Ab initio interatomic decay widths of excited states by applying Stieltjes imaging to Lanczos pseudospectra

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Electronically excited states of atoms and molecules in an environment may decay in interatomic processes by transferring excess energy to neighboring species and ionizing them. The corresponding interatomic decay width is the most important characteristic of the decay allowing to calculate its efficiency and the final states’ distribution. In this paper we present calculations of interatomic decay widths by the Fano–Stieltjes method applied to Lanczos pseudospectra, which has been previously shown to provide accurate autoionization widths in atoms and molecules. The use of Lanczos pseudospectra allows one to avoid the full diagonalization bottleneck and makes the method applicable to larger systems. We apply the present method to the calculation of interatomic decay widths in NeMg, NeAr and HCN-Mg, n = 1, 2 clusters. The results are compared with widths obtained analytically and by other ab initio methods where available. © 2011 American Institute of Physics. [doi:10.1063/1.3558739]

I. INTRODUCTION

Since its theoretical prediction1 the interatomic Coulombic decay (ICD) mechanism of electronically excited states in an environment has been the topic of extensive experimental2–10 and theoretical11–19 research. Electronically excited states participating in ICD may be produced in a variety of ways, e.g., through the ionization of an inner-valence electron, following the Auger decay of a core vacancy, or through a resonant excitation of inner- or outer-valence electrons, respectively. In ICD these states decay by transferring the energy and ionizing the environment. The most important characteristic of a decay process is the corresponding decay width. The knowledge of the latter allows one to estimate the efficiency of the decay into a particular channel and also makes possible calculating the distributions of the final states.19–23 There is a need of efficient and accurate methods for calculating the widths of decay processes involving electron emission. This is particularly important in the case of ICD processes where the number of environment species participating in and contributing to the decay is usually large.

The complexity of the interatomic decay, which involves the correlation of electronic motion on different weakly bound atoms or molecules, precludes the derivation of a general analytical formula for the decay width. However, once the distance between the excited moiety and neighboring species of the environment becomes large it is possible to obtain analytical expressions in the framework of the virtual photon transfer model.14, 18 These asymptotic decay widths are reasonably accurate at large interatomic distances, but are shown to underestimate the true widths at equilibrium geometries by as much as a few orders of magnitude.14, 18 However, since they can be expressed by the properties of the isolated excited moiety and environment species, whose values are often available in the literature, these asymptotic expressions provide an easy way for estimating the interatomic decay widths and can be used to verify ab initio results at asymptotic distances.

Apart from decay mechanisms based on nuclear rearrangements, excited states decay over time by photon or, if energetically allowed, electron emission. Such decaying states have complex energies \( E = E_R - i\Gamma /2 \), where \( \Gamma \) is the decay width, which is the sum over partial decay widths of the open decay channels, i.e., radiative, autoionization, interatomic Coulombic, etc. Since our primary interest lies in formulating a method suitable for calculating the widths of the decay processes arising due to electron correlation, i.e., interatomic Coulombic decay or autoionization widths, we will understand by the full width \( \Gamma \) the sum of the corresponding partial widths only. The property of resonances to have complex energies suggests a natural approach to compute \( \Gamma \): analytic continuation of the many-electron Hamiltonian into the complex energy plane. One way to achieve this is by adding a complex absorbing potential (CAP) to the Hamiltonian.24–26 In the case of electronic decay this Hamiltonian is represented using some many-electron ansatz, e.g., algebraic diagrammatic construction (ADC),27, 28 coupled cluster (CC),29 or configuration interaction (CI).30 The complex resonance energy is obtained by repeated diagonalization of the non-Hermitian complex symmetric Hamiltonian matrix for different CAP strengths. Since addition of a CAP discretizes the electronic continuum, CAP based methods have the advantage of being able to use \( \mathcal{C}^2 \) basis sets, such as Gaussian basis sets common in all standard methods for electronic structure studies.

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calculations, to represent the electronic continuum wave functions. The major drawbacks of the method are its numerical cost and the fact that a narrow resonance does not manifest itself in the results, until the underlying one-particle basis set becomes of considerable size.24

Another approach to calculate interatomic decay widths is based on the picture due to Fano31 and Feshbach32 of a resonance as a bound state embedded and interacting with the continuum. The coupling between the initial bound excited state and the ionization continuum of the environment is governed by interatomic electron correlation. The resulting decay width can be obtained from the corresponding golden-rule-like expression.31, 33, 34 The initial and final states of the decay may be constructed by a variety of techniques. To lowest order in perturbation theory they can be taken as spin-adapted Slater determinants of one-electron, e.g., Hartree–Fock, functions.35 The resulting calculations are very efficient numerically, but the neglect of electron correlation in the initial and final states may produce rather inaccurate results.16, 36 We improved this ansatz in calculations of the interatomic decay in systems having inversion symmetry, e.g., decay of inner-valence excited states in Ne2, by utilizing CI including single excitations to describe the initial state.37 Further improvement has been achieved employing the Fano ansatz,38 which allows one to consistently represent electron correlation in the initial and final states as well as the coupling between them to a desired accuracy. The main advantage of this family of methods is the ability to obtain the decay width directly after diagonalization of Hermitian matrices for any underlying one-particle basis. Moreover, the extension of these methods to the estimation of partial decay widths is possible,39 allowing us to calculate the autoionization and ICD widths separately.

The main disadvantage of the original Fano ansatz is the use of continuum electron wave functions whose asymptotic behavior and correct normalization cannot be reproduced by \( L^2 \) basis sets. This difficulty has been overcome in Ref. 38 by combining the Fano ansatz with the Stieltjes imaging technique.40–46 Employing this technique helps to evaluate decay widths by the Fano method using \( L^2 \) one-particle basis sets. The Stieltjes imaging technique allows to extract correctly normalized continuum quantities, e.g., decay widths or photoionization cross sections, from a discrete spectrum by calculating the spectral moments of the quantity in question and using them to construct consecutive approximations to the quantity itself. We have previously applied Stieltjes imaging to the calculations of the widths of states decaying by electron emission.14, 38, 47, 48 The standard implementation of the Stieltjes imaging requires the knowledge of a large part of the eigenspectrum of the corresponding Hamiltonian matrix and is, therefore, restricted to atomic or small molecular systems. This drawback of the Stieltjes imaging technique was realized at an early stage49 and a number of suggestions as to how it can be overcome exist in the literature.40–52 We proposed a general approach of employing the Stieltjes imaging technique in problems involving Hamiltonian matrices of large dimension. Our method53 is based on applying the Stieltjes imaging procedure to the block-Lanczos pseudospectra instead of the full spectra of the Hamiltonian. In the block Lanczos procedure one converges iteratively to a subspace of eigenvectors having nonzero overlap with a starting block of vectors.54 A judicious choice of the latter adapted to the problem at hand allows one to obtain continuum quantities of desired precision within reasonable computational time.

In this paper we extend the previous work by utilizing the combination of the Fano-ADC-Stieltjes procedure and the Lanczos method to calculate the decay widths of excited states undergoing interatomic (intermolecular) decay. The application of this method to the interatomic decay of singly and doubly ionized excited states is analogous. However, from the purely technical standpoint the calculations in the case of neutral excited states are more demanding than in the case of the ionized states due to the much larger dimensions of the Hamiltonian matrices for the same systems and one-particle basis sets. Our particular interest lies in the single excitations of inner- and outer-valence electrons which can be produced in single photon absorption. The interatomic decay of such excited states is known as resonant ICD (RICD) and excitation transfer ionization (ETI) in the case of inner- and outer-valence excitation, respectively, (see Fig. 1) and has been investigated theoretically in previous work.16, 17 The different names given to these processes are due to the fact that the excitation of an inner-valence electron leads to additional interatomic decay channels compared to the decay of an outer-valence excitation. The paper is structured as follows. Section II contains a short overview of the underlying theory. In Sec. III we consider a number of applications: in Subsection III A we calculate ETI widths in NeAr clusters, in Subsection III B we determine ETI widths in HCN-Mg and HCN-Mg2 clusters, and in subsection III C we apply our method to the

![FIG. 1. Schematic illustration of decay pathways following electronic excitations which are discussed in this work. The uppermost panel shows spectator resonant interatomic Coulombic decay, the middle panel depicts participant resonant interatomic Coulombic decay, and the lowermost panel illustrates the scheme of the excitation transfer ionization process. Note, that if we successively excite the electron to orbitals of higher and higher energies, decay by ETI or pRICD will eventually cease to exist, but the decay by sRICD will still be highly efficient.](Image)
calculation of RICD widths in NeMg clusters. The results obtained are compared, where possible, with those obtained by other \textit{ab initio} techniques or by the application of the analytical asymptotic formulas. Conclusions close this paper.

II. THEORY

Following Feshbach and Fano we consider a resonance state (decaying state) to be a bound state embedded in and interacting with the electronic continuum. The coupling to the electronic continuum is here by electron correlation. The width of the decaying state is given by \(^{31,33,34}\)

\[
\Gamma(E) = 2\pi\sum_{\beta} |\langle \phi_{\beta} | \hat{H} - E | \chi_{\beta,E}^+ \rangle|^2,
\]

(1)

where \(\hat{H}\) is the \(N\)-electron Hamiltonian, \(|\phi_{\beta}\rangle\) stands for the bound \(N\)-electron state and \(|\chi_{\beta,E}^+\rangle\) for the outgoing energy-normalized \(N\)-electron continuum state of energy \(E\), with \(\beta\) enumerating all open decay channels. The sum runs over all available final states at energy \(E\), and the relevant width is found by evaluating \(\Gamma(E)\) at \(E = E_r\), where \(E_r\) is the energy of the decaying state corrected for the interaction with the continuum. In the calculations presented in this paper we take \(E_r \approx E_d\), the energy of the bound state.

To determine \(|\phi_{\beta}\rangle\), \(|\chi_{\beta,E}^+\rangle\), and \(E_d\) we employ the algebraic diagrammatic construction \(^{35}\) (ADC) method for excited states \(^{46}\) to represent the Hamiltonian. We use the intermediate state representation approach to ADC (Ref. 57) which provides explicit schemes for constructing ADC representation of the Hamiltonian (in the following, the ADC Hamiltonian) using the basis of the so-called intermediate states \(|\tilde{\Psi}_J\rangle\).

These states are obtained by orthonormalization of the correlated excited states, \(|\Psi_{J0}\rangle\),

\[
|\Psi_{J0}\rangle = \hat{C}_J|\Psi_0\rangle,
\]

(2)

which result from the action of physical excitation operators \(\hat{C}_J\)

\[
\hat{C}_J = \{\hat{c}_a^\dagger \hat{c}_b, \hat{c}_c^\dagger \hat{c}_d, \hat{c}_e^\dagger \hat{c}_f, a < b, k < l; \ldots\},
\]

(3)

on the correlated ground state \(|\Psi_0\rangle\). Here \(a, b, \ldots\) denote particle and \(k, l, \ldots\) hole orbitals. The excitation operators divide the correlated states among excitation classes labelled by \([J]\), with \(J = 0\) referring to the ground state, \(J = ak\) \(([J] = 1)\) to the single hole–particle (1h1p) excitations, \(J = abkl\) \(([J] = 2)\) to the double hole–particle (2h2p) excitations, and so on. The orthonormalization of the \(|\Psi_{J0}\rangle\) proceeds in two steps. First, the states belonging to each excitation class are in turn orthogonalized to those of lower excitation classes by the Gram–Schmidt procedure to obtain precursor states \(|\Psi_{J0}\rangle\). For example, 1h1p precursor states \(([J] = 1)\) are obtained as

\[
|\Psi_{ak}\rangle = \hat{C}_k^\dagger |\Psi_0\rangle - |\Psi_0\rangle |\Psi_0\rangle \langle \Psi_0 | \hat{C}_k^\dagger |\Psi_0\rangle.
\]

(4)

Next, symmetric orthonormalization is performed within each excitation class. Taking again 1h1p states as an example, one has

\[
|\tilde{\Psi}_{ak}\rangle = \sum_{hl} |\Psi_{h}\rangle \langle S^{-1/2} |\Psi_{l}\rangle \langle S^{-1/2} |\Psi_{0}\rangle |\Psi_{0}\rangle.
\]

(5)

where \(S\) is the overlap matrix of the precursor states.

One can find the correlated ground state \(|\Psi_0\rangle\) correct up to \(n\)th order in perturbation theory by truncating its perturbation expansion

\[
|\Psi_0\rangle = |\Phi_{HF}^{0}\rangle + |\Psi_{0}^{(1)}\rangle + |\Psi_{0}^{(2)}\rangle + \cdots
\]

(6)

\(|\Phi_{HF}^{0}\rangle\) being the Hartree–Fock ground state. Correspondingly, one can construct an hierarchy of approximations, ADC\((n)\), \(n = 1, 2, \ldots\) in which the expansion of the Hamiltonian in the intermediate states of successive excitation classes \([J]\) is truncated in accordance with the correlated ground state \([Eq. (6)]\). Performing the orthonormalization procedure of Eqs. (4) and (5) approximately and consistently with the order of the many-body perturbation theory used for the construction of the correlated ground state [see Eq. (6)], one can express the Hamiltonian matrix elements of the type \langle\tilde{\Psi}_J|H|\tilde{\Psi}_J\rangle\) analytically using one-particle energies and the two-electron integrals. \(^{58,59}\)

The required one-particle orbitals are obtained in a restricted Hartree–Fock calculation. In this work, this task and the integral transformation needed to obtain the two-electron integrals are performed using \textsc{molcas6} quantum chemical program package. \(^{60}\) In the post Hartree–Fock calculations we employ the strict ADC(2) \([\text{or ADC(2)s}]\) and the extended ADC(2) \([\text{or ADC(2)x}]\) schemes. These schemes use second order perturbation theory for the correlated ground state and expand the excited states in the 1h1p and 2h2p excitation classes. Both ADC(2) schemes treat the 1h1p–1h1p and 1h1p–2h2p couplings in second and first order, respectively. The ADC(2)s scheme neglects the coupling between different 2h2p intermediate states, while the extended ADC(2)x scheme takes into account the 2h2p–2h2p interactions to first order. One obtains singly excited states correct to second order in both schemes, while doubly excited states are correct to zeroth or first order in the ADC(2)s and ADC(2)x schemes, respectively.

Within the Fano method the construction of ADC Hamiltonians for the initial and the final states require a selection scheme for configurations which span the corresponding subspaces. We denote by \(P\) (\(Q\)) the projector on the subspace of the final (initial) states and by \(P \hat{H} P\) (\(Q \hat{H} Q\)) the corresponding Hamiltonians. Some approaches for selecting the configurations corresponding to the closed and open channels of the decay have been described previously. \(^{38,47,48}\) We illustrate below a selection scheme suitable for describing the interatomic decay of excited states. Consider for example ETI in NeAr cluster following the \(2p^{-3}s\) excitation of Ne. This excitation is predominantly of 1h1p character, and to describe it we include in the subspace \(Q\) all 1h1p configurations with a vacancy in the Ne \(2p\) orbital. To improve the description with respect to intra-atomic electron correlation we additionally include all 2h2p configurations with two vacancies in the Ne \(2p\) orbitals. The energy of the \(2p^{-3}s\) excitation is located at the lower boundary of the \(\hat{Q} \hat{H} Q\) spectrum by construction and is relatively easy to obtain numerically accurately. The allowed final states of the process are 1h1p states having a hole in the Ar \(3p\) orbital and an electron in the continuum. To describe such states we add to the subspace \(P\) all 1h1p configurations with a vacancy in the Ar \(3p\) orbital. To account for correlation effects we also include
all 2h2p configurations with two vacancies in the Ar 3p orbitals. The final states of the decay are usually obtained by fully diagonalizing $P \hat{H} P$. However, for systems larger than a few atoms this step becomes very costly and can be avoided as discussed later on.

Having obtained the initial state and discrete quasicontinuum of final states, the next task is to evaluate the continuous quantity $\Gamma(E)$, which corresponds to the Stieltjes function of decay. This technique is based on the fact that $L^2$ wavefunctions corresponding to a discrete pseudospectrum approximate well the continuum functions in the vicinity of the system undergoing decay and can be used to reproduce the spectral moments, $M_n$, of $\Gamma$

$$M_n = 2\pi \langle \phi_d | (\hat{H} - E) \hat{H}^n (\hat{H} - E) | \phi_d \rangle.$$  \hspace{1cm} (7)

This assertion can be demonstrated by introducing the resolution of identity spanning the domain of the final states of the decay. Then the exact solution reads

$$M_n = 2\pi \sum_i E_i |\langle \phi_d | (\hat{H} - E) | \phi_i \rangle|^2 + 2\pi \int_{E_i}^{\infty} E^\pi |\langle \phi_d | (\hat{H} - E) | \phi_i \rangle|^2 dE,$$  \hspace{1cm} (8)

where $|\phi_i\rangle$ and $|\chi_{p,E}\rangle$ are the exact discrete and continuum functions, respectively, $E_i$ is the ionization threshold, and $E_i$ and $E$ are the energies of the discrete and continuum final states.

Since $|\phi_d\rangle$ is localized, the matrix elements in Eq. (8) do not get any significant contribution from the asymptotic region far from the system where the discrete representation of the continuum fails. Thus, the exact resolution of identity can be replaced by the one constructed with the discretized continuum functions $|\chi_{p,E}\rangle$, resulting in the following expression for $M_n$

$$M_n = 2\pi \sum_i E_i |\langle \phi_d | \hat{H} | \chi_{p,E} \rangle|^2.$$  \hspace{1cm} (9)

Those moments cannot be used to approximate the width $\Gamma$ directly, because $|\chi_{p,E}\rangle$ is unit normalized, whereas continuum functions are energy normalized. The Stieltjes imaging method employs the Stieltjes derivative to extract appropriately normalized continuum information from the discrete quasicontinuum $\{|\chi_{p,E}\rangle, \epsilon_j\}$. The Hamiltonian and theoretical aspects of the Stieltjes method can be found in Refs. 40, 41, 43, 44, and 61.

We mention here only two properties which are of particular interest in the present work. First, it can be shown that the knowledge of all $|\chi_{1,E}\rangle$ is necessary for the spectral moments’ calculation which seems to result in the need for the full diagonalization of the final state ADC Hamiltonian matrix.

This full diagonalization step can, however, be bypassed by replacing the full pseudospectrum $|\chi_{p,E}\rangle$ by a pseudospectrum obtained by the Lanczos diagonalization method. In this method, the Hamiltonian is represented in the basis of the so-called Lanczos states, $|\psi_j\rangle$, which are iteratively obtained from the Krylov states, $|\phi_k\rangle$, $k = 0, 1, \ldots, N$,

$$|\phi_k\rangle = \hat{H}^k |\phi_0\rangle, \quad k = 0, 1, \ldots, N,$$  \hspace{1cm} (10)

via the Gram–Schmidt orthonormalization procedure. The initial state $|\psi_0\rangle$ is usually chosen to have a large overlap with the Hamiltonian eigenstates that are of interest in a given physical problem, which ensures faster convergence to these states. The Lanczos states obtained after increasing numbers of iterations can be used to construct a series of approximations to the Hamiltonian. The $N$th order Lanczos approximation to $\hat{H}$ is of the form

$$\hat{H}^{(N)} = \sum_{i,j=0}^{N} |\psi_i\rangle \langle \psi_j | \hat{H} |\psi_j\rangle \langle \psi_j |,$$  \hspace{1cm} (11)

where $\langle \psi_i | \hat{H} |\psi_j \rangle$ is tridiagonal. The eigenvalues and eigenvectors of the operator $\hat{H}^{(N)}$ form the Lanczos pseudospectrum. With increasing $N$, the Lanczos pseudospectrum becomes a successively better approximation to the part of the spectrum of $\hat{H}$ having a nonzero overlap with $|\phi_0\rangle$. A generalization of the Lanczos technique to the case of several initial states, $|\phi_0^n\rangle$, is called block-Lanczos method. The block version is numerically more stable than the simple Lanczos method and, as will be shown below, the block version allows to define starting blocks having large overlap with the final states contributing mostly to the decay width.

The Lanczos technique can be also used for the calculation of the spectral moments of the type of Eq. (7). To this end, the original Hamiltonian has to be substituted by its Lanczos representation:

$$M_n = \langle \psi_d | (\hat{H} - E)^{\gamma} \hat{H}^n (\hat{H} - E) |\psi_d \rangle$$

$$\approx \langle \psi_d | (\hat{H} - E)^{\gamma} (\hat{H}^{(N)})^{\gamma} (\hat{H} - E) |\psi_d \rangle$$

$$= \sum_{i=0}^{N} (E_i^{(N)})^\gamma |\langle \psi_d | (\hat{H} - E) |\chi_i^{(N)} \rangle|^2,$$  \hspace{1cm} (12)

where $\chi_i^{(N)}$ are the eigenfunctions of $\hat{H}^{(N)}$ and $E^{(N)}$ their eigenvalues, while $\langle \hat{H} - E \rangle$ is the operator coupling the initial to the final state of the decay. While the non-negative moments of the order $0 \leq n \leq 2N$ can be calculated exactly by Eq. (13) with the appropriate choice of the initial state (or block of states), the negative moments required for the Stieltjes imaging can be calculated only approximately.

### III. APPLICATIONS

In order to demonstrate the efficiency and the accuracy of the Fano–Stieltjes–Lanczos method as applied to the calculations of interatomic decay widths we employ it in calculations of ETI (Ref. 17) widths in NeAr and HCN-Mg $n$, $n = 1, 2$. The calculations in the comparatively simple NeAr serve to test the selection schemes for the Q and P subspaces and to investigate the quality of the results with respect to the ADC scheme and the number of the final states used. Experimentally isolated HCN-Mg $n$ clusters provide us with a
realistic system where ETI is possible following an excitation of HCN. If available we compare the Fano–Stieltjes–Lanczos widths with those obtained previously for these clusters in CAP-ADC calculations. Subsequently, we use the Fano–Stieltjes–Lanczos method to determine RICD (Refs. 5 and 16) widths in NeMg clusters, calculated previously by the inferior Wigner–Weisskopf method. At large interatomic distances the numerical results are compared with the analytical widths obtained in the framework of the virtual photon transfer model.

A. Calculations of ETI widths in NeAr clusters

ETI is a nonradiative decay pathway of outer-valence excitations in clusters which sets in if the excitation energy is sufficient to ionize another cluster constituent. The outer valence excitation relaxes by transferring its energy to another cluster subunit and ionizing it (see Fig. 1). At interatomic distances of a few angstroms between the monomers this decay has been shown to be orders of magnitude faster than the competing radiative decay.

We start by calculating the widths of the optically allowed \( 2p^{-1} 3s \) \((^1 P)\) excitations of Ne in NeAr clusters. The excitation energy of the corresponding state in isolated Ne is 16.85 eV. \(^5\) The ionization potential of \( 3p \) electrons in isolated Ar lies at 15.76 eV. \(^6\) Therefore, the ETI channel is open at large interatomic separations in NeAr and we verified in a separate calculation that the channel remains open for all interatomic distances considered.

As a first step we define appropriate subspaces to describe the initial and the final states of the decay. The triply degenerate \(^1 P\) term of Ne splits in the dimer into \(^1\Sigma\) and \(^1\Pi\) states. We start by considering the decay of the \(^1\Pi\) state first. The electronic configurations of the ground state of Ne and Ar are \((\text{He})2s^22p^6\) and \((\text{Ne})3s^23p^6\), respectively. In the calculations the 1s orbital of Ne and the 1s2s2p orbitals of Ar were frozen. As mentioned earlier, to describe the initial \(2p^{-1} 3s\) \((^1\Pi)\) decaying state we include all configurations of 1h1p character of appropriate symmetry having a vacancy in the Ne \(2p\) orbital. To account for intra-atomic correlation effects we also include all 2h2p configurations with two vacancies in the Ne \(2p\) orbitals.

The excitation energy is above the first ionization potential of Ar but it is not sufficient to produce excited states of Ar\(^+\). The final states of the decay are thus 1h1p states with a vacancy in the Ar \(3p\) orbitals and an electron in the continuum. To describe these states we include all 1h1p configurations with a vacancy in the Ar \(3p\) orbitals. To account for intra-atomic correlation in the final states we add all 2h2p configurations with two holes in the Ar \(3p\) orbitals.

The calculations were carried out with the aug-cc-pVTZ Gaussian basis set \(^6\) augmented with 12s, 8p, 6d Rydberg-like Gaussian functions \(^6\) centered on Ne and the aug-cc-pVTZ Gaussian basis set \(^6\) augmented with 4s, 4p, 2d even-tempered diffuse Gaussian functions centered on Ar. Since by construction the decaying state lies near the lower spectral boundary of \(Q\hat{H}Q\), it can be easily computed accurately by the Davidson diagonalization method. The ADC(2)s energy of the \(2p^{-1} 3s\) \((^1\Pi)\) resonance is found to be 16.6 eV, in good agreement with the literature value of 16.85 eV. Using the ADC(2)s method, the Hamiltonian matrix representing the final states of the decay has a dimension of 20 200. The spectrum of final states was obtained by applying the block Lanczos method. The predominantly 1h1p character of the final states suggests that the best starting block consists of all 1h1p configurations of the final subspace (80 in this case). Using this starting block, we performed Lanczos diagonalization with 1, 5, 10, and 30 block iterations, obtaining 80, 400, 800, and 2400 final states, respectively. The calculated widths are given in Fig. 2. The figure shows that the decay width is converging extremely fast indicating an excellent choice of the starting vectors for the Lanczos procedure.

In order to check whether the Fano–Stieltjes–Lanczos method reproduces the dependence of the ETI rate on the symmetry of the initial state, \(^1\Pi\) correctly we applied it to the calculation of the width of the Ne \(2p^{-1} 3s\) \((^1\Sigma)\) excitation in the same cluster. We employed the same configuration subspaces and the same Gaussian basis sets as for the \(^1\Pi\) state. Although the resulting subspaces are not completely equivalent due to the different symmetry of the initial and final states, we utilized the parameters (block size 80 and 30 block Lanczos iterations) obtained from the study of convergence of the \(2p^{-1} 3s\) \((^1\Pi)\) excitations. For comparison we plotted both graphs in Fig. 3. One first notices that the width of Ne \(2p^{-1} 3s\) \((^1\Sigma)\) excitations is larger than the width of \(2p^{-1} 3s\) \((^1\Pi)\) excitations, in accordance with the theory. At interatomic distances R larger than 6 Å the widths are proportional to \(R^{-6}\) and the quotient of both widths is equal to four, which is exactly the value predicted by the virtual photon transfer model \(^6\) at large interatomic distances. The absolute values are also in good agreement with the analytical predictions. At small interatomic distances the width of Ne \(2p^{-1} 3s\) \((^1\Sigma)\) excitation increases faster than the width of the \(^1\Pi\) excitation due to the larger orbital overlap between the monomers for the states of \(\Sigma\) symmetry. The resulting lifetime of the Ne \(2p^{-1} 3s\) \((^1\Sigma)\) excitation in NeAr at the equilibrium distance of 3.5 Å is 55 fs, which is four orders of magnitude shorter than the life-time of the Ne \(2p^{-1} 3s\) \((^1\Pi)\) excitation in NeAr.
FIG. 3. The ETI widths of the Ne $2p^{-1}3s\left(^1\Pi\right), 2p^{-1}3s\left(^1\Sigma\right)$, and $2p^{-1}3p\left(^1\Delta\right)$ excitations in NeAr clusters as a function of the interatomic distance. We carried out 40 block Lanczos iterations with a block size of 80 (see the text for more details). The predictions of the asymptotic formula are depicted as dotted lines. Note the good agreement of the calculated widths and the analytical predictions. The dotted line close to the origin graphs the optically forbidden $\Delta$ excitation is proportional to $R^{-8}$.

of magnitude shorter than the 1.6 ns lifetime of the competing radiative decay.89

The interatomic decay widths have been calculated so far only for optically allowed initial states. However, we would like to further test the method by applying it to dipole forbidden but quadrupole allowed transitions. As has been demonstrated in Ref. 14 the ICD width of quadrupole allowed ionized initial states decreases with $R^{-8}$ at large interatomic distances. The expression for the ETI width derived here similarly to Ref. 14 and 18 reads

$$\Gamma = \frac{1323}{14\pi} c^6 \sigma(\omega) R^8 \Gamma_{\text{rad}},$$

where $\omega$ is the frequency of the virtual photon, $\sigma(\omega)$ is the photoionization cross section of the neighbor Ar, and $\Gamma_{\text{rad}}$ is the radiative width of the excited state of isolated Ne due to photon emission. In this instance, we would like primarily to check whether our approach can reproduce the correct asymptotic gradient and, in addition, check whether our approach works for very small numerical values of the width which occur in this case due to its fast decrease with $R$.

To this end we calculated the decay width of Ne $2p^{-1}3s\left(^1\Delta\right)$ excitations in NeAr (see Fig. 3). The energy value of this excitation is given in the literature with $18.63$ eV.65 We employed the same subspaces and the same Gaussian basis sets as in the calculations above. Using this setup we obtained an excitation energy of $18.8$ eV and the decay rate shown in Fig. 3. One can see that as the interatomic distance grows the decay width decreases much faster than the decay width of the optically allowed Ne $2p^{-1}3s$ excitations. This can be explained by the fact that the moment the orbital overlap becomes negligible, the rate falls off as $R^{-8}$ and not as $R^{-6}$ as in the previous case. It is notable that our \textit{ab initio} approach yields the correct $R^{-8}$ behavior even at very large interatomic distances where the absolute numbers are very small.

B. Calculations of ETI widths of HCN-Mg clusters

As a further test we apply the Fano–Stieltjes–Lanczos method to the calculation of ETI widths of the $5\sigma\pi^+$ excitation of the HCN molecule in HCN-Mg$_n$, $n = 1, 2$ clusters. The ETI widths of these systems have been calculated previously with the CAP-ADC method.17 In addition, all properties of the constituents necessary to evaluate the asymptotic formulas are known giving us the opportunity to compare the results. The first step is again to define the subspaces of the initial state and final states of the decay. The Hartree–Fock electronic configurations of the ground states of HCN and Mg are $1\sigma^22\sigma^23\sigma^24\sigma^25\sigma^21\pi^4$ and $(Ne)3\sigma^2$, respectively. By 5$\sigma$ we understand the nonbinding orbital on N. To describe the initial 1h1p 5$\sigma\pi^+$ excitation we include all configurations of 1h1p character with a vacancy in the 5$\sigma$ molecular orbital (MO). To account for electron correlation in the initial state we include, additionally, all 1h1p configurations with a vacancy in a 1$\pi$ MO and all 1h1p configuration with a vacancy in the 4$\sigma$ MO. We also add all 2h2p configurations with two vacancies in either 5$\sigma$, 4$\sigma$, or 1$\pi$ MOs, and all 2h2p configurations with one vacancy in the 5$\sigma$ and another in either the 4$\sigma$ MO, or in the 1$\pi$ MO.

The final states of the ETI process differ according to the number of neighboring Mg atoms. In the case of HCN-Mg the bound part of the final states consist of HCN in its ground state and Mg$^+$ in its ground state. To describe these states accounting for electron correlation, we include in the configuration space all 1h1p and 2h2p states with one or two holes in the Mg 3$s$ orbital. In the calculation of the final states we start as taking vectors of the Lanczos procedure all the 1h1p configurations. After the block Lanczos iterations we select Lanczos eigenvectors of predominantly 1h1p character and use them in the Stieltjes routine. In this way we ensure that no energetically forbidden doubly excited state contributes to the width. In the case of HCN-Mg$_2$, the final states consist of HCN in its ground state and the Mg dimer in a variety of ionized states. The energy of the initial state is sufficient to produce the ground and lower excited states of Mg$^+$ but not the doubly ionized Mg$^{2+}$. To span the corresponding subspace we include all 1h1p configurations with a vacancy either in the 3$\sigma_\text{g}$ or 3$\sigma_\text{u}$ MO of isolated Mg. We also add all 2h2p configurations with two holes in the 3$\sigma_\text{g}$, 3$\sigma_\text{u}$ orbital subset. In this case we take as starting block the 100 configurations which have the largest coupling to the initial state. We noticed that this coupling is generally much larger for the 1h1p than for the 2h2p configurations. We used all energetically permitted Lanczos eigenvectors in the Stieltjes calculation.

The calculations were carried out using the ADC(2)x method because we found the interactions among 2h2p configurations to be important to describe the initial and the final states of the decay. We employed the aug-cc-pVTZ Gaussian basis sets augmented with 1s, 1$\rho$, 1$d$ Rydberg-like Gaussians centered on H, C, and N and the aug-cc-pVTZ Gaussian basis sets augmented with 3s, 6$\rho$, 2$d$ even-tempered diffuse Gaussians centered on each Mg. Since by construction the decaying state lies near the lower spectral boundary, it can again be easily computed by the Davidson diagonalization method.58 The structure of HCN-Mg was
The ETI width of the out-of-plane $5\sigma^+\pi^*$ excitation in HCN-Mg$_2$ is also depicted in Fig. 4. At intermolecular distances larger than 20 Å, the width is proportional to $R^{-6}$ and, moreover, is in good agreement with the prediction of the asymptotic formula. Between 9 and 16 Å the width decreases roughly as $R^{-7}$. We found that the photoionization cross section of Mg$_2$ is roughly one order of magnitude larger than the photoionization cross section of Mg at the same energy of the virtual photon. Consequently, the $R^{-6}$ term in the ETI width of HCN-Mg$_2$ is approximately one order of magnitude larger than the one of HCN-Mg. Thus, both the $R^{-8}$ and $R^{-6}$ terms in Eq. (15) are of comparable size for $R$ between 9 and 16 Å which results in the observed $R^{-7}$ behavior of the width. At the equilibrium geometry we find an ETI lifetime of 40 fs. Our calculations are in good agreement with the results of Ref. 17 as one can see from the inset of Fig. 4.

FIG. 4. The ETI widths of the HCN $5\sigma^+\pi^*$ excitations in HCN-Mg (lower line) and HCN-Mg$_2$ (upper line) clusters as a function of the distance between N and Mg. The results are obtained by using starting blocks of the dimension 44 and 100, respectively, and 40 block Lanczos iterations. The predictions of the first term of Eq. (15) are shown as dotted lines. At equilibrium geometries, 3.95 and 3.8 Å of HCN-Mg and HCN-Mg$_2$, respectively, the estimated lifetimes are 385 and 40 fs, respectively. The inset depicts the comparison between the present results (full lines) and the widths obtained with the CAP-ADC method (dashed lines) where available. The CAP-ADC data is taken from Ref. 17.
vacancy is filled by an outer-valence electron of the same subunit (spectator RICD or sRICD) or by the electron promoted to the virtual orbital in the excitation step (participant RICD or pRICD), while the excess energy is used to ionize a neighboring cluster subunit. A schematic illustration of both processes is given in Fig. 1. The energy absorbed in exciting an inner-valence electron in an atom or molecule usually exceeds the first ionization potential thus enabling its autoionization. In the presence of neighbors the RICD and autoionization processes compete directly and can be of comparable efficiency. This stresses the importance of the accurate knowledge of both widths.

Here we apply our approach to the calculation of RICD widths in NeMg clusters following the $2s^{-1}3p$ excitation in Ne. The RICD widths of this relatively simple system have been previously obtained by the Wigner–Weisskopf approach and, moreover, all properties of the constituent atoms which are required to evaluate asymptotic formulas are known, thus, giving us the opportunity for independent assessment of the Fano–Stieltjes–Lanczos widths at large distances. As a first step we define the configuration subspaces for the initial and the final states of the decay. The electron configuration of the ground state of Ne is $(\text{He})^2$. To describe the $2s^{-1}3p$ initial state, we include all $1h1p$ configurations with the hole in the Ne 2s orbital and, to account for some electron correlation, all 2h2p configurations with two holes in the 2s2p shell. The subspace of the final states of the decay differs depending whether one considers pRICD, sRICD, or autoionization. The definition of the subspace of the final states of the decay in the case of autoionization has been described in Ref. 48.

In the case of pRICD the final states of the system consist of Ne in its ground state and the Mg atom in a variety of ionized states. The energy of the initial excitation is sufficient to produce the ground and excited states of Mg$^+$ as well as the ground state of Mg$^{++}$. Therefore, we take a final state subspace comprising all 1h1p and 2h2p configurations with holes in the Mg 3s orbital. The initial state couples in first order to the final states of 1h1p character, while it couples to the final states of 2h2p character only in second order, not accounted for by the ADC(2)x scheme. Usually these second order effects are small and we assume that they will not affect our results much.

In the case of sRICD the final states of the system consist of Ne in an excited $2p^{-1}3p$ state and the Mg atom in the same ionized states as in the pRICD case. Consequently, in this case the configuration subspace of the final states comprise all 2h2p configurations with one vacancy in a Ne 2p orbital and one in the Mg 3s orbital. To describe the shake-up and doubly ionized states of Mg following sRICD we would need 3h3p configurations. These configurations are not available in the ADC(2) scheme and appear for the first time in the ADC(4) scheme. However, the coupling to these states is of second order and is usually smaller than the first order coupling to the 2h2p states given above.

We have shown above how the starting block of the Lanczos procedure should be selected in case the final states are predominantly of 1h1p character. Thus, to calculate the widths of pRICD process we have chosen the subspace spanned by all 1h1p configurations as the starting block. In the case of sRICD the final states of the decay are of 2h2p character. The size of the subspace spanned by these configurations is usually extremely large. We thus used the 100 2h2p configurations with one vacancy in the Mg 3s and one in a Ne 2p orbital which have the largest coupling to the initial state.

As a first test, we calculated the sRICD width of the Ne $2s^{-1}3p$ ($^{1}P$) initial state as a function of the interatomic distance for different numbers of block Lanczos iterations (see Fig. 5). The calculations were carried out with an aug-cc-pCVTZ basis augmented with 12s, 8p, 6d Rydberg-like Gaussians centered on Ne and an aug-cc-pVTZ basis set augmented with 6s, 8p, 6d continuum-like Gaussians centered on Mg. To improve the description of the final 2h2p states we performed all calculations using the ADC(2)x scheme, which gives these states to first order in perturbation theory. The obtained energy of the Ne $2s^{-1}3p$ decaying state is 45.65 eV at large interatomic distances, in good agreement with the literature value of 45.54 eV (Ref. 65) for the isolated Ne. The resulting dimension of the final 2h2p subspace is 28 000. After five and ten block Lanczos iterations the decay width oscillates with R, becoming smooth after 30 or more block Lanczos iterations. For 60 and more iterations the width is converged at large interatomic distances but still increases slightly at interatomic distances where the orbital overlap is significant. Due to the observed slow convergence we tried to increase the size of the starting block, however, the convergence is not significantly improved by this.

We can offer two main reasons for the slow convergence at such interatomic distances. First, there is a large number of final states of 2h2p character contributing to a comparable degree to the decay width, thus, requiring many iterations to produce them. Second, since electron correlation is large among the final states of 2h2p character, many iterations are again needed to describe them accurately. Consequently, at interatomic distances close to the equilibrium geometry, the widths
To estimate the error introduced by the incomplete description compared with widths obtained by full diagonalization. The decay rate converged after 40 block Lanczos iterations with a starting block composed of all 80 1h1p configurations. The pRICD width of Ne 2s−13p (1Π) and Ne 2s−13p (1Σ) at large interatomic distances fall off as R−6 and differ roughly by a factor of four, in good agreement with the predictions of the virtual photon transfer model. At interatomic distances smaller than 9 Å the 1Π and the 1Σ widths increase—compared to the values predicted by the asymptotic formulas due to orbital overlap, whereas their ratio remains roughly four. At the equilibrium distance (4.4 Å) the Ne 2s−13p (1Π) and the Ne 2s−13p (1Σ) resonances have a width of 0.012 and 0.037 meV, respectively. Thus, they are roughly 4 and 13, respectively, times smaller than the corresponding sRICD width and two orders of magnitude larger than the corresponding values obtained with the Wigner–Weisskopf method. The significant difference can be explained by the fact that the description of the virtual orbitals of the initial and the final states are significantly improved in Fano–Stieltjes–Lanczos calculations.

The sRICD widths of the 2s−13p (1Π) and the 2s−13p (1Σ) states are virtually equal. This is because the excited electron, which determines the symmetry of the initial state, is not directly involved in the decay process. At large interatomic distances both widths are proportional to R−6 and in good agreement with the predictions of the virtual photon transfer model. At interatomic distances smaller than 8 Å both widths increase due to orbital overlap. At the equilibrium distance of 4.4 Å both width are at 0.16 meV and, therefore, roughly 70 times smaller than the autoionization width and eight times smaller than the sRICD width obtained by the Wigner–Weisskopf method. However, we would not like to draw definitive conclusions from the comparison between the Wigner–Weisskopf and the present Fano–Stieltjes–Lanczos sRICD widths, since the latter are not converged with the number of Lanczos states.

IV. CONCLUSIONS

We have presented an accurate and efficient scheme for calculating interatomic Coulombic decay widths based on the Fano formalism. The scheme can be applied to all problems allowing a physically meaningful definition of the subspaces of the initial (Q) and final (P) states of a decay. Its accuracy derives from the use of many-body methods accounting for electron correlation to obtain the initial and final states of the decay as well as the coupling between them. In this work we employed the ADC method but any other accurate quantum chemical method can also be used.

The efficiency is based on avoiding the full diagonalization bottleneck of the standard moment theory approach used to reconstruct a continuous function Γ(E) from the underlying $L^2$ pseudospectrum. Our scheme utilizes the
block-Lanczos diagonalization method to approximate the spectrum of the final states of the decay. Since decay widths are obtained by diagonalization of matrices of much smaller dimensions than the dimension of the final states’ subspace, our method is applicable to larger polyatomic systems.

We tested the proposed method by computing interatomic decay widths of outer-valence excited states in NeAr, HCN-Mg, n = 1, 2 and RICD widths in NeMg. The accuracy of the obtained results is well documented by the quality of the decay widths at large interatomic distances where they can be computed using analytical expressions containing only measurable properties of the excited atom (or molecule) and of its neighbor. The agreement of the predicted values with the analytic ones is very good and this fact can be, in reverse, exploited to extract properties of the fragments. In addition, in the case of HCN-Mg, n = 1, 2 we were able to compare the widths calculated by the present approach with widths obtained previously by the CAP-ADC method and the results are in good agreement.

The results obtained for the final states of predominantly 1h1p character converge fast with the number of block Lanczos iterations. A suitable choice for the starting block is given by configurations with the largest coupling to the initial state. The resulting band diagonal Lanczos matrices have significantly smaller dimensions than the full dimension of the final states’ subspace.

In the case of final states of 2h2p character, e.g., following sRICD, the starting block was chosen in the same way as in the 1h1p case. We have seen that in this case the convergence with the number of block-Lanczos iterations is fast at asymptotic distances, while it becomes slow at around the equilibrium geometry. This is explained by noting that a large number of doubly excited states contribute to the decay width and must all be recovered before the latter is converged. A different choice of the starting block may be helpful to overcome this shortcoming.

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