PHYSICAL REVIEW A VOLUME 36, NUMBER 9 NOVEMBER 1, 1987

Simple discretization method for autoionization widths. I. Theory

A. Macías, F. Martín, A. Riera, and M. Yáñez
Departamento de Química, Facultad de Ciencias, C-XIV, Universidad Autónoma de Madrid,
Cantoblanco, 28049 Madrid, Spain

(Received 29 December 1986)

A description of the theoretical basis is presented for a new method to calculate widths of two-electron Feshbach resonances, which employs discretization techniques for the continuum projection of the wave function. New features of our approach are the finite-difference expressions used to evaluate the density of states and the inverse interpolation procedure needed to achieve the required discrete-continuum degeneracy. Two following papers illustrate the use of our method to calculate resonance widths for atomic and molecular systems, respectively.

I. INTRODUCTION

Doubly excited states with two electrons, being the most fundamental systems that autoionize, have received continued attention as being best suited to theoretical investigation on resonance characteristics, as well as presenting difficult conceptual and computational problems. Because of their simplicity, they are used as benchmark cases for theoretical treatments of autoionization phenomena; a sample of these treatments is presented in Refs. 1–30, for atomic and molecular systems. From the experimental point of view, those states are also of great interest in several contexts, such as electron-impact measurements,[31] atomic processes in fusion plasmas,[32] beam-foil spectroscopy,[33,34] and single-collision beam experiments.[35–42]

In a series of papers,[23,25,28] we have proposed a new method for the calculation of resonance widths. Our procedure was claimed to be accurate, yet very simple—as compared, for example, to alternative, very precise techniques such as the complex rotation method.[43] Application of our approach to doubly excited states of He-like systems gave encouraging results, which warrant a detailed and systematic description of its fundamentals and computational details, which were presented in Refs. 25 and 28, in a rather concise and heuristic manner. This description is the purpose of the present work.

Starting from well-known Feshbach theory[44] (presented in Sec. II A), our approach uses a discretization technique for the continuum projection of the wave function; this will be described in detail in Sec. II B. In Sec. II C the reasoning underlying our approximation for the density of states is presented and exemplified. Then the necessity of using a *family* of basis sets, rather than a single one, is pointed out in Sec. II C. Discrete-continuum degeneracy, needed to apply the golden-rule formula, is achieved through an inverse interpolation procedure described in Sec. II D. This is followed by a summary of the basic steps of our method.

Our goal is to develop a procedure that is sufficiently simple to be applicable, without great computational effort, to the calculation of autoionization widths of molecular systems, as a complement to the research carried out by our group on molecular resonance energies.[26,27] Nevertheless, since it is for the atomic case that there exists a wealth of accurate data with which results of any proposed method should successfully compare, we present in a following paper[45] an explicit comparison of our results for positions and widths of resonances of the He isoelectronic series with those of other published work. As a further step towards our goal, in a third paper[46] of this series we extend our techniques to the calculation of molecular resonance positions and widths in the region of small internuclear distances where one-center expansions of the closed-channel wave functions are appropriate. Atomic units are used throughout.

II. METHOD

A. Use of golden rule

We shall first recall, following the theory of Refs. 44 and 47–50, the basic definitions of the Feshbach formalism that are needed to describe our implementation of it. We write the wave function ψ representing an autoionizing state of a two-electron system as the sum of two components describing open and closed channels:

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=P\psi+Q\psi \ , \tag{1}$$

where P is the projection operator having the property that $P\psi$ has the same asymptotic form as ψ when either of the two electronic coordinates $\mathbf{r}_1,\mathbf{r}_2$ tends to infinity, and $Q=1-P$. As is well known, in general the definition of these operators is, to some extent, a matter of choice,[48] but in the two-electron case an appropriate expression is readily inferred.[49,50] For example, for Feshbach resonances below the $n=2$ threshold of He-like systems, one can take[50]

$$Q=Q_1Q_2 \ , \tag{2}$$

where Q_i is the projector on the subspace spanned by all excited target states.

Inserting (1) in the Schrödinger equation yields the coupled equations

$$\begin{aligned}(H_{QQ}-E)Q\psi&=H_{QP}P\psi\ ,\\ (H_{PP}-E)P\psi&=H_{PQ}Q\psi\ ,\end{aligned} \tag{3}$$

where, in a standard notation, $H_{QQ}=QHQ$, $H_{PP}=PHP$, $H_{PQ}=H_{QP}^{\dagger}=PHQ$. The projected Hamiltonian H_{QQ} has a discrete spectrum below the excitation threshold, and the interaction H_{QP} permits the decay of $Q\psi$ into $P\psi$.

Equation (3) can be formally uncoupled by solving the first equation for $Q\psi$ and inserting it in the second:

$$(H_{PP}+V_{\text{opt}}-E)P\psi=0\ , \tag{4}$$

where V_{opt} is the generalized optical potential

$$V_{\text{opt}}=H_{PQ}(E-H_{QQ})^{-1}H_{QP}\ . \tag{5}$$

For E close to an eigenenergy of H_{QQ}, say, E_1^d,

$$(H_{QQ}-E_1^d)Q\phi_1=0\ . \tag{6}$$

Equation (4) can be written

$$\begin{aligned}&\left[H_{PP}+\sum_{n(\neq 1)}\frac{H_{PQ}\,|\,\phi_n\rangle\langle\phi_n\,|\,H_{QP}}{E-E_n^d}-E\right]P\psi\\ &\qquad\equiv(H'-E)P\psi=-\frac{H_{PQ}\,|\,\phi_1\rangle\langle\phi_1\,|\,H_{QP}}{E-E_1^d}P\psi\ .\end{aligned} \tag{7}$$

Then, letting χ_E be a solution of the homogeneous equation

$$(H'-E)P\chi_E=0\ , \tag{8}$$

we solve Eq. (7) in terms of the corresponding (standing-wave) Green's function for Eq. (8), and compare this solution to the Breit-Wigner resonance formula. The expression for the resonance width

$$\Gamma=2\pi\,|\,\langle\phi_1\,|\,H_{QP}\,|\,\chi_E\rangle\,|^2 \tag{9}$$

then follows, with $E=E_1^d$ in Eq. (8), and a normalization:

$$\langle\chi_E\,|\,\chi_{E'}\rangle=\delta(E-E')\ . \tag{10}$$

Also, the resonance position is given by

$$E_{\text{res}}=E_1+\Delta_1=E_1+\langle\phi_1\,|\,H_{QP}(E-H')^{-1}H_{PQ}\,|\,\phi_1\rangle\ , \tag{11}$$

where the standing-wave form of the Green's function is assumed.

Equation (9) is formally identical to Fermi's golden rule.[51] In applications, except when very accurate values for the resonance parameters are needed, the nonlocal part of H', and the energy shift Δ, which are quadratic in the interaction Hamiltonian H_{QP}, are neglected, so that χ_E is approximated by the solution of[51,52]

$$(H_{PP}-E)P\chi_E=0\ . \tag{12}$$

B. Discretization procedure

In our approach we aim at obtaining a good approximation to the resonance width Γ, rather than solving the scattering problem (12). Then we realize from Eq. (9) that the form of χ_E is only required in the region of configuration space where ϕ_1 is non-negligible, so that we can employ an L^2-integrable representation of χ_E in this region.

To obtain such a representation, powerful discretization techniques, involving a considerable computational effort, have been developed.[53–56] Here we shall simply diagonalize H_{PP} in a finite basis of L^2-integrable wave functions belonging to the orthogonal complement of the Q subspace, and covering (taking non-negligible values in) a domain D containing the region of configuration space where ϕ_1 is also non-negligible. To show that the wave functions obtained in the diagonalization procedure provide the sought-for representation of the open-channel functions χ_E, we shall follow Macías and Riera's approach in their work[57] on the basis of the stabilization method.

As in Ref. 57, to avoid mathematical complications related to the fact that χ_E does not belong to a Hilbert space, we first enclose the whole system in a very large box, or any other suitable device, so that the new eigenfunctions of H_{PP}, henceforth called $\bar{\chi}_E$, are identical to χ_E inside a very large domain $\mathcal{D}$ of configuration space, and are made to vanish quickly (either exponentially or abruptly) outside $\mathcal{D}$. In this respect, it is worth pointing out that, since tables and figures always have a finite precision, if so desired the box can be taken to be of macroscopic size so that there is no practical difference in the spectrum of H_{PP} when the boundary conditions change at the bounding surface of $\mathcal{D}$.

We are then left with a projected Hamiltonian whose spectral resolution is given by

$$H_{PP}=\sum_i\,|\,\bar{\chi}_{E_i}\rangle E_i\langle\bar{\chi}_{E_i}\,|\ , \tag{13}$$

that is, a sum over densely packed energy intervals of width $O(\varepsilon)$, where ε is extremely small.

When considering an expression containing χ_E which is a function of E, substituting the quasicontinuum function $\bar{\chi}_E$ for the continuum one χ_E replaces that function by an histogram, which will appear in practice as a continuous function. It is then more convenient to use a continuous interpolation function of the histogram. For example, the normalization condition (10) now reads

$$\langle\bar{\chi}_E\,|\,\bar{\chi}_{E'}\rangle=\delta_\varepsilon(E,E')\ , \tag{14}$$

where the interpolating function δ_ε is a member of a δ family (straightforward generalization of a δ sequence[58]). As usual, it is convenient to choose the area below this δ_ε function such that

$$\int dE'\delta_\varepsilon(E,E')=1 \tag{15}$$

and we have also, by construction,

$$\delta_\varepsilon(E_i,E_j)=0\ \text{ when }\ |\,E_i-E_j\,|>\varepsilon \tag{16}$$

so that

$$\langle \bar{\chi}_{E_i} \mid \bar{\chi}_{E_i} \rangle = \delta_\varepsilon(E_i, E_i) = O(\varepsilon^{-1}) \, . \tag{17}$$

Let us now diagonalize H_{PP} in a basis set of L^2-integrable functions

$$\{ \xi_j ; j = 0, 1, \ldots, N \} \tag{18}$$

covering a domain D of configuration space of atomic or molecular dimensions and which becomes complete in P space as $N \rightarrow \infty$. In practice, we shall have $D \subset\subset \mathcal{D}$, and the spectrum of the matrix $\mathbf{H}_{PP}$, given by the solution of

$$\mathbf{H}_{PP}\mathbf{C} = \mathbf{S}_{PP}\mathbf{C}\tilde{\mathbf{E}}, \quad \mathbf{C}^\dagger \mathbf{S}_{PP} \mathbf{C} = \mathbf{I} \, , \tag{19}$$

where $\mathbf{S}_{PP}$ is the overlap matrix in the representation (18), is formed by a discrete set of eigenvalues $\tilde{E}_n$, separated by energy differences which are much larger than ε (save for degeneracies).

Next we must establish the relationship between each wave function:

$$\tilde{\chi}_n(\mathbf{r}_1, \mathbf{r}_2) = \sum_j c_{jn} \xi_j(\mathbf{r}_1, \mathbf{r}_2) \tag{20}$$

formed from the eigencoefficients of Eq. (19), and fulfilling

$$\langle \tilde{\chi}_n \mid \tilde{\chi}_m \rangle = \delta_{nm} \, , \tag{21}$$

and the corresponding quasicontinuum one $\bar{\chi}_{\tilde{E}_n}$ of the same energy, normalized according to Eq. (14). This is a basic question, since at first sight it is not clear that they should be similar even inside the atomic domain D.

To answer this question, in Ref. 57 we first considered the formal limit of a complete basis set [$N \rightarrow \infty$ in (18)] and then passed on to the realistic case of a finite basis. Now the advantage of the small-grained discretization reached by the introduction of the box of size $\mathcal{D}$ becomes clear: The eigenfunctions $\bar{\chi}_E$ of H_{PP} belong to the Hilbert space of P functions and can be expanded in the complete set:

$$\{ \xi_j ; j = 0, 1, \ldots, \infty \} \, . \tag{22}$$

Then, in the limit $N \rightarrow \infty$ the eigenfunctions $\tilde{\chi}_n$ and $\bar{\chi}_{\tilde{E}_n}$ must coincide up to a normalization factor

$$\tilde{\chi}_n \underset{N \rightarrow \infty}{\longrightarrow} \delta_\varepsilon^{-1/2}(\tilde{E}_n, \tilde{E}_n) \bar{\chi}_{\tilde{E}_n} \tag{23}$$

so that Eq. (21) holds

$$\begin{aligned} \langle \tilde{\chi}_n \mid \tilde{\chi}_m \rangle &\underset{N \rightarrow \infty}{\longrightarrow} \delta_\varepsilon^{-1/2}(\tilde{E}_n, \tilde{E}_n) \delta_\varepsilon^{-1/2}(\tilde{E}_m, \tilde{E}_m) \langle \bar{\chi}_{\tilde{E}_n} \mid \bar{\chi}_{\tilde{E}_m} \rangle \\ &= \delta_\varepsilon^{-1/2}(\tilde{E}_n, \tilde{E}_n) \delta_\varepsilon^{-1/2}(\tilde{E}_m, \tilde{E}_m) \delta_\varepsilon(\tilde{E}_n, \tilde{E}_m) = \delta_{nm} \end{aligned} \tag{24}$$

since $|\tilde{E}_n - \tilde{E}_m| > \varepsilon$ for $n \neq m$. Hence, the normalization (23) is correct, and corresponds to the intuitively obvious fact that the amplitude of the S-normalized wave function $\tilde{\chi}_n$ must become progressively smaller when the basis set is enlarged. Then, we can see that the Heisenberg transform of $\tilde{\chi}_n$, which is given by the overlap

$$\begin{aligned} \langle \bar{\chi}_{E_i} \mid \tilde{\chi}_n \rangle &\underset{N \rightarrow \infty}{\longrightarrow} \delta_\varepsilon^{-1/2}(\tilde{E}_n, \tilde{E}_n) \langle \bar{\chi}_{E_i} \mid \bar{\chi}_{\tilde{E}_n} \rangle \\ &= \delta_{in} \delta_\varepsilon^{1/2}(\tilde{E}_n, \tilde{E}_n) \, , \end{aligned} \tag{25}$$

becomes completely concentrated about $\tilde{E}_n$. In other words, for large basis sets, $\tilde{\chi}_n$ has a maximum overlap with the continuum wave function $\bar{\chi}_{\tilde{E}_n}$. That this also holds to a good approximation for smaller basis sets was explicitly shown by Macías and Riera:[57] Provided that H_{PP} presents no resonance structure, the Heisenberg transform turns out to have a peaked structure with a maximum value for E close to $\tilde{E}_n$. This is equivalent to saying that one has

$$\tilde{\chi}_n(\mathbf{r}_1, \mathbf{r}_2) \simeq \rho^{-1/2}(\tilde{E}_n) \bar{\chi}_{\tilde{E}_n}(\mathbf{r}_1, \mathbf{r}_2) \quad \text{for } \mathbf{r}_1, \mathbf{r}_2 \in D \, , \tag{26}$$

where the normalization factor

$$\rho(\tilde{E}_n) \underset{N \rightarrow \infty}{\longrightarrow} \delta_\varepsilon(\tilde{E}_n, \tilde{E}_n) \tag{27}$$

increases indefinitely in the limit of a complete basis set, and can be formally assimilated to a density of states.

Substitution of expression (26) in Eq. (9) yields the golden-rule formula:

$$\Gamma \simeq 2\pi\rho(\tilde{E}_n) \, | \langle \phi_1 \mid H_{QP} \mid \tilde{\chi}_n \rangle |^2 \tag{28}$$

for $\tilde{E}_n = E_1^d$.

C. Density of continuum states

We have just seen that the coarse-grain discretization[57] of the spectrum of H_{PP}, achieved by its generalized diagonalization in a finite basis set (18), provides approximations to the wave functions $\bar{\chi}_E$, hence to χ_E, inside the domain D of configuration space covered by that basis set. As a consequence, it provides an approximation to the Feshbach projection operator P:

$$P = \sum_i | \chi_{E_i} \rangle \langle \chi_{E_i} | + \int dE \, | \chi_E \rangle \langle \chi_E | \tag{29}$$

taking the form

$$\tilde{P} = \sum_{n=0}^{N} | \tilde{\chi}_n \rangle \langle \tilde{\chi}_n | \tag{30}$$

$$\simeq \sum_{\substack{n \\ (\tilde{E}_n < E^0)}} | \bar{\chi}_{\tilde{E}_n} \rangle \langle \bar{\chi}_{\tilde{E}_n} | + \sum_{\substack{n \\ (\tilde{E}_n > E^0)}} \rho^{-1}(\tilde{E}_n) | \bar{\chi}_{\tilde{E}_n} \rangle \langle \bar{\chi}_{\tilde{E}_n} | \, , \tag{31}$$

where E^0 is the ionization threshold, and the projector in Eq. (31) is to be bracketed, to the left or to the right, by $\langle \mathbf{r}_1 \mathbf{r}_2 |$, with $\mathbf{r}_1, \mathbf{r}_2 \in D$. It is important to carefully distinguish this *coarse-grain discretization,* valid only inside D, from the *fine-grain discretization,* of Eq. (13), which is exact for all practical purposes.

To examine the nature of the quadrature[53,54] provided by (30) for the integral operator in (29), it is convenient to define an interpolating function $\mu(E)$, fulfilling

$$\begin{aligned} &(1) \;\; \mu(\tilde{E}_n) = n \, , \\ &(2) \;\; d\mu/dE \text{ continuous and monotonic} \, . \end{aligned} \tag{32}$$

Each such function μ can be used to define a quadrature operator for P:

$$P=\sum_{i} |\chi_{E_i}\rangle\langle\chi_{E_i}| + \int d\mu \frac{dE}{d\mu} |\chi_E\rangle\langle\chi_E|$$
$$\simeq \sum_{\substack{n \\ (\tilde{E}_n < E^0)}} |\bar{\chi}_{\tilde{E}_n}\rangle\langle\bar{\chi}_{\tilde{E}_n}| + \sum_{\substack{n \\ (\tilde{E}_n > E^0)}} \left.\frac{dE}{d\mu}\right|_{\tilde{E}_n} |\bar{\chi}_{\tilde{E}_n}\rangle\langle\bar{\chi}_{\tilde{E}_n}| \, . \qquad (33)$$

Comparison of (31) and (33) shows that, when bracketed by $\langle \mathbf{r}_1,\mathbf{r}_2 |$ with $\mathbf{r}_1,\mathbf{r}_2 \in D$, the former is a special case of the latter, with

$$\left.\frac{d\mu}{dE}\right|_{\tilde{E}_n} = \rho(\tilde{E}_n) \, . \qquad (34)$$

In fact, Eq. (34) provides a very useful way to approximate the normalization factor in Eq. (23), since, as will be seen below, it is not difficult to obtain finite-difference approximations to the left-hand side in that equation, when the basis set (18) is judiciously chosen.

In practice, those approximations can be reached in an empirical way, by inspection of the behavior of the eigenvalues as functions of the index n [see Eq. (32)]. However, it is interesting to consider the reasoning underlying their use, which we now outline.

To be specific, let us suppose we wish to describe a P state consisting of a bound electron, of energy E^0, and an unbound one which is represented by a standing wave. To reproduce this wave inside the D domain, we can employ an even-tempered[59] set of Slater (STO) or Gaussian (GTO) orbitals, whose exponents are in a geometrical progression:

$$\alpha_i = \alpha_0 \beta^i, \quad i=0,1,\ldots,N \qquad (35)$$

where β defines the density of the basis set. For such an orbital basis, one always finds that the eigenenergies of the secular equation (19) for the H_{PP} operator present a clear exponential pattern as functions of the index n [Fig. 1(a) illustrates this behavior]. To explain this empirical finding, we can work as follows.

Let us define[60] a *family* of configuration bases constructed from even-tempered sequences of STO's or GTO's:

$$\{\xi_j(\eta); j=0,1,\ldots,N\} \qquad (36)$$

depending upon a parameter η such that the orbital sequence is of the form

$$\alpha_i^{(\eta)} = \alpha_i^{(0)} \beta^{\eta} = \alpha_0 \beta^{\eta+i}, \quad i=0,1,\ldots,N \, . \qquad (37)$$

Each value of η then yields a different basis set, and a different secular equation (19). To a good approximation, the corresponding eigenenergies of this secular equation are of the form

$$\tilde{E}_n = E^0 + \tau_n(\eta) \, , \qquad (38)$$

that is, a sum of a bound electron energy and the kinetic energy of the "continuum" electron, which will depend on the basis set used, i.e., on the parameter η. Then, because of the homogeneous property of the kinetic-energy operator, we shall have, from (37),

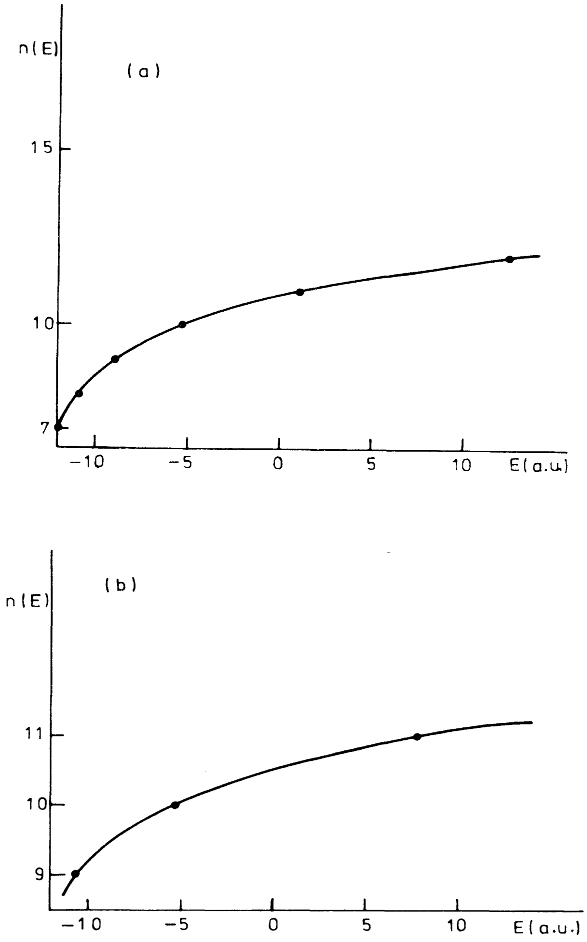

FIG. 1. Exponential behavior of the eigenvalues of $H_{PP},\tilde{E}_n$ of B^{3+}, as a function of the index n for (a) an even-tempered sequence of exponents [Eq. (35)], (b) a generalized sequence of exponents [Eq. (49)] (notice that the figure shows the inverse function, which is then logarithmic).

$$\tau_n(\eta) = \tau_n(0)\beta^{2\eta} = \tau_n(0) e^{\alpha\eta} \, , \qquad (39)$$

with $\alpha = 2\ln\beta$. In other words, for a fixed index n the eigenvalue $\tilde{E}_n(\eta)$ behaves exponentially as a function of the nonlinear parameter; an illustration of this fact is presented in Fig. 2(a).

Next, we shall assume that the basis set is not outrageously small, so that incorporating a new orbital with exponent α_{-1} or α_{N+1} [following the sequence (37)], or eliminating the first or last orbital with exponents α_0, α_N, respectively, yields the same eigenvalues $\tilde{E}_n$ for $1 \ll n \ll N$. Then we notice that

$$\{\xi_j(1); j=0,1,\ldots,N\} = \{\xi_j(0); j=1,2,\ldots,N+1\} \, , \qquad (40)$$

which, according to our assumption, should yield the same eigenvalues $\tilde{E}_n$ as the basis set (36), for $\eta=0$, and $1 \ll n \ll N$. We must then obtain

$$\tilde{E}_n(\eta=1)=\tilde{E}_{n+1}(\eta=0)\ , \tag{41}$$

that is,

$$\tau_n(1)=\tau_{n+1}(0)\ . \tag{42}$$

This procedure can be repeated $m \ll N$ times, yielding

$$\tau_n(m)=\tau_{n+m}(0)\ . \tag{43}$$

Taking Eq. (39) into account, one then has

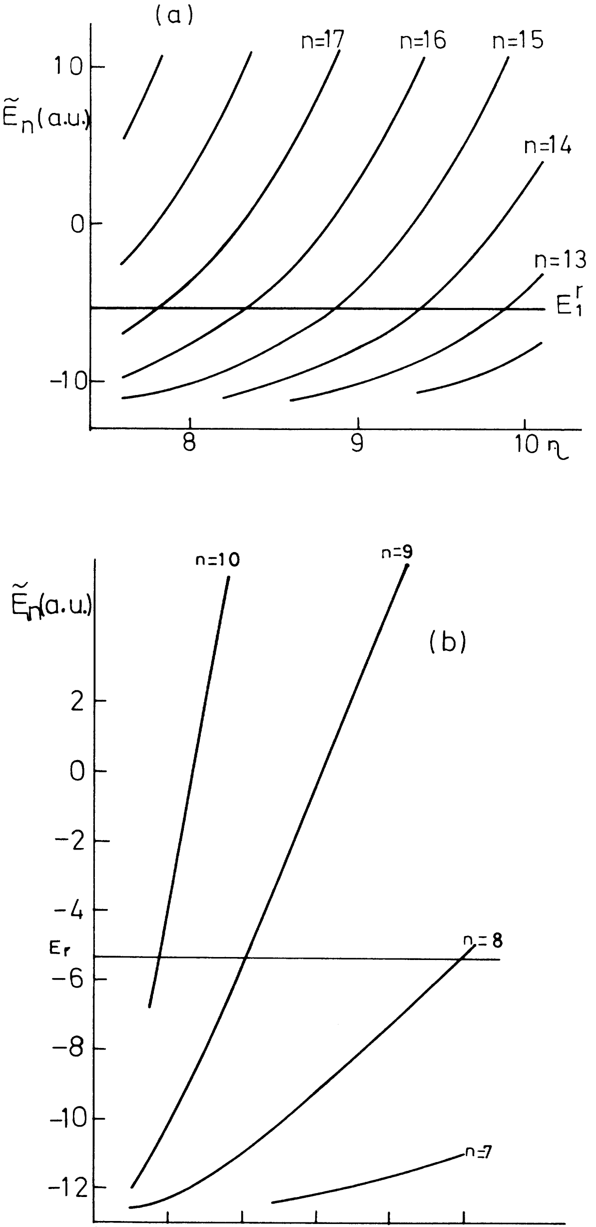

FIG. 2. Behavior of the eigenvalues of $H_{PP}, \tilde{E}_n$ of B^{3+}, as a function of the nonlinear parameter: (a) η defined in Eq. (37) for an even-tempered sequence of exponents [Eq. (35)], (b) γ defined in Eq. (54) for a generalized sequence of exponents [Eq. (49)].

$$\tau_{n+m}(0)=\tau_n(0)e^{\alpha m} \tag{44}$$

or

$$\tilde{E}_{n+m}=\tau_n(0)e^{\alpha m}+E^0\ , \tag{45}$$

that is, an exponential behavior of the eigenvalues $\tilde{E}_n$ as functions of the index n, for a given value of η, i.e., for a given basis set (36). The accuracy of Eq. (45) can be gauged from Fig. 1(a) and 1(b) by checking that the value of the gradient in a semilog fit of the eigenenergies versus n coincides with $\alpha=2\ln\beta$.

From the preceding reasoning, and taking into account that μ is an interpolation function for the index n [see Eq. (32)], it is clear that a good approximation to the left-hand side of Eq. (34) is

$$\left.\frac{d\mu}{dE}\right|_{\tilde{E}_n}=\frac{1}{\alpha(\tilde{E}_n-E^0)} \tag{46}$$

and we can employ a straightforward interpolation procedure, involving the nodes $\tilde{E}_{n-1}$, $\tilde{E}_n$, and $\tilde{E}_{n+1}$ to evaluate the density of states $\rho(\tilde{E}_n)$ in the golden-rule formula (28). In fact, for $\beta<2$, an extremely simple central difference expression[23,25,28] is sufficiently accurate for most purposes:

$$\rho(\tilde{E}_n)\simeq\frac{2}{\tilde{E}_{n+1}-\tilde{E}_{n-1}} \tag{47}$$

since

$$\tilde{E}_{n+1}-\tilde{E}_{n-1}=\tau_n(0)(e^{\alpha}-e^{-\alpha})\simeq 2(\tilde{E}_n-E^0)\alpha\ . \tag{48}$$

We notice that the use of Eq. (47) as an approximation to the density of states in Eq. (28) rests on the assumption that, inside the domain D, the basis set (18) is sufficiently close to completeness for $P=\tilde{P}$ of Eq. (31), and for Eq. (41), to hold. To test the accuracy of this assumption, two simple tests can be performed.

(a) Results obtained with two different basis sets $\{\xi_j(\eta)\},\{\xi_j(\eta+1)\}$ or indeed with $\{\xi_j(\eta')\}$ should be the same to a good precision. This test will be elaborated upon in Sec. II D.

(b) Convergence[23] of Γ with the size of the basis set N in Eq. (18) should have been reached, to the desired precision. In other words, further increasing the basis should modify the wave function [Eq. (26)] and the density of states [Eq. (47)] so as to leave the width [Eq. (28)] invariant. An illustration of this convergence is presented in Table I.

Incidentally, this second test brings forth a possible formal objection that can be raised, regarding the special kind of basis set chosen to illustrate our procedure, which is a point worthy of consideration. The objection is that even-tempered bases, though widely used in quantum chemistry, are known to be incomplete[61] in the limit $N\rightarrow\infty$ in Eq. (35). It is easy, however, to overcome this formal difficulty.

For this purpose, we can generalize the even-tempered exponent sequence (35) in many ways. A possible one is

TABLE I. Invariance test for the first ^1P resonance of B^{3+} regarding the size of the $\{\xi_i\}$ basis. Numbers in square brackets indicate power of ten.

		$E_1^d=-5.373\,54$ a.u.		
N	n	$\rho(\tilde{E}_n)$	$\langle\phi_1\|H\|\tilde{\chi}_n\rangle$	Γ (eV)
18	10	0.200 492	4.9208[-2]	8.30[-2]
28	15	0.218 717	4.7313[-2]	8.37[-2]

TABLE II. Invariance test for the first ^1P resonance of B^{3+} regarding the nonlinear parameter η. Numbers in square brackets indicate power of ten.

		$N=28$		
η	n	$\rho(\tilde{E}_n)$	$\langle\phi_1\|H\|\tilde{\chi}_n\rangle$	Γ (eV)
9.884	13	0.216 930	4.7531[-2]	8.38[-2]
9.367	14	0.218 112	4.7392[-2]	8.38[-2]
8.851	15	0.218 717	4.7313[-2]	8.37[-2]
8.337	16	0.218 237	4.7342[-2]	8.36[-2]
7.821	17	0.217 239	4.7419[-2]	8.35[-2]

$$\alpha_i=\alpha_0\beta^{[1-(1-\varepsilon)^i]/\varepsilon},\quad i=0,1,\ldots,M \tag{49}$$

which has an accumulation point as $M\rightarrow\infty$:

$$\alpha_\infty=\alpha_0\beta^{1/\varepsilon}\;. \tag{50}$$

The STO or GTO sets with the exponents in the sequence (49) become complete in the limit $M\rightarrow\infty$, according to Klahn and Bingel's theorem.[62] The geometrical sequence (35) is recovered from its generalization (49) in the limit $\varepsilon=0$. In fact, for $i\varepsilon\ll1$, the new and old orbitals, with exponents (49) and (35), respectively, are indistinguishable from each other; and for $N\varepsilon\ll1$ in Eq. (35), the even-tempered basis can be considered as a subset of the complete set with exponents given by (49) with $M=\infty$. This removes the objection.

Finally, it is worth pointing out that generalization (49) of the exponent sequence is not only of formal value as providing a justification for the use of even-tempered bases. As will be seen in the following papers, we have used to advantage in our calculations the fact that linear quasidependences between diffuse orbitals of the even-tempered set appear for larger values of β than for the generalized basis. For this generalized set, the density of states can be evaluated, making use of the fact that, for $(j-i)\varepsilon\ll1$,

$$\frac{1-(1-\varepsilon)^j}{\varepsilon}\simeq\frac{1-(1-\varepsilon)^i}{\varepsilon}+(1-\varepsilon)^i(j-i) \tag{51}$$

and therefore

$$\alpha_j\simeq\alpha_i\delta^{j-i}\;, \tag{52}$$

with

$$\delta=\beta^{(1-\varepsilon)^i}\;. \tag{53}$$

Thus, for small ε the new sequence is geometrical in a wide neighborhood of any given index i. As in the previous case, we can define a family of basis sets $\xi(\gamma)$ with

$$\alpha_i^{(\gamma)}=\alpha_i\gamma \tag{54}$$

for the discretized continuum orbital. As functions of the index n, the eigenvalues of Eq. (19), $\tilde{E}_n$, fulfill Eq. (45) to a very good approximation [see an illustration in Fig. 1(b)], and Eqs. (46) and (47) can likewise be applied for the new generalized basis of STO's or GTO's. Incidentally, as can be expected from Eqs. (38) and (54), the eigenvalues $\tilde{E}_n(\gamma)$ as functions of the parameter γ behave parabolically (proportional to γ^2), because of the homogeneous property of the kinetic-energy operator [see Fig. 2(b)].

D. Inverse interpolation procedure

In our proposed application of Eq. (28) to the evaluation of resonance widths, there still remains a last problem to be solved. It is that, in general, none of the eigenvalues of Eq. (19) coincides with E_1^d, whereas this degeneracy is a requirement for Eq. (28) to hold.

Our way out of this difficulty[23,25,28] is to employ, instead of a single basis set (18), a family of bases $\{\xi_j(\eta)\}$ or $\{\xi_j(\gamma)\}$, with STO or GTO exponents as defined in Eqs. (37) or (54). Then all matrices in the secular equation (19) are functions of the nonlinear parameter η (γ), and the η (γ) dependence of the eigenvalues can be used to impose that $\tilde{E}_n=E_1^d$, for any index n, by inverse interpolation, and to any desired precision. This is illustrated in Fig. 2(a) and 2(b) for several values of n.

Finally, we note that the very existence of several indexes $n,n',\ldots$ such that $\tilde{E}_n(\eta)=\tilde{E}_{n'}(\eta')=\ldots=E_1^d$ is fulfilled permits us to gauge the accuracy of our approximation for the density of states, in the sense that neighboring values should yield the same final width—thus providing an implementation of test (b) proposed in Sec. II C. An illustration of this test is presented in Table II.

III. SUMMARY

Before passing on in the following papers to applications of our method, it is useful to summarize the main practical steps of our procedure.

(1) Taking O'Malley and Geltman's form (2) for the Feshbach projection operator Q, we solve the eigenvalue equation (6) (in a finite representation). This yields (approximations to) the discrete wave function ϕ_1 and (to) its energy E_1^d.

(2) We define a finite basis (18) of L^2-integrable functions, all of which are orthogonal to ϕ_1, covering a domain D of configuration space that contains the region where ϕ_1 takes non-negligible values. Solving the secular equation (19) yields L^2-integrable approximations to the continuum wave functions χ_E of Eq. (12) inside D.

(3) A nonlinear parameter is varied in the basis set (18) of step (2) so as to achieve, by inverse interpolation, the degeneracy condition between discrete and continuum wave functions $\tilde{E}_n=E_1^d$, for a chosen value of n (Fig. 2).

(4) Provided that the discrete spectrum $\tilde{E}_n$ obtained in step (2) is such that a function $\mu(E)$ with the properties (32) can be defined (Fig. 1), a density of states $\rho(E)$ is evaluated with a finite-difference expression such as (47) [or (46)].

(5) The approximations for ϕ_1, χ_E, and ρ are introduced in the golden-rule formula (28). Overall checks are obtained by choosing neighboring values of n in step (3) (Table II), and increasing the discrete and continuum basis sets (Table I); in both tests the same final results should be reached to the desired precision. In practice, and somewhat paradoxically, in the application of our method[23,25,28] we have always found the convergence test to be considerably more straightforward for the continuum than for the discrete wave function.

Finally, some words may be appropriate with regard to the restrictions of the proposed method. Obviously, since it is an implementation of Feshbach's theory,[44] the well-known difficulties of this formalism apply. In particular, extension to systems with more than two electrons[49,63,64] is nontrivial, and the O'Malley-Geltman[50] form [Eq. (2)] for the Q operator is not immediately generalizable to targets with more than one electron.[65] Also, as is well known, construction of this Q operator for shape resonances is not straightforward, and to treat these resonances, perhaps our method should be implemented in the framework of the constrained variational approach of Macías and Riera[23,66,57] rather than of Feshbach's. Since, in our case, all tests refer to two-electron targets, the validity of the fit (46) [or (47)] for the density of states remains to be checked for systems with more than two electrons.

ACKNOWLEDGMENTS

This research has been partially supported by the Comisión Asesora de Investigación Científica y Técnica Project No. 890/84. Calculations have been performed at the Universidad Autónoma de Madrid IBM and Centro de Calculo centers, and at the Junta de Energía Nuclear (Madrid).

---

[1] R. P. Madden and K. Codling, Phys. Rev. **141**, 364 (1965).

[2] L. Lipsky and A. Russek, Phys. Rev. **142**, 59 (1966).

[3] J. Macek, J. Phys. B **1**, 831 (1968).

[4] E. Holøien and J. Midtal, J. Phys. B **5**, 1111 (1972).

[5] P. J. Hicks and J. Comer, J. Phys. B **8**, 1866 (1975).

[6] C. D. Lin, Phys. Rev. Lett. **35**, 1150 (1975); Phys. Rev. A **12**, 493 (1975).

[7] L. Lipsky, R. Anania, and M. J. Conneely, At. Data Nucl. Data Tables **20**, 127 (1977).

[8] L. Lipsky and M. J. Conneely, Phys. Rev. A **14**, 2193 (1976).

[9] L. Lipsky and M. J. Conneely, J. Phys. B **11**, 4135 (1978).

[10] R. L. Brooks and E. N. Pinnington, Phys. Rev. A **22**, 529 (1980).

[11] H. Klar and M. Klar, J. Phys. B **13**, 1057 (1980).

[12] G. Aspromalis, Y. Komninos, and C. A. Nicolaides, J. Phys. B **17**, 2451 (1982); **17**, L151 (1984).

[13] C. A. Nicolaides and E. Adamides, Phys. Rev. A **27**, 1691 (1983).

[14] A. K. Bhatia and A. Temkin, Phys. Rev. A **29**, 1895 (1984).

[15] Y. K. Ho, Phys. Rev. A **23**, 2137 (1981).

[16] Y. K. Ho, Phys. Rep. **99**, 1 (1983).

[17] L. A. Collins and B. I. Schneider, Phys. Rev. A **27**, 101 (1983).

[18] S. L. Guberman, J. Chem. Phys. **78**, 1404 (1983).

[19] H. Takagi and H. Nakamura, Phys. Rev. A **27**, 691 (1983).

[20] H. Bachau, J. Phys. B **17**, 1771 (1984).

[21] Y. K. Ho and J. Callaway, J. Phys. B **17**, L695 (1984).

[22] S. Hara and H. Sato, J. Phys. B **17**, 4301 (1984).

[23] A. Macías and A. Riera, Phys. Lett. **103A**, 377 (1984).

[24] D. H. Oza, J. Phys. B **18**, L321 (1985).

[25] A. Macías and A. Riera, Chem. Phys. Lett. **117**, 42 (1985).

[26] A. Macías, R. Mendizábal, F. Pelayo, A. Riera, and M. Yáñez, J. Mol. Struct. THEOCHEM. **107**, 245 (1984); Phys. Rev. A **33**, 242 (1986).

[27] F. Martín, A. Riera, and M. Yáñez, J. Chem. Phys. **84**, 5142 (1986).

[28] A. Macías and A. Riera, Europhys. Lett. **2**, 351 (1986); Phys. Lett. **119**, 28 (1986).

[29] N. Koyama, H. Fukuda, T. Motoyama, and M. Matsuzawa, J. Phys. B **19**, L331 (1986).

[30] S. Watanabe and C. D. Lin, Phys. Rev. A **34**, 823 (1986).

[31] A. Pochat, R. J. Tweed, M. Doritch, and J. Peresse, J. Phys. B **15**, 2269 (1982).

[32] R. A. Hulse, Nucl. Tech. Fusion **3**, 259 (1983).

[33] T. Andersen, S. M. Bentzen, and O. Poulson, Phys. Scr. **22P**, 119 (1980).

[34] H. Cederquist, M. Kisielinski, and S. Mannervik, J. Phys. B **16**, L479 (1983).

[35] R. Bruch, P. L. Altick, E. Trabert, and P. H. Heckmann, J. Phys. B **17**, L655 (1984).

[36] R. Bruch, Phys. Scr. **26**, 381 (1983).

[37] H. Van Sprong, H. H. Brangersma, and F. J. de Heer, Chem. Phys. Lett. **65**, 55 (1979).

[38] R. Morgenstern, A. Nieuhaus, and G. Zimmerman, J. Phys. B **13**, 4811 (1980); E. Boskamp, R. Morgenstern, and A. Nieuhaus, *ibid.* **15**, 4577 (1982); E. Boskamp, R. Morgenstern, P. Van der Straten, and A. Nieuhaus, *ibid.* **17**, 2823 (1984).

[39] C. L. Cocke, R. Dubois, T. J. Gray, E. Justiniano, and C. Can, Phys. Rev. Lett. **46**, 1671 (1981).

[40] S. Bliman, D. Hitz, B. Jacquot, C. Harel, and A. Salin, J. Phys. B **16**, 2849 (1983); S. Bliman, M. Bonnefoy, J. J. Bonnet, S. Dousson, A. Fleury, D. Hitz, and B. Jacquot, Phys. Scr. **T3**, 63 (1983).

[41] A. Itoh, T. Schneider, G. Schiwietz, Z. Roller, H. Platten, G. Notte, D. Schneider, and N. Stolterfoht, J. Phys. B **16**, 3965 (1983).

[42] M. Cormnille, J. Dubau, F. Bely-Dubau, S. Bliman, D. Hitz, M. Mayo, J. J. Bonnet, M. Bonnefoy, M. Chassevent, and A. Fleury, J. Phys. B **19**, L393 (1986).

[43] E. Balsev and J. M. Combes, Commun. Math. Phys. **22**, 280 (1971). For applications see whole issue in Int. J. Quantum Chem. **14**, No. 4 (1978), and Y. K. Ho, Ref. 16. For remarks on computational efforts see, e.g., K. T. Chung and B.

F. Davis, Phys. Rev. A **26**, 3278 (1982).

[44] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962).

[45] A. Macías, F. Martín, A. Riera, and M. Yáñez, following paper, Phys. Rev. A **36**, 4187 (1987).

[46] A. Macías, F. Martín, A. Riera, and M. Yáñez, this issue, Phys. Rev. A **36**, 4203 (1987).

[47] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[48] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

[49] A. Temkin and A. K. Bhatia, Phys. Rev. A **31**, 1259 (1985).

[50] T. F. O'Malley and S. Geltman, Phys. Rev. **137**, A1344 (1965).

[51] W. H. Miller, Phys. Rev. **152**, 70 (1966).

[52] W. H. Miller, Chem. Phys. Lett. **4**, 627 (1970).

[53] W. H. Bassichis, J. F. Reading, and R. R. Scheerbaum, Phys. Rev. C **11**, 316 (1975).

[54] J. T. Broad, Phys. Rev. A **18**, 1011 (1978); **26**, 3078 (1982).

[55] W. P. Reinhardt, Comput. Phys. Commun. **17**, 1 (1979).

[56] M. R. Hermann and P. W. Langhoff, J. Math. Phys. **24**, 541 (1983); Phys. Rev. A **28**, 1957 (1983).

[57] A. Macías and A. Riera, J. Phys. (Paris) **46**, 535 (1985).

[58] C. Cohen-Tannoudji, B. Diu, and F. Laloe, *Mécanique Quantique* (Hermann, Paris, 1980), Vol. I; I. Stackgold, *Boundary Value Problems of Mathematical Physics* (MacMillan, London, 1967), Vol. I.

[59] K. Ruedenberg, R. C. Raffenetti, and D. Bardo, in *Energy Structure and Reactivity,* Proceedings of the Conference on Theoretical Chemistry, Boulder, 1972 (Wiley, New York, 1975).

[60] A. Macías and A. Riera, Gazz. Chim. Ital. **108**, 329 (1978).

[61] B. Klahn and W. A. Bingel, Int. J. Quantum Chem. **11**, 943 (1977).

[62] B. Klahn and W. A. Bingel, Theor. Chim. Acta. **44**, 27 (1977).

[63] Y. Hahn, Ann. Phys. (N.Y.) **58**, 137 (1970).

[64] A. Berk, A. K. Bathia, B. R. Junker, and A. Temkin, Phys. Rev. A **34**, 4591 (1986).

[65] A. Temkin, A. K. Bhatia, and J. N. Bardsley, Phys. Rev. A **5**, 1663 (1972).

[66] S. C. Tucker and D. G. Truhlar, J. Chem. Phys. **86**, 6251 (1987).