (33)$$

whereas the Kronecker symbol $\delta_{m\{\tau k\}}$ selects the wave functions $|\Psi_m\rangle$ from the P subspace.

Taking Eqs. (30)–(32) into account, Eq. (29) can be rewritten as

$$\begin{aligned}
\hat{H}^{\alpha\beta}|\Psi_m^{anti}\rangle = & \hat{A} \sum_{m'} \left\{ \sum_j D_{ji'}^{\alpha\beta} \delta_{m'\{i'\}} V_{d_j}^{\alpha\beta} D_{ij}^{\alpha\beta\dagger} \delta_{m\{i\}} \right. \\
& + \sum_{\lambda} \int k dk d\Omega_k C_{\lambda\tau}^{\alpha\beta} \delta_{kk_m'} \delta_{m'\{\tau'k'\}} (V_{n_{\lambda}}^{\alpha\beta} + E_k) C_{\tau\lambda}^{\alpha\beta\dagger} \delta_{kk_m} \delta_{m\{\tau k\}} \\
& + \sum_{j,\lambda} \left(\int k dk d\Omega_k D_{ji'}^{\alpha\beta} \delta_{m'\{i'\}} V_{d_j,n_{\lambda}k}^{\alpha\beta} C_{\tau\lambda}^{\alpha\beta\dagger} \delta_{kk_m} \delta_{m\{\tau k\}} \right. \\
& \left. \left. + \int k dk d\Omega_k C_{\lambda\tau'}^{\alpha\beta} \delta_{kk_m'} \delta_{m'\{\tau'k'\}} V_{n_{\lambda}k,d_j}^{\alpha\beta} D_{ij}^{\alpha\beta\dagger} \delta_{m\{i\}} \right) \right\} |\Psi_{m'}\rangle. \quad (34)
\end{aligned}$$

Due to Eqs. (32) and (33), the integration in the last equation is carried out over \vec{k} instead of $\vec{k}^{\alpha\beta}$.

Equation (34) shows that the operation of the diatomic Hamiltonian $\hat{H}^{\alpha\beta}$ on the basis wave function $|\Psi_m^{anti}\rangle$ results in the sum of some terms [in the curly brackets in Eq. (34)], multiplied by the basis wave functions. Therefore, it can be written in matrix-multiplication form similar to Eq. (23). The operation of other fragment Hamiltonians in Eq. (18) on the basis function $|\Psi_m^{anti}\rangle$ can be written in a similar way. Finally, the operation of the total electronic Hamiltonian \hat{H}_e on the whole set of the basis functions $|\Psi_m^{anti}\rangle$ can be described by the Hamiltonian matrix \underline{H} ,

$$\hat{H}_e |\underline{\Psi}^{anti}\rangle = \underline{H} |\underline{\Psi}^{anti}\rangle, \quad (35)$$

where

$$\underline{H} = \begin{pmatrix} \underline{H}_d & \underline{V}_{dk'} & \underline{V}_{dk''} & \dots \\ \underline{V}_{k'd} & \underline{H}_n + E_{k'} \underline{I} & 0 & \dots \\ \underline{V}_{k''d} & 0 & \underline{H}_n + E_{k''} \underline{I} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (36)$$

Here the matrix

$$\underline{H}_d = \sum_{\alpha\beta} \underline{D}^{\alpha\beta\dagger} \underline{V}_d^{\alpha\beta} \underline{D}^{\alpha\beta} - (N-2) \sum_{\alpha} \underline{V}_d^{\alpha} \quad (37)$$

is the matrix for the calculation of the PESs of discrete states for the polyatomic anion, $\underline{V}_d^{\alpha\beta}$ is a diagonal matrix, the elements of which are the discrete-state potentials $V_{d_j}^{\alpha\beta}$ of a corresponding diatomic anion $\alpha\beta$. The matrix \underline{H}_d is constructed in a way similar to the conventional DIM method, but in Eq. (37) the potentials of the discrete states are used instead of the potentials of resonances for diatomic anions within the LCP approximation. By analogy,

$$\underline{H}_n = \sum_{\alpha\beta} \underline{C}^{\alpha\beta\dagger} \underline{V}_n^{\alpha\beta} \underline{C}^{\alpha\beta} - (N-2) \sum_{\alpha} \underline{V}_n^{\alpha} \quad (38)$$

is the matrix for the calculation of the PESs of the neutral polyatomic molecule, constructed within the standard DIM

method, $\underline{V}_n^{\alpha\beta}$ is a diagonal matrix, consisting of the potentials $V_{n_{\lambda}}^{\alpha\beta}$ of the neutral diatomic molecule $\alpha\beta$. \underline{I} is the unit matrix, and the matrices \underline{V}_{dk} and \underline{V}_{kd} are defined as

$$\underline{V}_{dk} = \sum_{\alpha\beta} \underline{D}^{\alpha\beta\dagger} \underline{V}_{dk}^{\alpha\beta} \underline{C}^{\alpha\beta} - (N-2) \sum_{\alpha} \underline{V}_{dk}^{\alpha}, \quad (39)$$

$$\underline{V}_{kd} = \underline{V}_{dk}^{\dagger}. \quad (40)$$

The matrix \underline{H} is infinite dimensional and exhibits block structure as indicated in Eq. (36).

The diagonalization of the matrix \underline{H}_d defined by Eq. (37) provides the matrix \underline{U} of the unitary transformation to the orthogonal wave functions of the discrete states in the Q subspace,

$$|\underline{\Psi}_d\rangle = \underline{U} |\underline{\Psi}_d^{anti}\rangle, \quad (41)$$

and the PESs \tilde{V}_{d_j} of the discrete states of the polyatomic anion

$$\underline{V}_d = \underline{U} \underline{H}_d \underline{U}^{\dagger}. \quad (42)$$

Note that the wave functions $|\underline{\Psi}_d\rangle$ are not eigenfunctions of the anion; they are coupled with continuum states.

The diagonalization of the matrix \underline{H}_n , Eq. (38), gives the matrix \underline{W} of the unitary transformation to the adiabatic wave functions of the polyatomic target molecule, which are the eigenfunctions of the corresponding Hamiltonian,

$$|\underline{\Psi}_n\rangle = \underline{W} |\underline{\Psi}_n^{anti}\rangle, \quad (43)$$

and the PESs $\tilde{V}_{n_{\lambda}}$ of the neutral molecule

$$\underline{V}_n = \underline{W} \underline{H}_n \underline{W}^{\dagger}. \quad (44)$$

The matrix \underline{H} defined by Eq. (36) is nondiagonal within the subblocks, being constructed by means of nonorthogonal basis functions within subsets. Performing block diagonalization separately in the Q and P subspaces, respectively, that is, making the transformation from the nonorthogonal wave functions $|\Psi_{d_i}^{anti}\rangle$ and $|\Psi_{n_{\tau}}^{anti}\rangle$ to the orthogonal (within the

subspaces Q and P) wave functions $|\tilde{\Psi}_{d_i}\rangle$ and $|\tilde{\Psi}_{n_\tau}\rangle$, one has the matrix $\underline{\tilde{H}}$, which gives the representation of the electronic Hamiltonian in orthogonal basis functions

$$\underline{\tilde{H}} = \begin{pmatrix} \underline{\tilde{V}}_d & \underline{\tilde{V}}_{dk'} & \underline{\tilde{V}}_{dk''} & \dots \\ \underline{\tilde{V}}_{k'd} & \underline{\tilde{V}}_n + E_{k'}I & 0 & \dots \\ \underline{\tilde{V}}_{k''d} & 0 & \underline{\tilde{V}}_n + E_{k''}I & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (45)$$

The matrices $\underline{\tilde{V}}_d$ and $\underline{\tilde{V}}_n$ are the diagonal ones defined above, and the matrices of couplings of discrete states with continua are defined as

$$\underline{\tilde{V}}_{dk} = \underline{U} \left[\sum_{\alpha\beta} \underline{D}^{\alpha\beta\dagger} \underline{V}_{dk}^{\alpha\beta} \underline{C}^{\alpha\beta} - (N-2) \sum_{\alpha} \underline{V}_{dk}^{\alpha} \right] \underline{W}^\dagger, \quad (46)$$

$$\underline{\tilde{V}}_{kd} = \underline{\tilde{V}}_{dk}^\dagger. \quad (47)$$

It is seen that the Hamiltonian matrix $\underline{\tilde{H}}$ of Eq. (45) has the form of an arrow matrix like in Eq. (6). The diagonal matrix elements are the PES of discrete states $\underline{\tilde{V}}_{d_i}$ and the energies of continuum states $\underline{\tilde{V}}_{n_\tau} + E_k$; the off-diagonal elements are nonzero only for couplings between discrete states and continua as defined by Eq. (46). The matrix $\underline{\tilde{H}}$ has a clear structure: the matrix $\underline{\tilde{V}}_d$ is the matrix representation of the operator \hat{H}_{QQ} in Eq. (5), which operates in the Q subspace, the matrices $\underline{\tilde{V}}_{dk}$ and $\underline{\tilde{V}}_{kd}$ correspond to the operators \hat{H}_{PQ} and \hat{H}_{QP} coupling the discrete and continuum states, and the rest represents the \hat{H}_{PP} operator in the P subspace.

Taking into account the form of the Hamiltonian matrix, Eq. (45), the Hamiltonian operator can be written in the projection-operator form

$$\begin{aligned} \hat{H}_e = & \sum_i |\tilde{\Psi}_{d_i}\rangle \tilde{V}_{d_i} \langle \tilde{\Psi}_{d_i}| \\ & + \sum_\tau \int k dk d\Omega_k |\tilde{\Psi}_{n_\tau}\rangle |k\rangle (\tilde{V}_{n_\tau} + E_k) \langle k| \langle \tilde{\Psi}_{n_\tau}| \\ & + \sum_{i,\tau} \int k dk d\Omega_k (|\tilde{\Psi}_{d_i}\rangle \tilde{V}_{d_i,n_\tau,k} \langle \tilde{\Psi}_{n_\tau}| \langle k| \\ & + |\tilde{\Psi}_{n_\tau}\rangle |k\rangle \tilde{V}_{n_\tau,k,d_i} \langle \tilde{\Psi}_{d_i}|), \end{aligned} \quad (48)$$

which is the natural generalization of Eq. (5) for the case of several discrete states and several continua. The formulas (37), (38), (42), (44), (46), and (47) allow one to achieve the PO description of the polyatomic anion from the corresponding information of atomic and diatomic anions.

Thus, the generalized DIM method consists of the following: in the spirit of DIM, the matrix \underline{H}_d for discrete states of a polyatomic anion is constructed by means of Eq. (37)

based on discrete-state potentials of diatomic and atomic anions; the diagonalization of this matrix provides the PESs of discrete states \tilde{V}_{d_i} and the matrix of the unitary transformation \underline{U} ; the matrix \underline{H}_n for the neutral polyatomic molecule is constructed within the standard DIM method by means of Eq. (38), which gives the PESs \tilde{V}_{n_τ} of the neutral molecule and the transformation matrix \underline{W} ; continuum states are associated with the PESs \tilde{V}_{n_τ} ; then couplings between discrete states of a polyatomic anion and continua are calculated by means of Eq. (46); and finally, the fixed-nuclei Hamiltonian within the projection-operator formalism is given by Eq. (48).

It is worth pointing out that the coupling-matrix elements of the diatomic discrete states with diatomic continua depend on both the corresponding internuclear distance $R_{\alpha\beta}$ and the electron energy E_k : $V_{d_i,n_\tau,k}^{\alpha\beta} = V_{d_i,n_\tau,k}^{\alpha\beta}(R_{\alpha\beta})$. As a result, the matrix elements \tilde{V}_{dk} of the coupling between polyatomic discrete states and polyatomic continua depend on the whole set of internuclear distances (for example, three distances for a triatomic anion: R_{ab} , R_{bc} , R_{ca}) and on an electron energy E_k : $\tilde{V}_{d_i,n_\tau,k} = \tilde{V}_{d_i,n_\tau,k}(\mathbf{R})$. \mathbf{R} stands for the set of coordinates describing the nuclear configuration in a multidimensional space (three dimensional for a triatomic anion).

As mentioned above, the PESs \tilde{V}_{d_i} of the discrete states, the neutral-molecule PESs \tilde{V}_{n_τ} , and the discrete-continuum couplings $\tilde{V}_{d_i,n_\tau,k}$ allow one to perform the dynamical treatment of both electron-molecule scattering and negative-ion-molecule collisional processes in the framework of the nonlocal complex-potential formalism. In analogy to Eqs. (14)–(16), the nonlocal complex effective potential for the polyatomic collision complex is given by the nonlocal matrix

$$V_{ij}^{eff}(\mathbf{R}, \mathbf{R}'; E) = V_{d_i}(\mathbf{R}) \delta_{ij} \delta(\mathbf{R} - \mathbf{R}') + F_{ij}(\mathbf{R}, \mathbf{R}'; E), \quad (49)$$

$$\begin{aligned} F_{ij}(\mathbf{R}, \mathbf{R}'; E) = & \sum_\tau \int k dk d\Omega_k \tilde{V}_{d_i,n_\tau,k}(\mathbf{R}) \\ & \times \tilde{G}_{n_\tau}^{(+)}(\mathbf{R}, \mathbf{R}'; E - k^2/2) \tilde{V}_{n_\tau,k,d_j}(\mathbf{R}'), \end{aligned} \quad (50)$$

where

$$\tilde{G}_{n_\tau}^{(+)}(\mathbf{R}, \mathbf{R}'; E) = \langle \mathbf{R} | (E - \hat{T}_N - V_{n_\tau} + i\eta)^{-1} | \mathbf{R}' \rangle \quad (51)$$

is the Green's function for nuclear motion in the target state τ . Equations (49)–(51) make explicit that the polyatomic nonlocal complex-potential matrix is completely determined by the functions $\tilde{V}_{d_i}(\mathbf{R})$, $\tilde{V}_{n_\tau}(\mathbf{R})$, and $\tilde{V}_{d_i,n_\tau,k}(\mathbf{R})$.

If the LCP approximation is used for the dynamical treatment, the LCPs can be derived within the present formalism on the basis of Eq. (48) [or Eq. (45)]. As described in Sec. II, the LCPs are defined as the poles of the corresponding T or S matrices in the complex k plane, and can be obtained by

using the approach of Refs. [72,77]. The poles are the complex solutions of the following equation, which is the generalization of Eq. (9):

$$\det \left| \frac{k^2}{2} \underline{I} + \underline{\tilde{V}}_n - \underline{\tilde{V}}_d(\mathbf{R}) - \underline{F}^t(\mathbf{R}, k) \right| = 0, \quad (52)$$

and the elements of the matrix $\underline{F}^t(\mathbf{R}, k)$ are defined as

$$F_{ij}^t(\mathbf{R}, k) = \sum_{\tau} F_{ij}^{\tau}(\mathbf{R}, k), \quad (53)$$

$$F_{ij}^{\tau}(\mathbf{R}, k) = \int k' dk' d\Omega_{k'} \frac{\tilde{V}_{d_i, n_{\tau}, k'}(\mathbf{R}) \tilde{V}_{n_{\tau}, k', d_j}(\mathbf{R})}{\frac{k^2}{2} - \frac{k'^2}{2}}. \quad (54)$$

The LCPs are then given by

$$V_{res}(\mathbf{R}) = \frac{k_{res}^2}{2} + \tilde{V}_{n_0}(\mathbf{R}), \quad (55)$$

k_{res} being the solution of Eq. (52) associated with the ground-state potential \tilde{V}_{n_0} of the neutral molecule. If the state is bound, the potential V_{res} is real. If $\text{Re}(\frac{1}{2}k_{res}^2) > 0$, the potential is complex and describes an electron-molecule resonance.

If the position of the resonance is defined as the singularity of the K matrix, then its position is given by the solution of the following equation for real E_k :

$$\det | E_k \underline{I} + \underline{V}_n - \underline{V}_d(\mathbf{R}) - \underline{\Delta}^t(\mathbf{R}, E_k) | = 0, \quad (56)$$

where $\Delta_{ij}^t(\mathbf{R}, E_k) = \text{Re} F_{ij}^t(\mathbf{R}, E_k)$. In this case the width of the resonance is obtained in a similar way as given by Eq. (11).

V. APPLICATION OF THE GENERALIZED DIM METHOD TO H_3^-

Let us apply the formalism derived in the previous section to the H_3^- collisional complex. According to Eq. (48), the construction of the electronic Hamiltonian of H_3^- in the projection-operator form requires (i) the PESs $\tilde{V}_{n_{\tau}}$ of the neutral H_3 molecule, (ii) the potential-energy surfaces \tilde{V}_{d_i} of discrete states of the H_3^- anion, and (iii) the couplings $\tilde{V}_{d_i, n_{\tau}, k}$ between discrete states and continua.

The H_3 PESs can be taken from *ab initio* calculations [3,4]. The construction of the $\tilde{V}_{d_i, n_{\tau}, k}$ matrix elements from diatomic information requires also the knowledge of the expansion-coefficient matrices $\underline{C}^{\alpha\beta}$ and \underline{W} for H_3 . In the present work they are calculated with the conventional DIM method with the minimum basis set, which consists of only two states [78],

$$|\Psi_{n_1}\rangle = \frac{1}{\sqrt{2}} (|\tilde{\chi}_H^a\rangle |\chi_H^b\rangle - |\chi_H^a\rangle |\tilde{\chi}_H^b\rangle) |\chi_H^c\rangle,$$

$$|\Psi_{n_2}\rangle = \frac{1}{\sqrt{6}} (2|\chi_H^a\rangle |\chi_H^b\rangle |\tilde{\chi}_H^c\rangle - |\chi_H^a\rangle |\tilde{\chi}_H^b\rangle |\chi_H^c\rangle - |\tilde{\chi}_H^a\rangle |\chi_H^b\rangle |\chi_H^c\rangle), \quad (57)$$

where $|\chi_H^{\alpha}\rangle$ and $|\tilde{\chi}_H^{\alpha}\rangle$ (the superscript $\alpha = a, b, \text{ or } c$ labels the nuclei $A, B, \text{ or } C$) represent the hydrogen-atom ground states with positive and negative spin quantum number, respectively. The matrices \underline{C}^{ab} , \underline{C}^{bc} , and \underline{C}^{ca} can easily be obtained from the basis (57), e.g., $\underline{C}^{ab} = \underline{I}$. The basis (57) provides a 2×2 matrix \underline{H}_n in accordance with Eq. (38). The input information here are the diatomic adiabatic potentials of the $\text{H}_2(X^1\Sigma_g^+)$ and $\text{H}_2(a^3\Sigma_u^+)$ states, which are known with high accuracy [79,80]. The diagonalization of \underline{H}_n gives the matrix \underline{W} [see Eq. (44)] and the two lowest surfaces $\tilde{V}_{n_{\tau}}$, which are then replaced by the *ab initio* PESs [4]. The construction of the continuum basis states $|\Phi_{n_{\tau}, k}\rangle$, required for the total basis set of Eq. (26) for the singlet states of H_3^- , from the basis states (57) is straightforward.

The minimum basis set for the low-lying singlet discrete states of the H_3^- anion consists of the following three states:

$$|\Psi_{d_1}\rangle = \frac{1}{\sqrt{2}} |\chi_{H^-}^a\rangle (|\tilde{\chi}_H^b\rangle |\chi_H^c\rangle - |\chi_H^b\rangle |\tilde{\chi}_H^c\rangle),$$

$$|\Psi_{d_2}\rangle = \frac{1}{\sqrt{2}} |\chi_{H^-}^b\rangle (|\tilde{\chi}_H^a\rangle |\chi_H^c\rangle - |\chi_H^a\rangle |\tilde{\chi}_H^c\rangle), \quad (58)$$

$$|\Psi_{d_3}\rangle = \frac{1}{\sqrt{2}} |\chi_{H^-}^c\rangle (|\tilde{\chi}_H^a\rangle |\chi_H^b\rangle - |\chi_H^a\rangle |\tilde{\chi}_H^b\rangle),$$

$|\chi_{H^-}^{\alpha}\rangle$ being the ground state of H^- . This leads to easily computable matrices \underline{D}^{ab} , \underline{D}^{bc} , \underline{D}^{ca} , and finally to a 3×3 matrix \underline{H}_d defined by Eq. (37). The input information here is the binding energy of H^- (the experimental value of 0.75 eV [81] is used in the present calculations) as well as the diatomic potentials of the $^2\Sigma_u^+$ and $^2\Sigma_g^+$ discrete states of H_2^- (see below and Appendix). The difference between the present generalized DIM approach and the LCP DIM method for H_3^- [17,18] is that the diatomic potentials $V_{d_j}^{\alpha\beta}$ and atomic energies $V_{d_j}^{\alpha}$ for the discrete states are used in Eq. (37) instead of the positions of the resonances. The output is the potential energies of the discrete states instead of the real parts of the LCP PESs. According to Eq. (42), the diagonalization of the matrix \underline{H}_d provides the PESs \tilde{V}_{d_i} of the three lowest singlet states of H_3^- and the matrix \underline{U} .

At each energy E_k the couplings between the three discrete states of H_3^- and the continua associated with the two lowest states of a neutral H_3 molecule are determined by a matrix \tilde{V}_{dk} defined by Eq. (46). As follows from this equation, the following input is needed: the matrices $\underline{D}^{\alpha\beta}$ and $\underline{C}^{\alpha\beta}$ for the construction of the DIM Hamiltonian matrices for both H_3^- discrete states and H_3 bound states from di-

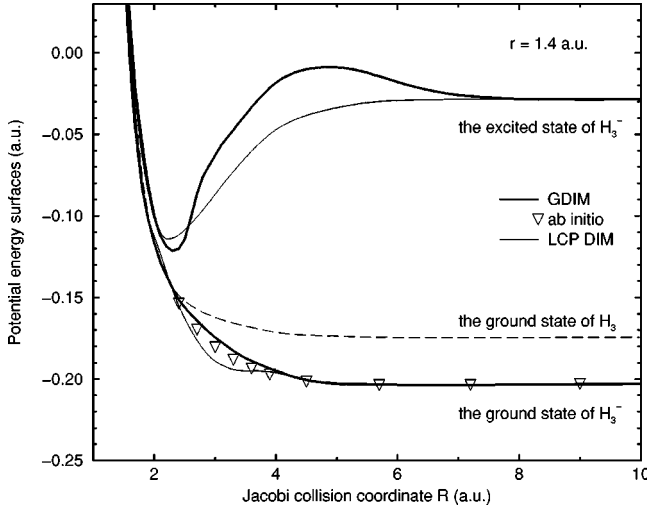


FIG. 1. The real parts of the local complex potentials of the ground and the first excited states of the H_3^- anion (solid lines) and the ground-state PES of the neutral H_3 molecule [4] (dashed line) for collinear geometry at the Jacobi internal coordinate $r=1.4$ a.u. as a function of the Jacobi collision coordinate. The thick lines are the real parts of PESs calculated by means of the generalized DIM method, the thin solid curves are the calculations within the LCP DIM method. The symbols are the *ab initio* data for the ground state of H_3^- [16], which are in agreement with the results of other *ab initio* calculations [13–15].

atomic potentials [Eqs. (37) and (38)], the matrices $V_{dk}^{\alpha\beta}$ and V_{dk}^α consisting of the coupling-matrix elements between discrete states and continua for the diatomic and atomic anions, and the transformation matrices \underline{U} and \underline{W} , obtained from the

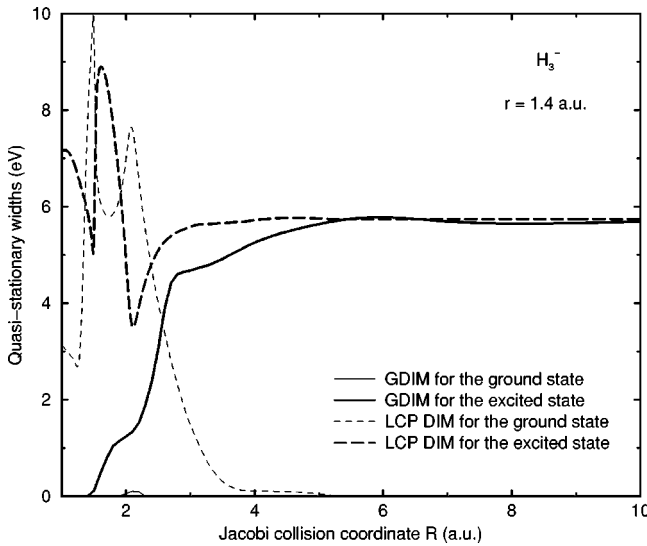


FIG. 2. The width functions of the ground and the first excited states of H_3^- for collinear geometry at the Jacobi internal coordinate $r=1.4$ a.u. as a function of the Jacobi collision coordinate. The thin and thick solid lines correspond to the widths of the ground and the first excited states obtained by means of the generalized DIM method, respectively; the thin and thick dashed curves are the calculations within the LCP DIM method for the ground and the first excited states.

diagonalization of the DIM matrices \underline{H}_d and \underline{H}_n [Eqs. (42) and (44)], respectively.

In contrast to the neutral hydrogen molecule, the data for the bound and resonant states of the H_2^- anion are not readily available. The potential-energy function of the $\text{H}_2^-(^2\Sigma_u^+)$ discrete state and the coupling between this discrete state and the $\text{H}_2(X^1\Sigma_g^+)$ *p*-wave continuum (as a function of both the internuclear distance R and the electronic energy) are known from the *ab initio* calculation for $R < 3$ a.u. [74]. When combined with *ab initio* data for the bound $\text{H}_2^-(^2\Sigma_u^+)$ state at $R > 3$ a.u. [82], this information allows us to construct the discrete-state potential and the corresponding coupling over the whole range of the internuclear distance and electronic energy [67]. Unfortunately, this information is not available for the $\text{H}_2^-(^2\Sigma_g^+)$ discrete state, which is coupled with the $\text{H}_2(X^1\Sigma_g^+)$ and $\text{H}_2(a^3\Sigma_u^+)$ continua. There exist several calculations of the LCP of the $\text{H}_2^-(^2\Sigma_g^+)$ resonance [83–88], as well as empirical LCPs obtained by fitting of experimental data [89,90]. In general, the LCP is not sufficient for the extraction of the complete information about the discrete-state potential and the couplings with the continua. Therefore, an *ab initio* calculation of these data for the $\text{H}_2^-(^2\Sigma_g^+)$ resonance is highly desirable. In the present work, the recent LCP obtained by an *R*-matrix calculation [88] is used for the construction of a model potential for the $\text{H}_2^-(^2\Sigma_g^+)$ discrete state and its couplings with the $\text{H}_2(X^1\Sigma_g^+)$ and $\text{H}_2(a^3\Sigma_u^+)$ continua. In order to avoid computational problems, a new simplified model for the $\text{H}_2^-(^2\Sigma_u^+)$ resonance also has been derived based on the *ab initio* calculation [74,82] and the model of Ref. [67]. The nonlocal diatomic models used in the present work for both the $\text{H}_2^-(^2\Sigma_u^+)$ and $\text{H}_2^-(^2\Sigma_g^+)$ resonances are specified in the Appendix.

The procedure described above allows us to obtain the electronic Hamiltonian of the H_3^- anion in the projection-operator form, Eq. (48). As mentioned above, this form provides the basis for a treatment of the nuclear dynamics beyond the LCP approximation. The same form of the electronic Hamiltonian can be used for calculating the LCP energy surfaces by means of Eqs. (52) or (56).

As an example, the calculated local complex potentials for the two lowest singlet states of H_3^- are shown in Figs. 1 and 2 for collinear geometry at the Jacobi internal coordinate $r=1.4$ a.u. as a function of the Jacobi collision coordinate R . The full three-dimensional surfaces obtained by the generalized DIM method will be reported in a separate publication. In the present calculations the real parts of the LCPs (the positions of the resonances) have been determined as the poles of *K* matrix, that is, as the solutions of Eq. (56) for real $E_k(\mathbf{R})$. The quasistationary widths $\Gamma_i(\mathbf{R})$ of the resonances are obtained from the imaginary parts of diagonal matrix elements $F_{ii}^t(\mathbf{R}, E_k)$, the energies $E_k(\mathbf{R})$ being given by the solution of Eq. (56): $\Gamma_i(\mathbf{R}) = -2 \text{Im} F_{ii}^t(\mathbf{R}, E_k(\mathbf{R}))$.

Figure 1 displays the real parts of the LCPs: the thick solid lines are the results of the calculations carried out by means of the generalized DIM method, while the thin solid curves are the real PESs obtained within the LCP DIM

method.³ The symbols are the *ab initio* data [16] for the ground state of H_3^- , and the dashed line corresponds to the ground state PES of H_3 [4]. It is seen that there is good agreement between the *ab initio* and the present calculations for the ground state of H_3^- , which asymptotically ($R \rightarrow \infty$) correlates to $\text{H}^- + \text{H}_2(X^1\Sigma_g^+)$. The quasistationary widths of the LCPs of the same states are shown in Fig. 2; the thin and thick solid lines correspond to widths of the ground and the first excited states of H_3^- obtained by means of the generalized DIM method, respectively, while the thin and thick dashed curves represent the calculations carried out within the LCP DIM method for the ground and the first excited states. The ground-state PES of H_3^- lies mainly below the PES of the ground state of H_3 at this geometry and, hence, is real in the generalized DIM calculations, except for a small region around $R=2$ a.u. where it is slightly above the ground-state H_3 PES. The *ab initio* calculations [16] also exhibit a crossing of the H_3^- and H_3 PESs in this region. It is seen from Fig. 1 that the LCP DIM potentials qualitatively reproduce the real parts of the LCPs, but the imaginary parts of the LCPs obtained by means of the LCP DIM method are not correct: the ground-state LCP is complex for $R < 5$ a.u., although the state is bound (see Fig. 2). In contrast to this, the generalized DIM method yields automatically a potential-energy surface, which is real for a bound state and complex for a resonance. An example of the latter case is the PES of the first excited state of H_3^- which asymptotically ($R \rightarrow \infty$) corresponds to the $\text{H} + \text{H}_2(^2\Sigma_u^+)$ configuration (see Fig. 1); it is located above the ground-state PES of the neutral H_3 molecule and has a nonzero imaginary part plotted in Fig. 2. Except for the asymptotic region, the magnitudes of the quasistationary widths calculated within the LCP DIM method are much larger than the ones obtained by means of the generalized DIM method, even when the real parts of the LCPs are close to each other. Thus, the LCP DIM method does not provide reliable results for imaginary parts of complex potentials. As mentioned above, the generalized DIM method developed in the present work is reliable and free of such artifacts as a complex potential for a bound state.

It has recently been shown by classical-trajectory [62] and wave-packet [65] calculations that the quasistationarity of the excited state (as well as the nonadiabatic transitions between the ground state and the first excited state) is responsible for the electron detachment process in low-energy $\text{H}^- + \text{H}_2$ collisions. While the calculation of the real part of the excited-state PES has been performed earlier [17,18] by means of the LCP DIM method, the present work represents the first calculation of the imaginary part.

It should be pointed out that the $\text{H}_2(^2\Sigma_g^+)$ resonance is short lived and the resonant electron energy is close to the threshold with respect to the $\text{H}_2(a^3\Sigma_u^+)$ continuum. As mentioned above, the LCP approximation breaks down in this case. For this reason the model for the $\text{H}_2(^2\Sigma_g^+)$ resonance,

obtained from the LCP [88], needs to be improved. In addition, it is pointed out in Ref. [88] that there is nonadiabatic coupling between the $\text{H}_2(^2\Sigma_g^+)$ resonance and another higher-lying resonance. To obtain more accurate PES of H_3^- , an extension of the basis set and more *ab initio* data for the $\text{H}_2(^2\Sigma_g^+)$ resonance are required.

VI. CONCLUSIONS

In the present paper the concept of the combination of the projection-operator approach and the diatomics-in-molecules method has been developed. The result is a generalized formulation of the diatomics-in-molecules method, which yields a description of potential-energy functions of both quasistationary and bound states for polyatomic anions. The derived approach is also applicable for quasistationary states of neutral and positively charged polyatomic systems. The proposed theory allows one to calculate potential-energy surfaces of both discrete states and discrete-continuum coupling elements from the corresponding data of the atomic and diatomic fragments, that is, to obtain the complete information for quasistationary and bound states of polyatomic anions. The ground as well as excited states of polyatomic anions can be described with this approach.

The extension of the projection-operator formalism to polyatomic systems obtained in this way provides the basis for a rigorous treatment of the nuclear dynamics of electron-molecule scattering, including resonance effects, and for ion-molecule collisions in terms of energy-dependent, complex, and nonlocal effective potentials. More approximate local complex potential-energy surfaces of quasistationary states also can be obtained with the generalized DIM method via the determination of the poles of the multichannel electron-molecule scattering matrix in the fixed-nuclei limit.

In previous calculations of the LCPs by means of the DIM method, the LCP approximation has been used first, and then the Hamiltonian matrix has been constructed with the conventional DIM method, based on the atomic and diatomic LCPs. This LCP DIM method cannot assure reliable LCP PESs in the vicinity of thresholds. It may yield, for example, nonzero imaginary parts of PESs for bound states. In the generalized DIM method, the Hamiltonian matrix as well as the projection-operator form of the Hamiltonian are constructed first based on the DIM philosophy, and then the LCP approximation is employed if the LCP PESs are desired. This strategy leads to consistent potentials with proper threshold behavior of the widths.

The input data needed for the generalized DIM method are the adiabatic energies of neutral atomic and diatomic fragments, the potential-energy functions of discrete states of atomic and diatomic anions, as well as energy- and distance-dependent couplings between the discrete states and the electron-molecule continua. This information is very limited at present, and more data of this kind are highly desirable.

In order to illustrate the concepts derived, the generalized DIM method has been applied to the ground and the first excited states of the H_3^- anion, making use of information that is available for the bound and resonance states of H^-

³Note that in the present work different positions of the $\text{H}_2(^2\Sigma_{u,g}^+)$ resonances are used than in the previous LCP DIM calculations [17,18,54].

TABLE I. The parameter $b_1(R)$ of the nonlocal model for the $\text{H}_2^- (^2\Sigma_u^+)$ resonance at small internuclear distances R .

R (a.u.)	b_1 (a.u.)	R (a.u.)	b_1 (a.u.)	R (a.u.)	b_1 (a.u.)	R (a.u.)	b_1 (a.u.)	R (a.u.)	b_1 (a.u.)
0.2	2.280	0.7	3.137	1.4	3.569	2.4	4.707	4.0	6.253
0.3	2.399	0.8	3.060	1.6	3.897	2.6	4.763	4.5	6.977
0.4	2.536	0.9	3.031	1.8	4.220	2.8	4.884	5.0	7.798
0.5	2.688	1.0	3.071	2.0	4.485	3.0	5.101	5.5	8.486
0.6	2.834	1.2	3.275	2.2	4.641	3.5	5.639		

and H_2^- . The LCP PES calculated in this way are physically consistent and in reasonably good agreement with the *ab initio* calculations as far as the latter are available [13–16].

ACKNOWLEDGMENTS

The financial support from the Deutsche Forschungsgemeinschaft making this work possible during the stay of A.K.B. at the Institute of Physical and Theoretical Chemistry, Technical University of Munich is gratefully acknowledged. A.K.B. is also thankful to Dr. P. J. Kuntz for fruitful discussions and to the Max-Planck-Institute for Quantum Optics (Garching, Germany) for hospitality and partial financial support.

APPENDIX

1. Nonlocal models for the $\text{H}_2^- (^2\Sigma_{u,g}^+)$ resonances

The description of resonances in electron-molecule scattering requires the following functions to be known (see, for example, [53]): (i) the potential energies $V_{n_\lambda}(\mathbf{R})$ of the considered states of the neutral molecule, (ii) the potential energies $V_{d_i}(\mathbf{R})$ of the relevant discrete states of the anion, and (iii) the discrete-continuum coupling elements $V_{d_i, n_\lambda k}(\mathbf{R})$ as functions of both nuclear configuration coordinates \mathbf{R} and continuum electron parameters. In the case of a diatomic anion, the nuclear configuration is described by the internuclear separation R . For the $\text{H}_2^- (^2\Sigma_{u,g}^+)$ resonances, the target states are the ground state $X^1\Sigma_g^+$ and the lowest triplet state $a^3\Sigma_u^+$ with the well-known potential energies $V_{n_1}(R)$ and $V_{n_2}(R)$ [79,80]. For the $\text{H}_2^- (^2\Sigma_u^+)$ resonance, the discrete-state potential, the quasistationary width, and the energy shift have been calculated with *ab initio* methods as functions of the electron kinetic energy $E = k^2/2$ for a grid of seven inter-

nuclear distances R , ranging from 1.4014 to 2.75 a.u. [74]. Based on these data a short-range ($1 \text{ a.u.} < R < 3 \text{ a.u.}$) nonlocal model has been obtained [91], that is, analytic fits have been obtained for the discrete-state potential $V_{d_1}(R)$ and for the matrix element $V_{d_1, n_1 k}(R)$, which couples the $\text{H}_2^- (^2\Sigma_u^+)$ discrete state with the $\text{H}_2(X^1\Sigma_g^+)$ continuum. By a combination with *ab initio* calculations of the bound $\text{H}_2^- (^2\Sigma_u^+)$ potential for $R > 3$ a.u. [82], a nonlocal model for the $\text{H}_2^- (^2\Sigma_u^+)$ resonance over the whole range of the internuclear separation and the electronic energy has been obtained [67]. In both models [67,91], the $V_{d_1, n_1 k}(R)$ coupling is represented by a sum of three terms, which leads to six terms for the energy shift [see Eq. (8)]. In order to simplify the calculations, a new nonlocal model for the $\text{H}_2^- (^2\Sigma_u^+)$ resonance based on the *ab initio* calculations [74,82,91] and on the model of Ref. [67] has been developed in the present work. In the new model described below, the discrete-continuum coupling element consists of a single, albeit nonseparable, term.

In contrast to the $\text{H}_2^- (^2\Sigma_u^+)$ resonance, few calculations have been performed for the $\text{H}_2^- (^2\Sigma_g^+)$ resonance. Only LCP information is available [83–90], which is not sufficient for the construction of a nonlocal model. In the present work, a preliminary nonlocal model for the $\text{H}_2^- (^2\Sigma_g^+)$ resonance is obtained, based on a recent R -matrix calculation of the short-range (from 0.8 to 4 a.u.) local complex potential [88] as well as on the long-range ($R > 4$ a.u.) empirical LCP [90] obtained by the fitting of experimental data.

Atomic units are assumed in all formulas given in the following.

2. The $\text{H}_2^- (^2\Sigma_u^+)$ resonance

The discrete-state potential $V_{d_1}(R)$ for the p -wave $^2\Sigma_u^+$ resonance in electron- H_2 scattering is taken from the model of Ref. [67]. The analytic form of the potential is

$$V_{d_1}(R) = \begin{cases} 1.74e^{-2.37R} - \frac{94.4e^{-22.5/R}}{((R-2.54)^2 + 3.11)^2} + E^- & \text{for } R \leq 10.6 \text{ a.u.}, \\ -0.00845Re^{-0.35R} - \frac{2.25}{R^4} - \frac{97}{R^6} + E^- & \text{for } R > 10.6 \text{ a.u.}, \end{cases} \quad (\text{A1})$$

TABLE II. The short-range part of the potential $V_{d_2}(R)$ for the $\text{H}_2^-(^2\Sigma_g^+)$ discrete state as a function of the internuclear distance R .

R (a.u.)	V_{d_2} (a.u.)	R (a.u.)	V_{d_2} (a.u.)	R (a.u.)	V_{d_2} (a.u.)	R (a.u.)	V_{d_2} (a.u.)	R (a.u.)	V_{d_2} (a.u.)
0.20	2.25000	2.00	0.19822	3.80	0.01890	5.40	-0.01137	8.01	-0.02348
0.40	1.10000	2.20	0.15600	4.00	0.01347	5.60	-0.01369	8.40	-0.02407
0.60	0.70500	2.40	0.12128	4.20	0.00911	5.86	-0.01601	8.74	-0.02449
0.80	0.50167	2.60	0.09042	4.40	0.00506	6.12	-0.01783	9.11	-0.02486
1.00	0.38683	2.80	0.06828	4.50	0.00306	6.40	-0.01925	9.50	-0.02519
1.20	0.33322	3.00	0.05367	4.70	-0.00006	6.71	-0.02046	10.0	-0.02554
1.40	0.29433	3.20	0.04287	4.84	-0.00311	7.03	-0.02143	10.5	-0.02582
1.60	0.26658	3.40	0.03366	5.00	-0.00580	7.38	-0.02229	11.2	-0.02615
1.80	0.23742	3.60	0.02556	5.17	-0.00843	7.68	-0.02290		

where $E^- = -0.0277$ a.u. is the binding energy of H^- .

In order to be able to perform the calculation of the complex level-shift [see Eq. (54)] analytically, the discrete-continuum coupling is parametrized as

$$V_{d_1, n_1 k}(R) = \frac{1}{\sqrt{2\pi}} E^{3/4} e^{-b_1(R)E} g_1(R), \quad E = \frac{k^2}{2}. \quad (\text{A2})$$

This ansatz fulfills the Wigner threshold law for p -wave scattering [92]. The function $g_1(R)$ is given by

$$g_1(R) = 3.5 \exp(-0.0346 R^2). \quad (\text{A3})$$

To allow the approximation of the discrete-continuum coupling by the single term (A2), the coefficient b_1 is chosen to be R dependent. For $R < 5.5$ a.u., this dependence is given numerically in Table I. Otherwise it has the analytic form

$$b_1(R) = \frac{A_1 - A_2}{1 + \exp\left(\frac{R - R_0}{\Delta R}\right)} + A_2, \quad R > 5.5 \text{ a.u.}, \quad (\text{A4})$$

where $A_1 = 2.198$, $A_2 = 10.654$, $R_0 = 3.883$, and $\Delta R = 1.518$.

3. The $\text{H}_2^-(^2\Sigma_g^+)$ resonance

The short-range ($R \leq 11.2$ a.u.) discrete-state potential $V_{d_2}(R)$ for the $\text{H}_2^-(^2\Sigma_g^+)$ resonance has been obtained numerically and is given in Table II. At long range, the potential has the analytic form

$$V_{d_2}(R) = 0.008 R e^{-0.35R} - \frac{2.25}{R^4} - \frac{97}{R^6} + E^- \quad \text{for } R > 11.2 \text{ a.u.} \quad (\text{A5})$$

This discrete state is coupled with the $\text{H}_2(X^1\Sigma_g^+)$ ground-state and the lowest triplet-state ($a^3\Sigma_u^+$) continua by the following matrix elements:

$$V_{d_2, n_1 k}(R) = \frac{1}{\sqrt{2\pi}} E^{1/4} e^{-b_2 E} g_2(R), \quad (\text{A6})$$

$$g_2(R) = \sum_{j=1}^2 h_j^{(1)} \exp(-t_j^{(1)} [R - R_j^{(1)}]^2), \quad (\text{A7})$$

$$V_{d_2, n_2 k}(R) = \frac{1}{\sqrt{2\pi}} E^{3/4} e^{-b_3 E} g_3(R), \quad (\text{A8})$$

$$g_3(R) = \sum_{j=1}^2 h_j^{(2)} \exp(-t_j^{(2)} [R - R_j^{(2)}]^2). \quad (\text{A9})$$

The parameters of the model have the following values: $b_2 = 2.7212$, $b_3 = 15.0$, $h_1^{(1)} = 0.33$, $h_2^{(1)} = 0.22$, $t_1^{(1)} = 1.2$, $t_2^{(1)} = 0.7$, $R_1^{(1)} = 1.85$, $R_2^{(1)} = 4.0$, $h_1^{(2)} = 5.8$, $h_2^{(2)} = 4.67$, $t_1^{(2)} = 1.8$, $t_2^{(2)} = 0.15$, $R_1^{(2)} = 1.74$, $R_2^{(2)} = 3.1$. The formulas (A6) and (A8) fulfill the Wigner threshold law for s and p waves, respectively.

The described nonlocal model yields both the position and the width of the $\text{H}_2^-(^2\Sigma_g^+)$ resonance in accordance with the data of [88,90].

[1] W. H. Miller, *Annu. Rev. Phys. Chem.* **41**, 245 (1990).
 [2] J. Z. H. Zhang, *Theory and Application of Quantum Molecular Dynamics* (World Scientific, New York, 1998).
 [3] P. Siegbahn and B. Liu, *Chem. Phys.* **68**, 2457 (1978).
 [4] A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, *J. Chem. Phys.* **86**, 6258 (1987).
 [5] A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.* **241**, 229 (1995).

[6] J. R. Hiskes, *Comments At. Mol. Phys.* **19**, 59 (1987).
 [7] U. Hege and F. Linder, *Z. Phys. A* **320**, 95 (1985).
 [8] M. Zimmer and F. Linder, *Chem. Phys. Lett.* **195**, 153 (1992).
 [9] M. Zimmer and F. Linder, *J. Phys. B* **28**, 2671 (1995).
 [10] H. Müller, M. Zimmer, and F. Linder, *J. Phys. B* **29**, 4165 (1996).
 [11] E. Haufler, S. Schlemmer, and D. Gelflich, *J. Phys. Chem. A* **101**, 6441 (1997).

- [12] M. S. Huq, L. D. Doverspike, and R. L. Champion, *Phys. Rev. A* **27**, 2831 (1983).
- [13] O. K. Kabbaj, F. Volatron, and J.-P. Malrieu, *Chem. Phys. Lett.* **147**, 353 (1988).
- [14] H. H. Michels and J. A. Montgomery, Jr., *Chem. Phys. Lett.* **139**, 535 (1987).
- [15] G. Chałasinski, R. A. Kendall, and J. Simons, *J. Phys. Chem.* **91**, 6151 (1987).
- [16] J. Stärck and W. Meyer, *Chem. Phys.* **176**, 83 (1993).
- [17] A. K. Belyaev, D. T. Colbert, G. C. Groenenboom, and W. H. Miller, *Chem. Phys. Lett.* **209**, 309 (1993).
- [18] A. K. Belyaev and A. S. Tiukanov, *Chem. Phys.* **220**, 43 (1997).
- [19] F. A. Gianturco, S. Kumar, and F. Schneider, *J. Chem. Phys.* **105**, 156 (1996).
- [20] R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966).
- [21] J. R. Taylor, *Scattering Theory* (Wiley, New York, 1972).
- [22] J. Z. H. Zhang, S.-I. Chu, and W. H. Miller, *J. Chem. Phys.* **88**, 6233 (1988).
- [23] W. Domcke, M. Berman, C. Mündel, and H.-D. Meyer, *Phys. Rev. A* **33**, 222 (1986).
- [24] M. McCartney, P. G. Burke, L. A. Morgan, and C. J. Gillan, *J. Phys. B* **23**, L415 (1990).
- [25] T. N. Rescigno, A. E. Orel, and C. W. McCurdy, *J. Chem. Phys.* **73**, 6347 (1980).
- [26] J. G. Lauderdale, C. W. McCurdy, and A. U. Hazi, *J. Chem. Phys.* **79**, 2200 (1983).
- [27] S. Mahalakshmi and M. K. Mishra, *Chem. Phys. Lett.* **296**, 43 (1998).
- [28] U. V. Riss and H.-D. Meyer, *J. Phys. B* **26**, 4503 (1993).
- [29] F. O. Ellison, *J. Am. Chem. Soc.* **85**, 3540 (1963).
- [30] J. C. Tully, in *Semiempirical Methods of Electronic Structure Calculations*, edited by G. A. Segal (Plenum, New York, 1977), p. 173.
- [31] P. J. Kuntz, in *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum Press, New York, 1979), p. 79.
- [32] C. J. Margulis, D. A. Horner, S. Bonella, and D. F. Coker, *J. Phys. Chem. A* **103**, 9552 (1999).
- [33] C. J. Margulis and D. F. Coker, *J. Chem. Phys.* **113**, 6113 (2000).
- [34] D. Babikov, E. A. Gislason, M. Sizun, F. Aguillon, and V. Sidis, *J. Chem. Phys.* **112**, 7032 (2000).
- [35] S. F. Alberti, J. Echave, V. Engel, N. Halberstadt, and J. A. Beswick, *J. Chem. Phys.* **113**, 1027 (2000).
- [36] C. J. Margulis and D. F. Coker, *J. Chem. Phys.* **114**, 6744 (2001).
- [37] V. S. Batista and D. F. Coker, *J. Chem. Phys.* **105**, 4033 (1996).
- [38] A. V. Nemukhin, B. L. Grigorenko, E. Ya. Ekasyrskaya, I. A. Topol, and S. K. Burt, *J. Chem. Phys.* **112**, 513 (2000).
- [39] V. S. Batista and D. J. Coker, *J. Chem. Phys.* **106**, 6923 (1997).
- [40] J. B. Giorgi, F. Y. Naumkin, J. C. Polanyi, S. A. Raspopov, and N. S.-K. Sze, *J. Chem. Phys.* **112**, 9569 (2000).
- [41] V. S. Batista and D. F. Coker, *J. Chem. Phys.* **106**, 7102 (1997).
- [42] B. L. Grigorenko, A. V. Nemukhin, I. A. Topol, and S. K. Burt, *J. Chem. Phys.* **113**, 2638 (2000).
- [43] M. Y. Niv, M. Bargheer, and R. B. Gerber, *J. Chem. Phys.* **113**, 6660 (2000).
- [44] A. Herzenberg, *J. Phys. B* **1**, 548 (1968).
- [45] W. H. Miller, *J. Chem. Phys.* **52**, 3563 (1970).
- [46] R. Polak, I. Paidarova, and P. J. Kuntz, *J. Chem. Phys.* **82**, 2352 (1985).
- [47] M. Sizun, E. A. Gislason, and G. Parlant, *Chem. Phys.* **107**, 311 (1986).
- [48] C. J. Margulis, D. F. Coker, and R. M. Lynden-Bell, *J. Chem. Phys.* **114**, 367 (2001).
- [49] J. Vojtik and I. Paidarova, *Chem. Phys. Lett.* **99**, 93 (1983).
- [50] J. Vojtik, I. Paidarova, and F. Schneider, *Chem. Phys.* **114**, 369 (1987).
- [51] I. Paidarova and J. Vojtik, *Chem. Phys.* **122**, 89 (1988).
- [52] J. H. Bardsley, *J. Phys. B* **1**, 349 (1968).
- [53] W. Domcke, *Phys. Rep.* **208**, 97 (1991).
- [54] A. K. Belyaev and A. S. Tiukanov, *Chem. Phys. Lett.* **302**, 65 (1999).
- [55] F. A. Gianturco and S. Kumar, *J. Chem. Phys.* **103**, 2940 (1995).
- [56] F. A. Gianturco and S. Kumar, *J. Phys. Chem.* **99**, 15 342 (1995).
- [57] S. Mahapatra, N. Sathyamurthy, S. Kumar, and F. A. Gianturco, *Chem. Phys. Lett.* **241**, 223 (1995).
- [58] S. Mahapatra and N. Sathyamurthy, *J. Phys. Chem.* **100**, 2759 (1996).
- [59] F. A. Gianturco and S. Kumar, *J. Phys. B* **30**, 3031 (1997).
- [60] S. Mahapatra and N. Sathyamurthy, *Faraday Discuss.* **110**, 228 (1998).
- [61] W. H. Ansari and N. Sathyamurthy, *Chem. Phys. Lett.* **289**, 487 (1998).
- [62] A. K. Belyaev and A. S. Tiukanov, *Chem. Phys. Rep.* **18**, 1289 (2000).
- [63] T. Takayanagi and Y. Kurosaki, *Phys. Chem. Chem. Phys.* **2**, 665 (2000).
- [64] S. Mahapatra, *Phys. Chem. Chem. Phys.* **2**, 671 (2000).
- [65] F. Aguillon, A. K. Belyaev, V. Sidis, and M. Sizun, *Phys. Chem. Chem. Phys.* **2**, 3577 (2000).
- [66] R. Jaquet and M. Heinen, *J. Phys. Chem. A* **105**, 2738 (2001).
- [67] M. Čížek, J. Horáček, and W. Domcke, *J. Phys. B* **31**, 2571 (1998).
- [68] H. Feshbach, *Ann. Phys. (N.Y.)* **5**, 357 (1958).
- [69] H. Feshbach, *Ann. Phys. (N.Y.)* **19**, 287 (1962).
- [70] U. Fano, *Phys. Rev.* **124**, 1866 (1961).
- [71] R. J. Eden and J. R. Taylor, *Phys. Rev.* **133**, B1575 (1964).
- [72] M. Ohno and W. Domcke, *Phys. Rev. A* **28**, 3315 (1983).
- [73] M. Berman, L. S. Cederbaum, and W. Domcke, *J. Phys. B* **16**, 875 (1983).
- [74] M. Berman, C. Mündel, and W. Domcke, *Phys. Rev. A* **31**, 641 (1985).
- [75] M. Čížek, J. Horáček, and W. Domcke, *Phys. Rev. A* **60**, 2873 (1999).
- [76] T. Beyer, B. M. Nestmann, and S. D. Peyerimhoff, *J. Phys. B* **33**, 4657 (2000).
- [77] A. L. Sobolewski and W. Domcke, *J. Chem. Phys.* **88**, 5571 (1988).
- [78] F. O. Ellison, N. T. Huff, and J. C. Patel, *J. Am. Chem. Soc.* **85**, 3544 (1963).
- [79] W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964).

- [80] W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).
- [81] H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975).
- [82] J. Senekowitsch, P. Rosmus, W. Domcke, and H.-J. Werner, *Chem. Phys. Lett.* **111**, 211 (1984).
- [83] I. Eliezer, H. S. Taylor, and J. K. Williams, *J. Chem. Phys.* **47**, 2165 (1967).
- [84] B. D. Buckley and C. Bottcher, *J. Phys. B* **10**, L636 (1977).
- [85] J. N. Bardsley and J. S. Cohen, *J. Phys. B* **11**, 3645 (1978).
- [86] D. T. Stibbe and J. Tennyson, *J. Phys. B* **29**, 4267 (1996).
- [87] D. T. Stibbe and J. Tennyson, *J. Phys. B* **30**, L301 (1997).
- [88] D. T. Stibbe and J. Tennyson, *J. Phys. B* **31**, 815 (1998).
- [89] J. C. Y. Chen and J. L. Peacher, *Phys. Rev.* **167**, 30 (1968).
- [90] J. N. Bardsley and J. M. Wadehra, *Phys. Rev. A* **20**, 1398 (1979).
- [91] C. Mündel, M. Berman, and W. Domcke, *Phys. Rev. A* **32**, 181 (1985).
- [92] E. P. Wigner, *Phys. Rev.* **73**, 1002 (1948).