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ATOMIC AND MOLECULAR AUTOIONIZING STATES. A THEORETICAL APPROACH

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Resumé - Nous présentons une nouvelle méthode qui permet l'obtention des positions et durées de vie des états résonants, atomiques ou moléculaires, avec deux électrons actifs. Cette procédure, est basée sur une analogie formelle entre le formalisme de Feshbach et la méthode du pseudopotentiel de Phillips et Kleinman. Elle produit des résultats en très bon accord avec ceux de la méthode de Feshbach avec un calcul beaucoup plus simple, spécialement pour le cas où l'état résonant se trouve au dessus de plusieurs seuils d'ionisation. Cette méthode peut être généralisée facilement au traitement des états doublement excités des systèmes isoélectroniques du Be, c'est-à-dire, des systèmes avec un coeur de couche fermée $1s^2$. Dans notre application de la méthode la fonction d'onde de la composante ouverte s'obtient en utilisant une technique de discrétisation du continu, dont les bases sont présentées en détail. On utilise aussi une méthode d'interpolation inverse pour remplir la condition de dégénération discret-continu qui est nécessaire pour appliquer la règle d'or et obtenir la largeur. Nous présentons quelques illustrations pour des états résonants de systèmes Heliumoïde et Berylliumoïde qui sont au dessus de plusieurs seuils d'ionisation et aussi pour des résonances moléculaires de systèmes homo et heteronucléaires à deux électrons.

Abstract - We present a progress report on a new method to calculate positions and widths of two-electron atomic (molecular) resonances. This procedure, based on a formal analogy between the Feshbach formalism and the Phillips-Kleinman pseudopotential approach, yields results in very good agreement with those obtained with the standard Feshbach formalism, but requires a considerably smaller computational effort in cases where the resonant states of interest lie above several ionization thresholds. This method can be very easily generalized to the treatment of doubly excited states of Be-like systems, that is containing a closed shell $1s^2$ core. In our implementation of the method, the open channel wavefunction is obtained from using a discretization procedure, whose theoretical basis we present in some detail, and an inverse interpolation method to achieve the discrete-continuum degeneracy which is needed to apply the golden rule formula to calculate the width. We present some illustrations for He-like and Be-like resonances lying above one or several ionization thresholds, and for molecular resonances of homo and heteronuclear two-electron systems.

1 - INTRODUCTION

Doubly excited states of atoms and molecules have received a great deal of attention because they are involved in a considerable number of experimental phenomena such as beam-foil spectroscopy /1,2/, electron-impact experiments /3/, atomic processes in fusion plasmas /4/, and single-collision beam experiments /5-12/.

One of the most powerful tools to obtain the positions and widths of this kind of resonances is the well known Feshbach formalism /13/, whose fundamental definitions are summarized in section 2. In this approach the

wavefunction representing the autoionizing state of a (formal) two-electron system is written as the sum of a closed channel, $Q\psi$, and an open channel $P\psi$, components. Solutions of the closed channel equation have been reported for He-like resonances lying above the first ionization limit /14-18/; on the other hand, results for resonances which are above several ionization thresholds are scarce /19/, because the method becomes computationally cumbersome. Likewise, only very recently theoretical results for $(1s^2 nln'l')$ resonant states of Be-like systems have been reported /20/ in the literature and there is a complete lack of theoretical information on $(1snln'l')$ resonances of Li-like systems, because, although these states are of an increasing interest, the Feshbach approach is extremely difficult to implement for systems with more than two electrons.

We present in this paper a progress report on an alternative method we have recently proposed that yields positions and widths /21,22/ in very good agreement with those obtained with the Feshbach formalism while requiring a considerably smaller computational effort. Our method is based /23/ on a formal analogy between the Feshbach theory and the Phillips-Kleinman pseudopotential approach /24/ to be described in Section 3. We shall show in Section 4 that this procedure constitutes a general method which permits to obtain, through an adequate definition of this pseudopotential, either the energies of the valence states of species with a closed-shell core or the positions of autoionizing states of systems with or without a core and lying above one or several ionization thresholds.

To approximate the open channel wavefunction and calculate its interaction with the corresponding closed channel component, we have developed a discretization procedure /25/ whose theoretical basis will be summarized in section 5. The calculation of the width will be explained in section 6 and in section 7 we shall present some illustrations for He-like /26/ and Be-like /20/ resonances lying above several ionization thresholds and discuss the extension of this theoretical treatment to the study of molecular resonances /27/.

2 - FESHBACH THEORY FOR TWO-ELECTRON SYSTEMS

In order to better understand the new theory presented in section 4, it is worth to recall the basic definitions of the Feshbach formalism /13/.

In this theory the wave function representing a two-electron resonant state is written as a sum of open and closed channel components:

$$\psi(r_1, r_2) = P\psi + Q\psi \quad (1)$$

where P is a projection operator such that $P\psi$ behaves asymptotically like ψ when either r_1 or r_2 tends to infinity; and $Q = 1 - P$. For two-electron systems the O'Malley-Geltman form /28/ for Q is generally used:

$$Q = Q_1 Q_2 \quad (2)$$

where

$$Q_i = 1 - P_i = 1 - \sum_{\alpha} |\Psi_{\alpha}(i)\rangle \langle \Psi_{\alpha}(i)| = 1 - \sum_{\alpha} P_{\alpha}(i) \quad (3)$$

and where the sum in eq. (3) runs over the N_c threshold states, whose energies lie below the doubly excited state considered, and are defined by the hydrogenic orbitals Ψ_{α} .

Inserting eq. (1) in the Schrödinger equation yields the coupled equations:

$$\begin{aligned} (H_{QQ} - E) Q\psi &= -H_{QP}P\psi \\ (H_{PP} - E) P\psi &= -H_{PQ}Q\psi \end{aligned} \quad (4)$$

where $H_{QQ} = QHQ$; $H_{PP} = PHP$ and $H_{PQ}^+ = H_{QP} = PHQ$.

The projected Hamiltonian H_{QQ} has a discrete spectrum below the N_c+1 ionization limit and the interaction H_{QP} permits the decay of the closed channel $Q\psi$ into the continuum state $P\psi$.

Then, the closed channel wavefunction is obtained as the eigenfunction of:

$$(H_{QQ} - E_{n'}) \psi_{n'} = 0 \quad (5)$$

When more than one open channel is open we can define the partial width corresponding to each ionization threshold, α , as:

$$\Gamma_{n\alpha} = 2\pi |\langle \phi_n | H_{QP} | \chi_{E\alpha} \rangle|^2 \quad (6)$$

where the corresponding open channel component $\chi_{E\alpha}$ is (neglecting terms quadratic in H_{QP}) the eigenfunction of the equation:

$$(P_\alpha H P_\alpha - E^c) \chi_{E\alpha} = 0 \quad (7)$$

for $E^c = E_n^c$ and

$$P_\alpha = P_\alpha(1) + P_\alpha(2) - P_\alpha(1)P_\alpha(2) \quad (8)$$

The total width is given by /13/:

$$\Gamma_n = \sum_\alpha \Gamma_{n\alpha} \quad (9)$$

In the $\{\phi_n, \chi_{E\alpha}\}$ representation, the Hamiltonian can be symbolically written as:

$$H = \begin{pmatrix} E^c & H_{QP} \\ H_{PQ} & E^c \end{pmatrix} \quad (10)$$

where E^c and E^c are diagonal matrices. As indicated above, the elements of E^c are discrete below the N_c+1 threshold, and correspond to the closed channel energies of Eq. (5). The E^c matrix contains a discrete part, which corresponds to the Rydberg series converging to the first ionization limit and an open channel continuum part, which corresponds to the ionization continua.

In practice, the closed channel equation (eq. (5)) is usually solved by using either:

a) the exact solutions of a separable Hamiltonian such as:

$$H^c = H - r_{12}^{-1} = H^c(1) + H^c(2) \quad (11)$$

as a basis set, or

b) a standard CI method, with configurations built from Slater or Gaussian-type atomic orbitals that have been orthogonalized to the set $\{\psi_\alpha\}$ in Eq. (3).

Both implementations become considerably complicated when more than one ionization threshold is open: in a) because of slow convergence and substantial programming complication; in b) because the orbital basis used to build the configurations must be simultaneously orthogonalized to the different sets $\{\psi_\alpha\}$ involved in the definition of Q , which makes the procedure very difficult to apply.

3 - FESHBACH THEORY FOR SYSTEMS WITH A CLOSED-SHELL CORE

Let us consider now the particular case of the resonant states of a system with a closed-shell core. To be specific, let us assume that we are interested in the $(1s^2 3l3l')$ autoionizing states of Be-like systems. As indicated in the Introduction, the Feshbach formalism is extremely difficult to implement for a four-electron system. On the other hand, we can take into account that the core $1s^2$ electrons play an almost passive role, and use a model potential /29/ to account for the core-valence effects. This provides a practical alternative to the full-electron treatment, since it reduces the problem to a formal two-electron case, and the Feshbach formalism outlined in the previous section can be applied. In this approach we replace the four-electron Hamiltonian by a model one of the form:

$$H_M = H^c(1) + H^c(2) + V_M(1) + V_M(2) + r_{12}^{-1} \quad (12)$$

where H^c is a hydrogenic Hamiltonian and V_M a suitable model potential /30-32/ that accounts for the core-valence effects. We can then carry out a variational calculation for H_M solving the corresponding secular equation in a representation of configurations of the form:

$$\psi_{k_1, k_2} = 1/2 [\psi_{k_1}(1) \psi_{k_2}(2) \pm \psi_{k_2}(1) \psi_{k_1}(2)] \quad (13)$$

where ψ_k are one-electron wavefunctions and the spin functions have been factored out for simplicity. A well-known /30-32/ peculiarity of model potential calculations is that the valence states of the system are not described by the lowest eigenvalues of (12), but are, from a formal point of view, infinitely excited. This is because, below the valence states ($2s^2$, $2s2p$, $2p^2$...) of the system there exists a infinite number of unphysical "core" or "virtual" states, which belong to the unphysical Rydberg series $1s'^2$, $1s'2s'$, $1s'2p'$... converging to a pseudoionization $1s'$ limit. The consequence is that, in this approximation, the valence states of this atomic system will lie above this pseudoionization threshold and are therefore embedded in the virtual continuum of the model Hamiltonian.

We notice that the previous feature of the simplified theory implies that in this model there is no difference whatsoever between the two-electron valence states ($1s^2 2l 2l'$) and the ($1s^2 3l 3l'$) autoionizing ones. Actually the only difference is that while the latter lie above several ionization thresholds ($1s'$, $2s$ and $2p$, one of which is non-physical) the former lies above a single ($1s'$) threshold. This difference becomes even less significant if we consider a system as Mg where the two-electron valence states would lie above several pseudoionization ($1s'$, $2s'$ and $2p'$) thresholds.

We see then that the model potential approach provides an analogy /23/ between doubly excited resonant and two-electron valence states. As a consequence, the latter can be obtained with the same methodology as the former, e.g., by solving an equation similar to Eq. (5). This would also mean that the difficulties indicated at the end of section 2 to implement the Feshbach formalism for resonances lying above several ionization thresholds will also apply here.

4 - FESHBACH-PSEUDOPOTENTIAL APPROACH

In the model potential approach, there is however a simpler way to calculate the valence energies which consists in adding to the model Hamiltonian (12) a level shift operator or pseudopotential V_{PS} ,

$$H_{eff} = H_M + V_{PS} \quad (14)$$

so that the lowest eigenvalue of H_{eff} corresponds to the two-electron state of interest. According to our analogy, this way can be also applied /21,22/ to obtain the resonance energies of doubly excited states.

To see the implementation of the method let us consider again, for instance, a Be-like system. We can chose V_{PS} as a generalization of the Phillips-Kleinman projection /24/ operator:

$$V_{PS} = |1s'(1)\rangle M \langle 1s'(1)| + |1s'(2)\rangle M \langle 1s'(2)| \\ - |1s'(1)1s'(2)\rangle M \langle 1s'(1)1s'(2)| \quad (15)$$

which takes the form of a sum of one-electron pseudopotentials, minus a correction term which prevents states with two electrons in the core to be shifted twice, and where M is a suitable large positive number. Introduction of this pseudopotential in H_{eff} shifts up the energies of all virtual core states, so that the first eigenvalue of the effective Hamiltonian corresponds to the ground valence state of the system.

On the other hand, if one is interested in doubly excited states of the system lying above the $2s$ and $2p$ thresholds, one can generalize Eq. (15) and write:

$$V_{PS} = MP \quad (16)$$

where

$$P = \sum_{\alpha} |\varphi_{\alpha}(1)\rangle \langle \varphi_{\alpha}(1)| + \sum_{\beta} |\varphi_{\beta}(2)\rangle \langle \varphi_{\beta}(2)| \\ - \sum_{\alpha\beta} |\varphi_{\alpha}(1)\varphi_{\beta}(2)\rangle \langle \varphi_{\alpha}(1)\varphi_{\beta}(2)| \quad (17)$$

is just the projection operator as defined by $P = 1 - Q$ and Eqs. (2), (3) and the summations involve the $1s'$, $2s$ and $2p$ ionization thresholds. Then the first eigenvalue of Eq. (14) corresponds to the lowest ($1s^2 3l 3l'$) autoionizing state. In summary, we may adopt for our pseudopotential operator the form of Eqs. (16) and (17) where the summations in (17) run over as many thresholds as needed depending on the state of interest.

Comparison of Eq. (16) with Eqs. (3), (5) shows that the effective Hamiltonian can be written in the $\{\phi_n, \chi_{E\alpha}\}$ representation in the following symbolic form:

$$H_{\text{eff}} = \begin{pmatrix} E^c & H_{QP} \\ H_{PQ} & E^c + MI \end{pmatrix} \quad (18)$$

We notice the parallelism between this symbolic matrix and that obtained within the Feshbach-O'Malley theory (See Eq. (10)). However, the most important fact is that the practical solution of the closed channel equation now becomes quite simple because it is no longer necessary to explicitly construct the Q projection operator, and a CI calculation can be carried out directly for the effective Hamiltonian (14). Moreover, the goodness of the approximation will only depend on the quality of the basis set used [23].

Finally it should be noticed that this procedure can also be applied to resonant states of two-electron systems lying above several ionization thresholds. It suffices to set $V_M \equiv 0$ in Eq. (12).

5 - DISCRETIZATION FOR THE CONTINUUM PROJECTION OF THE WAVEFUNCTION

To solve the open channel equation, Eq. (7), we follow the work of Refs [16-18, 25-27 and 33]. We take into account that, from Eq. (6), the form of the open channel component, $\chi_{E\alpha}$, is only needed in the region of configuration space where the closed channel component, ϕ_n , which is degenerate with it is non-negligible. This allows us to employ an L^2 -integrable representation of $\chi_{E\alpha}$ in this region. Let us assume for the sake of simplicity that we are in a single continuum, so that we can drop the subindex α from our notation.

To obtain the L^2 representation of χ_E we can diagonalize H_{PP} in a finite basis of L^2 -integrable wave functions belonging to the complement of Q subspace. To avoid mathematical complications derived from the fact that χ_E does not belong to a Hilbert space, and is normalized according to Dirac's delta function

$$\langle \chi_E | \chi_{E'} \rangle = \delta(E - E') \quad (19)$$

we follow the procedure of Macías and Riera [16-18] and enclose the whole system in a very large box, so that the new eigenfunctions of H_{PP} hereafter called χ_{E_i} , are identical to χ_E inside a very large domain of configuration space. Under these conditions the spectral resolution for the projected Hamiltonian is given by:

$$H_{PP} = \sum_i |\chi_{E_i}\rangle E_i \langle \chi_{E_i}| \quad (20)$$

Then, we may consider any arbitrary function of χ_E as, for instance, the bracketed expression $\langle f | \chi_E \rangle$; while this term is a function of the continuous variable E, the corresponding expression $\langle f | \chi_{E_i} \rangle$ takes values for discrete E_i only and may be represented by a histogram. However, our discretization is dense enough (say energy separation $O(\epsilon)$) for the energy differences to be so small that the histogram may be replaced by a continuous interpolation function. For example, our discretization will replace the normalization (19) by:

$$\langle \chi_E | \chi_{E'} \rangle = \delta_\epsilon(E, E') \quad (21)$$

where the interpolation function $\delta_\epsilon(E, E')$ is a member of a δ -family, which tends to $\delta(E - E')$ as $\epsilon \rightarrow 0$. It is convenient to choose the area under this δ_ϵ as

$$\int \delta E' \delta_\epsilon(E, E') = 1 \quad (22)$$

we have also by construction

$$\delta_\epsilon(E_i, E_j) = 0 \quad \text{when } |E_i - E_j| > \epsilon \quad (23)$$

The advantage of introducing the fine grained discretization (20) will now be apparent, because χ_{E1} can be approximated, as well as desired, by a basis expansion, which is not the case for χ_E . Let us consider now a practical situation in which we diagonalize H_{PP} in a basis set of L^2 integrable functions:

$$\{f_j; j=0,1,\dots,N\} \quad (24)$$

which is complete in P space as $N \rightarrow \infty$. Its spectrum is formed by a discrete set of eigenvalues E_n and each eigenfunction will be given by:

$$\chi_n = \sum_j c_{jn} f_j \quad (25)$$

where the coefficients c_{jn} are obtained by solving the corresponding secular equation:

$$H_{PP}C = S_{PP}CE, \quad C^+ S_{PP}C = I \quad (26)$$

From Eq. (26) the χ_n wave functions are normalized according to the delta of Kronecker:

$$\langle \chi_n | \chi_m \rangle = \delta_{mn} \quad (27)$$

Since the χ_{E1} wavefunctions belong to the Hilbert space of P functions and can be expanded in the complete set (24), in the limit $N \rightarrow \infty$ the eigenfunctions χ_n and χ_{En} must coincide up to a normalization factor

$$\chi_n \rightarrow \delta^{-1/2}(E_n, E_n) \chi_E \quad \text{as } N \rightarrow \infty \quad (28)$$

so that Eq. (27) holds

$$\begin{aligned} \langle \chi_n | \chi_m \rangle &\xrightarrow{N \rightarrow \infty} \delta^{-1/2}(E_n, E_n) \delta^{-1/2}(E_m, E_m) \langle \chi_{En} | \chi_{Em} \rangle \\ &= \delta^{-1/2}(E_n, E_n) \delta^{-1/2}(E_m, E_m) \delta(E_n, E_m) = \delta_{mn} \end{aligned} \quad (29)$$

If we take now the Heisenberg transform of χ_n

$$\begin{aligned} \langle \chi_{E1} | \chi_n \rangle &\xrightarrow{N \rightarrow \infty} \delta^{-1/2}(E_n, E_n) \langle \chi_{E1} | \chi_{En} \rangle = \\ &= \delta_{1n} \delta^{-1/2}(E_n, E_n) \end{aligned} \quad (30)$$

we find that $\langle \chi_{E1} | \chi_n \rangle$ is completely concentrated about E_n , i.e., for large enough basis, χ_n has a maximum overlap with the continuum wavefunction χ_{En} . It has also been proved /34/ that this is so, to a good approximation, for smaller basis sets. This is equivalent to write:

$$\chi_n \approx \rho^{-1/2}(E_n) \chi_{En} \quad (31)$$

We further notice that formal discretization of the continuum spectrum of H_{PP} substitutes the projection operator:

$$P = \int dE |\chi_E\rangle \langle \chi_E| \quad (32)$$

by the quadrature:

$$P = \sum_n \Delta E_n |\chi_{En}\rangle \langle \chi_{En}| \quad (33)$$

For a complete set, condition (28) is fulfilled and we can write:

$$P \xrightarrow{N \rightarrow \infty} \sum_n \delta^{-1}(E_n, E_n) |\chi_n\rangle \langle \chi_n| = \sum_n \rho^{-1}(E_n) |\chi_n\rangle \langle \chi_n| \quad (34)$$

and, since the spectra associated to $\{\chi_E\}$ and $\{\chi_n\}$ are identical in the limit $N \rightarrow \infty$, Eqs. (31) and (33) show that $\rho(E_n)$ may be taken as a density of states

$$\rho(E_n) \approx \Delta n / \Delta E_n \quad (35)$$

As a consequence of the relationship (30) in this discretization approach the golden rule formula becomes:

$$\Gamma = 2\pi\rho(E_n) |\langle \phi_1 | H_{GF} | \chi_n \rangle|^2 \quad (36)$$

for $E_n = E_1^0$.

The problem now is how to evaluate this density of states. To illustrate our procedure /25-27,33/ let us consider a particular case, supposing that we diagonalize H_{FF} in a basis of configurations built from even-tempered sequences of STO's or GTO's

$$\{f_j(\eta)\}; j = 0, 1, \dots, N \quad (37)$$

depending upon a non-linear parameter η such that the exponent sequence is

$$\alpha_i(\eta) = \alpha_1(0) \beta^i = \alpha_0 \beta^{i+1}, \quad i = 0, 1, \dots, N \quad (38)$$

To a good approximation the corresponding eigenenergies are the sum of a bound electron energy, E^0 , and the kinetic energy of the "continuum" electron:

$$E_n = E^0 + \tau_n(\eta) \quad (39)$$

Fig. 1 - Exponential behavior of the eigenvalues of H_{FF} , E_n as a function of the index n .

and present a clear exponential pattern as functions of the index n (See Fig. 1). Actually, it is easy to show /25/, from the homogeneous property of the kinetic-energy operator, that these eigenvalues fulfill the equation:

$$E_{n+m} = \tau_n(0) e^{\alpha m} + E^0 \quad (40)$$

and that, to a very good approximation /25,33/, the density of states can be evaluated by the very simple expression:

$$\rho(E_n) = 2 / (E_{n+1} - E_{n-1}) \quad (41)$$

Furthermore, the accuracy of this procedure can be gauged by two very simple tests:

- 1) Results obtained with two different basis sets (i.e. different values of the parameter η) should yield the same results, to a good precision.
- 2) Convergence of Γ with the size of the basis set N should have been reached to the desired precision.

6 - THE CALCULATION OF Γ

As stated in the previous section, we approximate the width corresponding to the ionization into a given continuum of the resonant state by Eq. (36). However, it is clear that, in general, none of the eigenvalues of H_{FP} obtained by solving the corresponding secular equation (26) coincides with $E_{i^{\infty}}$, unless some additional condition is imposed. In our procedure this is easily done by using a basis set as the one defined by Eq. (38) which depends on a non-linear parameter η . Then, all matrices in the secular equation (26) are functions of this parameter and so are the eigenvalues (see Fig. 2).

Fig. 2 - Behavior of the eigenvalues of H_{FP} as a function of the nonlinear parameter η .

Therefore we only need to choose this parameter by inverse interpolation so that $E_n = E_{i^{\infty}}$. Figure 2 clearly shows that the resonance condition can be achieved for different values of n and this fact permits to gauge the accuracy of our approach, in the sense that densities of states evaluated at neighbour values of n should yield equal values for the width.

At this point it is worth to summarize the main steps of our procedure.

1) We carry out a CI calculation for the effective Hamiltonian (14) using configurations built from a finite basis of STO's or GTO'S. For two-electron systems, V_M is zero, while for those systems consisting of a core and two valence electrons V_M is a model potential [29] which accounts for core-valence effects. We take it to be of the single form [30-32]:

$$V_M = (-2/r_1) (1 - \alpha r_1) e^{-2\alpha r_1} \quad (42)$$

where the parameter α is chosen by fitting the exact energy of the lowest valence state of the ionized system which has the same symmetry as the resonant state of interest. In all cases M was taken to be 100 a.u. in Eq. (16) and it was checked that increasing M up to 1000 a.u. did not change

our data. Thus we obtain approximations to the (valence and) closed channel wave functions ϕ_n and to their energies E_n .

2) For each projector P_α (Eq. (8)) we carry out a CI calculation in a finite basis of L^2 -integrable functions spanning a manifold projected onto by P_α . This is equivalent to include in each configuration one of the hydrogenic orbitals ψ_α entering the definition of P_α (See Eq. (3)). For instance, if we are interested in evaluating (31,31') resonances of He-like systems, ψ_α is either of the 1s, 2s, $2p_{+1}$, $2p_{-1}$ and $2p_0$ hydrogenic orbitals of the corresponding ionized system. We then obtain L^2 -integrable approximations, χ_n , to the continuous wave functions, $\chi_{E\alpha}$ associated to each open channel.

3) A non-linear parameter is varied in the basis set used in step 2) to achieve, by inverse interpolation, the degeneracy condition between discrete and continuum components.

4) the density of states in Eq. (36) is evaluated using Eq. (41)

5) the matrix element $\langle \phi_n | H_{GF} | \chi_{E\alpha} \rangle$ is evaluated and introduced in Eq. (36) together with the corresponding value of ρ , to evaluate the partial width to that continuum. The total width of the autoionizing state of interest then follows from Eq. (9).

7 - ILLUSTRATIONS

We shall illustrate the performance of our theoretical approach for:

a) resonant states of He-like systems lying above the first or above several ionization thresholds. In particular, we shall present results for the first resonant states of 'P symmetry above the $n = 1$ threshold of Helium and the first two (31,31') 'P resonant states of N^{5+} whose energies lie above several ionization limits.

b) resonant states of Be-like systems; more specifically we shall present the energy positions and widths for the (1s²3131') 'P resonant states of C^{2+} and Ne^{5+} ions, which are of great experimental interest /35-39/.

c) molecular resonances of two-electron homo- and heteronuclear systems; in particular we shall show how the pseudopotential approach yields energy positions for molecular resonances for the whole range of internuclear distances, and we shall also present some widths for the range of very short internuclear distances where one-center expansions are sufficiently accurate to describe the molecular wave function.

7.1 - He-LIKE SYSTEMS

7.1.1 - RESONANCES UNDER $n = 2$

To obtain the positions and widths of the first ten 'P resonant states of He above $n=1$, we have carried out a direct CI calculation for the effective Hamiltonian (12) with $V_M \equiv 0$ and $M = 100$ a.u..

Table 1 - Resonance energies (A) and widths (B) for the 'P states of He above the $n = 1$ threshold. a) Feshbach-pseudopotential approach; b) conventional Feshbach method /18/.

A)	-E (a.u.)		B)	Γ (eV)	
	a)	b)		a)	b)
(2, 2a)	0.69200	0.69213	(2, 2a)	3.82(-2)	3.74(-2)
(2, 3b)	0.59730	0.59730	(2, 3b)	1.46(-4)	1.43(-4)
(2, 3a)	0.56376	0.56379	(2, 3a)	8.60(-4)	8.45(-3)
(2, 3c)	0.54701	0.54701	(2, 3c)	3.12(-4)	3.03(-5)
(2, 4b)	0.54613	0.54613	(2, 4b)	2.12(-5)	2.10(-5)
(2, 4a)	0.53423	0.53425	(2, 4a)	3.68(-3)	3.62(-3)
(2, 4c)	0.52755	0.52755	(2, 4c)	1.33(-5)	1.28(-5)
(2, 5b)	0.52711	0.52711	(2, 5b)	1.03(-5)	1.03(-5)
(2, 5a)	0.52141	0.52142	(2, 5a)	1.95(-3)	1.91(-3)
(2, 5c)	0.51787	0.51787	(2, 5c)	9.27(-6)	8.60(-6)

The corresponding configurations were built from the basis set of STO's of Ref. /18/. The corresponding discretized continuum wave function was obtained by solving the secular equation (26) in the basis of configurations described in Ref. /18/. The results obtained /20/ have been summarized in Table 1 where comparison with values obtained using the conventional Feshbach method /18/ is very encouraging.

7.1.2 - RESONANCES LYING ABOVE SEVERAL THRESHOLDS

Our results /21/ for positions, total and partial widths for the first two ($3131'$) 1^1P resonant states of N^{5+} whose energies lie above three ionization limits ($1s$, $2s$, $2p$) are presented in Table 2, along with results obtained with the conventional Feshbach method /19, 22/.

Table 2 - Resonance energies and widths for the 1^1P states of N^{5+} above $n = 2$ threshold. a) Feshbach-pseudopotential approach. b) Conventional Feshbach method /19,22/

$-E(a. u.)$				
	a)	b)		
1^1P^0	5.02844	5.020		
2^1P^0	4.69834	4.720		
$\Gamma(eV)$				
1^1P^0	4.00(-1)(**)	4.38(-1)		
2^1P^0	1.13(-1)(**)	1.14(-1)		
(**) Partial widths:				
	Γ_{1sep}	Γ_{2sep}	Γ_{2p1s}	Γ_{2p2d}
1^1P^0	3.37(-3)	1.25(-1)	1.93(-1)	7.78(-2)
2^1P^0	1.67(-3)	4.31(-3)	5.63(-3)	1.02(-1)

Overall agreement is very good, just as for resonances lying above a single ionization threshold. In this respect it is worth stressing again that conventional Feshbach calculations are, for these cases, much more involved from the computational point of view and much more time consuming. The basis sets used for both the discrete and the continuum wave function are given in Table 3.

Table 3 - STO basis sets and configurations used in the calculation of closed- and open-channel wave functions of 1^1P symmetry. The definition for each STO is: $\varphi_m(n, l, m, \xi, r) = N_l r^{n-1} e^{-\xi r/2} Y_l^m(\theta, \phi)$.

Closed-channel wave function(**)											
$l=0$		$l=1$		$l=2$		$l=3$					
n	$\mathcal{S}_i(1)$	n	$\mathcal{S}_i(1)$	n	$\mathcal{S}_i(1)$	n	$\mathcal{S}_i(1)$				
1	1.0	2	1/2	3	1/3	4	1/6				
1, 2	1/2	2, 3	1/3	3 to 6	2/15	4, 5	2/15				
1 to 3	1/3	3 to 6	2/15	7, 8	0.1						
3 to 6	2/15	7 to 9	0.1								
7 to 9	0.1										
Open-channel wave function(**)											
$1sep$ and $2sep$				$2pes$				$2ped$			
n	α_N	β	N	n	α_N	β	N	n	α_N	β	N
2	2.5	1.6	8	2	2.5	1.6	8	2	2.5	1.6	8
4	1.25	1.6	8	4	1.25	1.6	8	5	1.25	1.6	8

(*) Configurations included: All $nsn'p$ with $n \leq 3$ or $n' \leq 4$; all $npn'd$ with $n < 5$; all $ndn'f$ with $n < 6$.

(**) Configurations included: Full CI

7.2 - Be-LIKE SYSTEMS

In order to obtain the positions and widths of ($1s^2 3l 3l'$) $^1,^3P$ resonances of C^{2+} and Ne^{6+} the first step is to adjust the model potential of Eq. (42) so as to reproduce the exact energy of the lowest 2S states of C^{2+} ($\alpha = 3.7300$) and Ne^{6+} ($\alpha = 6.3943$), respectively. The secular equation for the effective hamiltonian (12) was then set up in a representation of configurations built from the basis set of STO's given in Table 4. This table also contains the STO basis employed to solve the corresponding open channel equations (26).

Table 4 - STO basis sets and configurations used in the calculation of closed- and open-channel wave functions of $^1,^3P$ symmetry of Be-like systems

$l=0$		$l=1$		$l=2$		$l=3$	
n	ζ_l	n	ζ_l	n	ζ_l	n	ζ_l
1-3	$\frac{1}{2}$	2-3	$\frac{1}{2}$	3	$\frac{1}{2}$	4	$\frac{1}{2}$
4-6	$\frac{1}{2}$	4-6	$\frac{1}{2}$	4-6	$\frac{1}{2}$	5-7	$\frac{1}{2}$
7-9	$\frac{1}{2}$	7-9	$\frac{1}{2}$	7-8	$\frac{1}{2}$		

Discrete $^1,^3P$ states

Configurations: All $nsn'p$ with $n \leq 3$ or $n' \leq 3$
 All $npn'd$ with $n' \leq 7$
 All $ndn'f$

$2sep$				Continuum $2pes$				$2ped$			
n	a_N	β	N	n	a_N	β	N	n	a_N	β	N
2	2.5	1.6	8	2	2.5	1.6	8	3	2.5	1.6	8
4	1.25	1.6	8	4	1.25	1.6	8	5	1.25	1.6	8

Configurations: Full configuration-interaction

Our results /20/ for positions, partial and total widths are presented in Table 5. In this case there are no conventional Feshbach results to compare with. However, for the particular case of 1P resonance positions comparison with the experimental outcomes of Mack /35/ is very good, once our results have been corrected to take into account the post collisional interaction shift which affects the experimental outcomes /20/.

Table 5 - Resonance energies and total and partial widths for $^1,^3P$ states of berylliumlike systems above the $1s^2 2p$ threshold.

	1^1P	2^1P	1^3P	2^3P
	$-E$ (a.u.)			
C^{2+}	1.621883	1.433512	1.684652	1.513232
Ne^{6+}	6.828589	6.387434	6.964866	6.577623
	Γ (eV)			
C^{2+}	0.22815	0.66209(-1)	0.76196(-1)	0.37109(-1)
Ne^{6+}	0.30392	0.14453	0.89977(-1)	0.51413(-1)

Partial widths:

		Γ_{2sep}	Γ_{2pu}	Γ_{2pd}
C^{2+}	1^1P	0.72785(-1)	0.13233	0.23033(-1)
	2^1P	0.18307(-2)	0.43199(-2)	0.60058(-1)
	1^3P	0.30691(-1)	0.43522(-1)	0.19825(-1)
	2^3P	0.35218(-2)	0.91620(-2)	0.24425(-1)
Ne^{6+}	1^1P	0.10340	0.15578	0.44736(-1)
	2^1P	0.19899(-2)	0.11379(-1)	0.13116
	1^3P	0.41664(-1)	0.43476(-1)	0.48370(-2)
	2^3P	0.35188(-2)	0.15963(-1)	0.31931(-1)

7.3 - MOLECULAR RESONANCES

7.3.1 - POSITIONS

We have chosen as a suitable model system for our illustration the 1Σ resonant states of the LiHe^{3+} quasimolecule which are involved in $\text{Li}^{3+} + \text{He}(1s^2)$ collisions. These states lie above two Rydberg series $\{\text{Li}^+(1snl) + \text{He}^{2+}\}$ and $\{\text{Li}^{2+}(1s) + \text{He}^+(nl)\}$, both converging to the first ionization limit $\text{LiHe}^{4+}(1s\sigma)$. For the sake of consistency the corresponding effective Hamiltonian (12) was diagonalized in a configuration basis identical to that employed in the conventional Feshbach calculations of Ref. /40/. The results /23/ are plotted in Fig. 3. The agreement between these data and those of Ref. /40/ is so good that both curves are indistinguishable from each other in the whole range of internuclear distances considered.

Fig. 3 - Electronic energies of the autoionizing states of the LiHe^{3+} quasimolecule obtained with either the Feshbach or pseudopotential methods (both sets of values are indistinguishable in this figure)

We have also evaluated the 1Σ - 2Σ radial coupling which determines the mechanism of charge exchange in $\text{Li}^{3+} + \text{He}(1s^2)$ collisions.

Fig. 4 - Radial coupling between the 1Σ and 2Σ resonant states of the LiHe^{3+} quasimolecule obtained with either the Feshbach or pseudopotential methods (both sets of values are indistinguishable in this figure)

As for the energy positions, the coupling given in Fig. 4 is practically indistinguishable from that obtained in Ref. /40/ using the conventional Feshbach method.

7.3.2 - WIDTHS

We have employed the scheme presented in Section 6 to calculate the width for the region of very small internuclear distances, of the $^1\Sigma$ resonant states of LiHe^{3+} and HeH^+ quasimolecules which are correlated in the UA limit to $^1P(2s2p)$, as well as for the first $^1\Sigma^+$ resonant state of H_2 and He_2^{2+} as typical benchmark homonuclear systems.

In the region of small internuclear distances one-center expansions for ϕ_n are a sensible choice, the only problem being how to choose their origin in the heteronuclear case. We have adopted as the intuitively most reasonable choice the center of nuclear charge. For both LiHe^{3+} and H_2 the same basis sets of Ref. /27/ have been used. The corresponding open channel wave functions were approximated as linear combinations of configurations built from the set of STO's of Ref. /41/ and also centered at the center of nuclear charge.

Fig. 5 - Variation of the width of the first $^1\Sigma^+$ resonant state of H_2 with the internuclear distance.

Fig. 6 - Variation of the width of the $^1\Sigma$ resonant state correlated in the UA limit to $^1P(2s2p)$ of LiHe^{3+}

For the sake of conciseness we shall discuss only the widths obtained for LiHe^{2+} and H_2 molecules [27] which are presented in Figs. 5 and 6 respectively. Both increase considerably with R . This can be understood [27] by analyzing the shape (See Fig. 7) of the ϵp continuum orbital which describes the outgoing electron.

Fig. 7 - Evolution with the internuclear distance of the shape of the ϵp orbital which describes the outgoing electron of the He_2^{2+} molecule

Fig. 8 - Variation of the energy of the first $1\Sigma_u^+$ resonant state He_2^{2+} and of He_2^{2+} ($1s\sigma_g$) ionization limit as function of the internuclear distance.

Fig. 7 shows that, as R increases, this orbital presents less oscillations in the molecular region and as a consequence its interaction with the closed channel component becomes more effective and greater the width. This increase of the average wavelength of the continuum orbital is a consequence of the fact that, as R increases, the energy difference between the resonance and the ionization threshold (See Fig. 8) decreases very rapidly and so the kinetic energy of the outgoing electron. As in atomic cases, there is full agreement between these results and those obtained from conventional Feshbach calculations /27/.

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