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# Simple discretization method for autoionization widths. III. Molecules

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We apply a new method to calculate widths of two-electron Feshbach resonances, which was described in detail and applied to atomic systems in preceding articles (this issue), to molecular and quasimolecular autoionizing states. For simplicity in the programming effort, we restrict our calculations to the small-$R$ region where one-centered expansions are sufficiently accurate to describe the wave functions. As test cases, positions and widths for the $H_2$, $He_2^{2+}$, $HeH^+$, and $LiHe^{3+}$ resonances of lowest energy are computed for $R<0.6$ a.u. The advantage of using block-diagonalization techniques to define diabatic resonant states instead of generalizing the Feshbach formalism is pointed out.

## I. INTRODUCTION

An *ab initio* treatment of processes such as Penning ionization,[1-4] electron impact,[5-8] electron detachment,[9,10] dissociative recombination,[11-13] dissociative attachement,[14] and atomic collisions involving molecular autoionizing states at low impact energies[15-22] requires knowledge of lifetimes of electronic molecular resonances. This has stimulated theoretical work, which has concentrated on two-electron molecular systems, as suitable benchmark cases for this type of calculations.[6-8,23-30] However, published work in this field is more scarce than for atomic systems, mainly due to the difficulties in the determination of the open-channel wave function describing an outgoing electron; moreover, one finds that most publications deal with homonuclear systems where treatment is simpler—actually, we are aware of only one calculation for a heteronuclear system.[27]

We present in this paper an extension to two-electron diatomic molecules and quasimolecules of a method proposed by Macías and Riera,[31] used by these authors in Refs. 32 and 33, and whose fundamentals have been explained in detail in a preceding article, hereafter called paper I.[34] In a following article,[35] henceforth called paper II, we have presented a systematic application of the method to doubly excited states of the He isoelectronic series, compared our results with published accurate data whenever available, studied the accuracy of the approximations involved, and exemplified the use of different analytical forms of the basis employed to approximate the open-channel wave functions and of different exponent sequences. A summary of the main steps of our procedure was given in Sec. III of paper I.

For a molecular or quasimolecular system the two extreme regions of the correlation diagram, namely, the united-atom (UA) and separated-atom (SA) regions, correspond to clear situations where we test our method first, since in both exact limits $R=0$ and $R=\infty$ (with $R$ the internuclear distance), the corresponding values of the resonance widths ($\Gamma$) are known with good precision, because of the atomic character of the system. In this paper we shall deal with the small-$R$ region where single-center expansions provide good approximations to the closed-channel electronic wave functions, because this requires only moderate changes in our programs developed for atoms. In particular, we shall treat $^1\Sigma$ resonant states which are correlated for $R\rightarrow 0$ to the $^1P(2s2p)$ state of the united-atom limit. As suitable model systems we have chosen two homonuclear molecules ($H_2$,$He_2^{2+}$) and two heteronuclear ones ($HeH^+$,$LiHe^{3+}$).

From the practical point of view, further interest of our results comes from the fact that there is an almost complete lack of published values for resonance widths in this small-$R$ region. Indeed, most of the calculations reported in the literature[23-25,27-30] have been carried out for values of $R$ greater than 1 a.u., and, in this sense, our results are a complement to these calculations.

Before presenting our results (in Sec. III), however, it is worth dealing with a characteristic of molecular resonances—absent in the atomic case—which is that their positions, as functions of $R$, can pseudocross.[26,36] At the pseudocrossing region, it may happen that the usual Feshbach treatment breaks down, because of overlapping of the resonances. While extension of this treatment to the case of overlapping resonances is possible,[37-39] the difficulty can be very easily overcome by using diabatic states instead of adiabatic ones to describe dynamical processes. Since this point is not clear in the bibliography, a description of the analysis carried out in Ref. 36 will be presented in Sec. II. Throughout this paper we use the notation (I.$n$) and (II.$n$) for equations $n$ of papers I and II, respectively. Atomic units are used unless otherwise stated.

## II. AUTOIONIZING DIABATIC STATES

Before presenting our results for the resonance positions and widths of molecular systems, it is convenient to draw a distinction between general autoionizing states and the special case of autoionizing *diabatic* states, especially since this distribution does not arise for atomic systems.

In a series of pioneering articles,[38,40,41] O'Malley argued that in order to describe electronic recombination (the inverse of autoionization) processes, one should not use the exact, *adiabatic* eigenstates of the Born-Oppenheimer Hamiltonian, but instead bound electronic states imbedded in the ionization continuum; he then introduced a special version of Feshbach theory in which the energy shift [see Eq. (I.11)] vanishes, to define those bound states as being represented by the eigenfunctions of the projected Hamiltonian $H_{QQ}$. Similarly, the treatment of phenomena such as charge-exchange and excitation processes in atomic collisions is often greatly simplified through the use of bound states imbedded in the ionization continuum.[3,10,42,43]

For neutral and positively ionized systems, the spectrum of the projected Hamiltonian $H_{PP}$ [Eq. (I.12)] is discrete below the ionization threshold, and continuous above it. The discrete spectrum corresponds to one, or more, Rydberg series converging to a parent ion state, and for molecular systems it is formed by energy curves lying parallel and converging to the ionization threshold. Since these Rydberg series are projected out by the $Q$ projection operator, some eigenvalues of $H_{QQ}$ can cross, as functions of the internuclear distance $R$, both the ionization threshold and the energies of the Rydberg series, since the noncrossing rule does not apply to the crossing between an eigenenergy of $H_{QQ}$ and one of $H_{PP}$. Since this behavior corresponds precisely to that of *diabatic* states as introduced by Lichten,[42,43] O'Malley concluded[41] that his proposal yielded an exact definition of Lichten's qualitative reasoning.

However, in their general analysis on the definitions and characteristics of diabatic states, Macías and Riera[36] pointed out that O'Malley's definition could [and in fact did (see Ref. 26)] yield resonance energies presenting sharp pseudocrossings, thereby violating a usual requirement on diabatic states.[42]

To explain this point in more detail, we shall employ a generalization of Landau and Lifshitz's treatment[44] of the Wigner-Von Neumann noncrossing rule. To span the $Q$ space, we use a basis of configurations, which we group according to their symmetry, and to their type or character (like $\sigma_g^2$, $\sigma_u^2$, etc.).[36] To each such set corresponds a projection operator $Q^{(i)}$, and we have

$$Q = \sum_i Q^{(i)} \ , \tag{1}$$

$$Q^{(i)} Q^{(j)} = Q^{(i)} \delta_{ij} \ , \tag{2}$$

so that the projected Hamiltonian $H_{QQ}$ can be written

$$H_{QQ} = \begin{bmatrix} H_{QQ}^{(1,1)} & H_{QQ}^{(1,2)} & \cdots \\ H_{QQ}^{(2,1)} & H_{QQ}^{(2,2)} & \cdots \\ H_{QQ}^{(3,1)} & H_{QQ}^{(3,2)} & \cdots \\ \cdots & & \end{bmatrix} , \tag{3}$$

with $H_{QQ}^{(i,j)} = Q^{(i)} H Q^{(j)}$.

Let us now consider two eigenfunctions of $H_{QQ}^{(1,1)}$ and $H_{QQ}^{(2,2)}$ of the same symmetry, fulfilling

$$\begin{aligned} &(H_{QQ}^{(1,1)} - E_1^D) Q^{(1)} \phi_1^D = 0 \ , \\ &(H_{QQ}^{(2,2)} - E_2^D) Q^{(2)} \phi_2^D = 0 \ , \end{aligned} \tag{4}$$

and having energies $E_1^D, E_2^D$ that cross as functions of the internuclear distance $R$. Then, the corresponding eigenenergies of $H_{QQ}$,

$$\begin{aligned} &(H_{QQ} - E_1^d) Q \phi_1 = 0 \ , \\ &(H_{QQ} - E_2^d) Q \phi_2 = 0 \ , \end{aligned} \tag{5}$$

avoid crossing[44] because of the nonvanishing interaction term $\langle \phi_1^D \mid QHQ \mid \phi_2^D \rangle$. This will happen irrespectively of whether the states are imbedded or not in the ionization continuum, showing that, to yield diabatic states, O'Malley's definition must be generalized to account for the (not uncommon) situation of avoided crossings between the eigenenergies of $H_{QQ}$.

In this respect, it was pointed out in Ref. 36 that, whenever applicable, the block-diagonalization procedure introduced by Macías *et al.*[45,46] to define diabatic states is equivalent, in the present context, to the required generalization of the Feshbach treatment (see paper I). We can write

$$H = \begin{bmatrix} H_{QQ}^{(1,1)} & H_{QQ}^{(1,2)} & \cdots & H_{QP}^{(1)} \\ H_{QQ}^{(2,1)} & H_{QQ}^{(2,2)} & \cdots & H_{QP}^{(2)} \\ \cdots & & & \\ H_{PQ}^{(1)} & H_{PQ}^{(2)} & \cdots & H_{PP} \end{bmatrix} \tag{6}$$

in an obvious notation, and the eigenfunctions of the diagonal operators $H_{QQ}^{(i,i)}$ [as in Eq. (4)] can be used, instead of the eigenfunctions of $H_{QQ}$ [as in Eq. (5)], in the vicinty of sharp avoided crossings between the energies of the latter operator. A further advantage is that this definition is trivially extended below the ionization threshold.

Thus the diabatic states introduced in Refs. 45 and 46 provide a nondiagonal representation of the electronic Hamiltonian $H$, being coupled between themselves through the operators of $H_{QQ}^{(i,j)}$ type and, above the ionization threshold, to the background continuum through those of type $H_{QP}^{(i)}$. Moreover, they present the advantage that the Feshbach theory, and our implementation of it presented in paper I, can be directly applied to them, whereas an extension is required[37-39] for overlapping resonances corresponding to the pseudocrossing eigenenergies of $H_{QQ}$.

Then, since the $\{\phi_1, \phi_2\}$ and $\{\phi_1^D, \phi_2^D\}$ sets, spanning the same manifold, provide entirely equivalent representation[47] to describe any physical process, whenever appropriate we have chosen the latter representation in this paper, and we have used the theory of paper I to calculate the resonance positions and widths of the corresponding autoionizing molecular states.

## III. ONE-CENTER CALCULATIONS

As in paper II, lifetimes of autoionizing states for two-electron molecular systems were obtained through an approximate calculation of the golden-rule formula:

$$\Gamma_k = 2\pi\rho(\tilde{E}_n)\,|\,\langle \phi_k \,|\, H_{QP} \,|\, \tilde{\chi}_n \rangle\,|^2 \equiv 2\pi\rho(\tilde{E}_n)V^2 \;, \quad (7)$$

which defines the interaction term $V$. For notation, see papers I and II.

Just as in the atomic case, we have chosen the projection operator $P$ according to O'Malley's definition:[48]

$$P = P_1 + P_2 - P_1P_2 \;, \quad (8)$$

where

$$P_k = \,|\, 1s\sigma(k) \rangle \langle 1s\sigma(k) \,|\; . \quad (9)$$

The extension to molecules of the techniques employed in the atomic calculations reported in paper II is considerably simplified if the atomic character of the orbital entering the definition of $P_k$ is preserved. Since, for small internuclear distances, a good approximation to the $1s\sigma$ molecular orbital is provided by the corresponding UA $1s$ atomic orbital, in the calculations reported here we have made use of this approximation. We stress the point that this is only made for the sake of simplification of our programming effort, and it is inessential to our approach and, in particular, to the theory developed in paper I. Obviously, this approximation can be eliminated with the help of some additional programming effort through the introduction of a projection operator $P_k$ defined in terms of the exact $1s\sigma$ molecular orbital.

As indicated in the Introduction, in the present paper we restrict our calculations to the region of short internuclear distances where the use of a one-center basis to expand the discrete component $\phi_k$ of Eq. (7) is useful. The validity range of this one-center expansion depends on each particular system, and calculations carried out by Salas[49] indicate that for "reasonably" sized Slater-type orbital (STO) basis sets this range follows the empirical rule

$$(Z_A + Z_B)R < 3 \text{ a.u.} \quad (10)$$

for molecular orbitals (MO's), and is somewhat shorter for two-electron wave functions.[49] In practice, the accuracy reached with one-center expansions obviously depends upon the chosen center $C$, which, in our approach, we identify with that of the $1s$ orbital involved in the projection operator $P_k$ of Eqs. (8) and (9). In the homonuclear case, the choice is clear: The midpoint between the nuclei is the position required to preserve $g$ and $u$ symmetry. In heteronuclear systems there is no *a priori* privileged origin, although the intuitively most reasonable choice would seem to be the center of nuclear charge.

In our approach, therefore, the closed-channel wave function $\phi_k$ is approximated as

$$\phi_k = \sum_i d_{ki} Q\psi_i \;, \quad (11)$$

where the coefficients $d_{ki}$ are calculated by solving the secular equation for the $H_{QQ}$ matrix in the $Q\psi_i$ representation:

$$Q\psi_i(l_1,l_2,l;m_1,m_2,m) = \sum_{m_1,m_2} C(l_1,l_2,l;m_1,m_2,m)\|Q_1\varphi_{l_1m_1}Q_2\varphi_{l_2m_2}\| \;, \quad (12)$$

where $C(l_1,l_2,l;m_1,m_2,m)$ are the corresponding Clebsch-Gordan coefficients,[50] and

$$Q_k\varphi_{lm}(k) = (1-P_k)\varphi_{lm}(k) \;, \quad (13)$$

where $\varphi_{lm}(k)$ are Slater-type orbitals (STO's) centered at the common origin $C$.

The open-channel wave function is approximated as [see Eq. (I.20)]

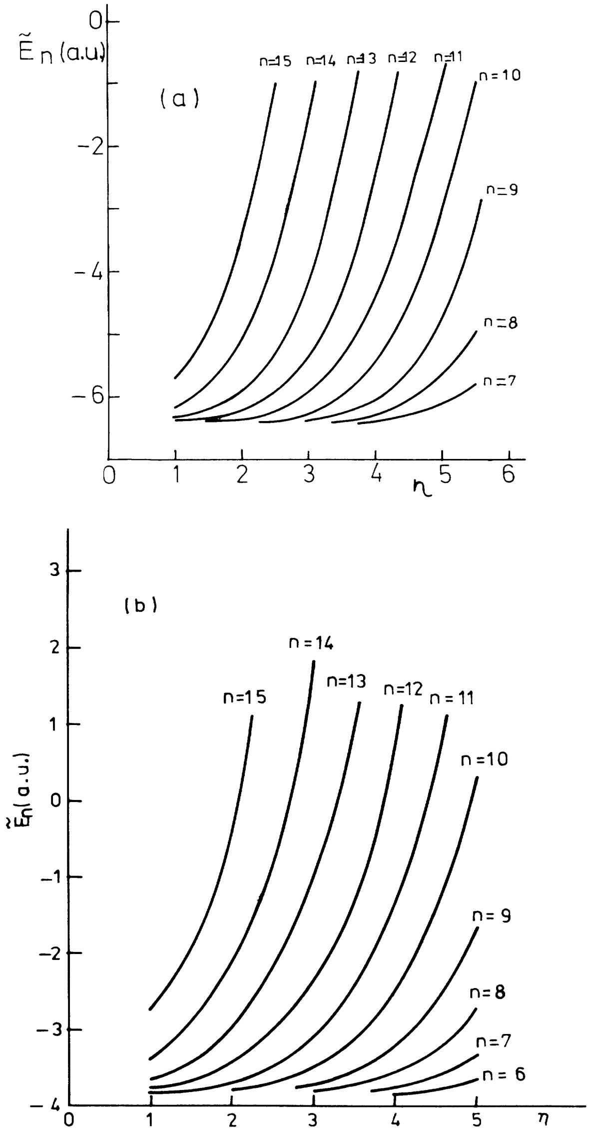

FIG. 1. Exponential behavior of the eigenvalues of $H_{PP}, \tilde{E}_n(\eta)$ as a function of the nonlinear parameter $\eta$ for (a) a homonuclear case ($He_2^{2+}$ for R = 0.25 a.u.), (b) a heteronuclear case ($HeH^+$ for $R=0.3$ a.u.). This figure can be compared with Fig. 2(a) of paper I.

$$\tilde{\chi}_n = \sum_i c_{ni} \xi_i \ , \tag{14}$$

where each configuration $\xi_i$ is built from a set of STO's centered at $C$ and the $c_{ni}$ coefficients are obtained by solving the secular equation for the $H_{PP}$ matrix [Eq. (I.19)].

For the sake of consistency, we have used in our calculations the same basis of STO's $\{\varphi_{lm}\}$ [Eq. (II.9)] and configurations as those employed in paper II for the calculation of positions and widths of the corresponding UA $[{}^1P(2s2p)]$ resonant states (see Table II of that reference). Accordingly, the set $\{\xi_i\}$ has been taken to be of the form $\| 1s\varepsilon_i p \|$ and the nonlinear parameter $\eta$ varied to achieve the resonance condition $\tilde{E}_n(\eta) \simeq E_k^d$ is defined as in Eq. (II.12).

When a one-center expansion is employed to construct (11) and (14), there only appears a new kind of integral which must be evaluated in addition to those required in atomic calculations (paper II); they are of the type:

$$\langle \varphi_c \mid -Z_A/r_A - Z_B/r_B \mid \varphi_c \rangle \ , \tag{15}$$

where $C$ refers to expansion center. These integrals were analytically calculated following Roothaan's algorithm.[51,52]

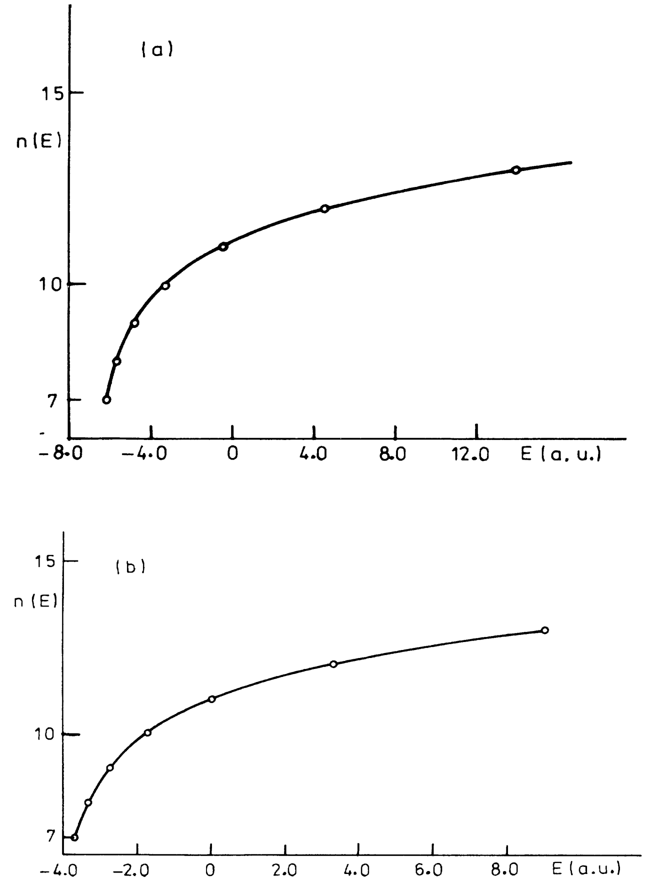

FIG. 2. Exponential behavior of the eigenvalues of $H_{PP}, \tilde{E}_n(\eta)$ as a function of the index $n$ for (a) a homonuclear case (${\rm He_2}^{2+}$, corresponding to $\eta = 4.9358$ and $R = 0.25$ a.u.); (b) a heteronuclear case (${\rm HeH}^+$, corresponding to $\eta = 4.4155$ and $R = 0.3$ a.u.). This figure can be compared with Fig. 1(a) of paper I.

TABLE I. Invariance tests for the first ${}^1\Sigma_u^+$ resonance of ${\rm He_2}^{2+}$ regarding (a) the size of the $\{\xi_i\}$ basis and (b) the nonlinear parameter $\eta$. Compare with Tables I and II of paper I.

| (a) | | | |
|---|---|---|---|
| $N^{\rm a}$ | $\rho(\tilde{E}_n)$ | $\langle \phi_k \mid H \mid \tilde{\chi}_n \rangle$ | $\Gamma$ (eV) |
| 8 | 0.450 67 | 4.9040[−2] | 0.1853 |
| 14 | 0.486 04 | 4.7607[−2] | 0.1883 |
| (b) $N^{\rm a}=8$ | | | |
| $\eta$ | $\rho(\tilde{E}_n)$ | $\langle \phi_k \mid H \mid \tilde{\chi}_n \rangle$ | $\Gamma$ (eV) |
| 6.044 | 0.441 34 | 4.9579[−2] | 0.1855 |
| 5.487 | 0.449 30 | 4.9089[−2] | 0.1851 |
| 4.936 | 0.450 67 | 4.9040[−2] | 0.1853 |
| 4.384 | 0.446 87 | 4.9434[−2] | 0.1867 |
| 3.828 | 0.435 57 | 4.9963[−2] | 0.1859 |

[a] $N$ is defined in Table II of paper II.

Just as in the atomic case (paper II), we have performed, for both homonuclear and heteronuclear systems, the tests proposed in paper I to check the validity of our assumptions.

(1) Exponential behavior of the eigenvalues of $H_{PP}$, $\tilde{E}_n(\eta)$ [Eq. (I.45)], as function of $\eta$ and $n$. This is illustrated in Figs. 1 and 2, respectively, which can be compared with Figs. 1(a) and 2(a) of paper I. Since we have used a value of the scaling parameter $\beta = 1.6 < 2$, the central difference expression (I.47) is used to calculate the density of states $\rho(\tilde{E}_n)$.

(2) Results obtained with two different basis sets fulfilling the resonance condition $E_k^d \simeq \tilde{E}_n(\eta) \simeq \tilde{E}_{n'}(\eta')$ are the same to a good precision [see Table I(a), to be compared with Table II of paper I].

(3) The convergence of our calculated value of $\Gamma$ with the size of $\{\xi_i\}$ has been reached to the precision desired [see Table I(b), to be compared with Table I of paper I].

## IV. RESULTS

### A. Homonuclear case

Table II presents our results for energies and widths of the first ${}^1\Sigma_u^+$ state of $H_2$ and ${\rm He_2}^{2+}$ for values of the internuclear distance up to 0.5 a.u. Although we have found no results in the literature for either positions or widths of this state for $R < 0.5$ a.u., Hara and Sato[30] have reported values for the $H_2$ molecule for $R \geq 1.0$ a.u., obtained with a three-center expansion of contracted Gaussian-type orbitals (GTO's) to describe the discrete wave functions and a close-coupling expansion for the continuum orbital, where the couplings between different partial waves were neglected. Figure 3 presents our calculated resonance positions, together with those of Hara and Sato,[30] which we have corrected by adding the energy of the ionization limit ($E_{1s\sigma}$) reported by the

TABLE II. Energies and widths for the first resonant ${}^1\Sigma_u^+$ state of (a) $H_2$ and (b) $He_2{}^{2+}$ molecules in the region of small internuclear distances.

| $R$ (a.u.) | $H_2$<br>$E$ (a.u.) | $\Gamma$ (eV) |
|---|---|---|
| | (a) $H_2$ | |
| 0.0 | −0.692 125 | 0.037 44 |
| 0.1 | −0.691 255 | 0.039 66 |
| 0.2 | −0.689 754 | 0.045 92 |
| 0.3 | −0.688 980 | 0.056 38 |
| 0.4 | −0.689 590 | 0.072 41 |
| 0.5 | −0.691 748 | 0.096 95 |
| | (b) $He_2{}^{2+}$ | |
| 0.0 | −3.314 115 | 0.073 82 |
| 0.1 | −3.296 573 | 0.089 26 |
| 0.2 | −3.282 705 | 0.138 61 |
| 0.3 | −3.294 580 | 0.261 16 |
| 0.4 | −3.329 103 | 0.640 84 |
| 0.5 | −3.376 594 | 1.3290 |

same authors in Ref. 53. It can be seen that both sets of values join very smoothly. Even more significantly, our results for $\Gamma$ also join very smoothly to those of these authors, as shown in Fig. 4. In this figure we have extended the calculations presented in Table II up to $R=0.7$ a.u., to illustrate the fact that, while the representation of the $1s\sigma_g$ orbital in Eq. (9) by a $1s$ atomic orbital with UA exponent, $\alpha=2.0$, becomes inadequate in the present case for $R>0.5$ a.u., when the exponent of this $1s$ atomic orbital is optimized to better reproduce the $1s\sigma_g$ orbital for this range of internuclear distances ($\alpha=1.85$), the values obtained for $\Gamma$ smoothly merge with those of Hara and Sato.[30]

The variation of $\Gamma$ with $R$ for the first ${}^1\Sigma_u^+$ resonance of $He_2{}^{2+}$ is plotted in Fig. 5. As indicated above, no data have been reported in the literature for this state; it may be remarked, however, that our results are of the same order, and present the same increasing behavior, as those calculated by Hara and Sato[26] for the first ${}^1\Sigma_g^+$ resonance of the same system. On the other hand, this comparison should not be carried out too far, because (i) the characters of the $\Sigma_g$ and $\Sigma_u$ states are different and (ii) while the first ${}^1\Sigma_u^+$ resonant state does not present avoided crossings, because the next resonance of the same symmetry is quite separate in energy, Hara and Sato's ${}^1\Sigma_g^+$ resonance positions do present pseudocrossings in the small-$R$ region.[26] As explained in Sec. II, in the latter situation it is necessary either to use diabatic wave functions for the closed channels, or to use a generalization of the Fesbach formalism for the case of overlapping resonances; otherwise, the values of $\Gamma$ obtained by a naïve approach using the golden rule of Eq. (7) are of doubtful physical significance in the pseudocrossing region.[26]

It can be seen in Figs. 4 and 5 that for both $H_2$ or $He_2{}^{2+}$ systems the width of the first ${}^1\Sigma_u^+$ resonance in-

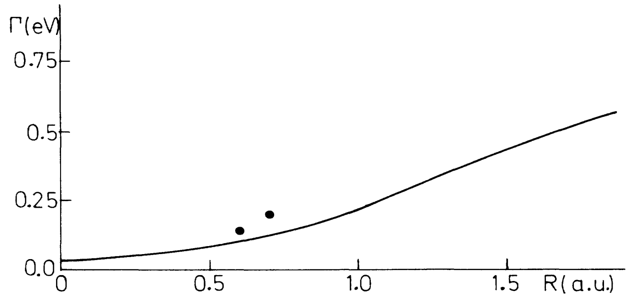

FIG. 4. Variation of the width of the first ${}^1\Sigma_u^+$ resonant state of $H_2$ with the internuclear distance. Values of $\Gamma$ for $R\leq 0.5$ a.u. from this work; values of $\Gamma$ for $R\geq 1.0$ a.u. taken from Ref. 30. ●, values of $\Gamma$ obtained with the UA exponent for the $1s$ orbital in Eq. (9) (see text).

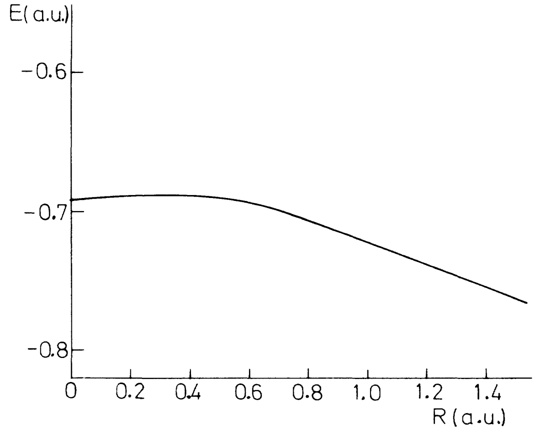

FIG. 3. Energy position, as a function of the internuclear distance, for the first ${}^1\Sigma_u^+$ resonant state of $H_2$. For $R\leq 0.5$ a.u., values calculated in this work; for $R\geq 1.0$ a.u., values taken from Ref. 30.

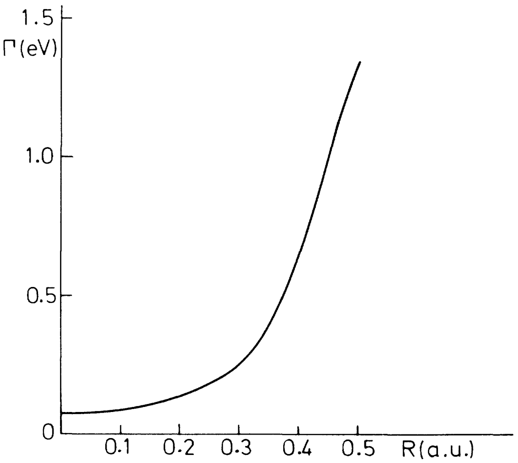

FIG. 5. Variation of the width of the first ${}^1\Sigma_u^+$ resonant state of $He_2{}^{2+}$ with the internuclear distance.

creases considerably with $R$. This can be heuristically understood by analyzing the shape (see Fig. 6) of the $\varepsilon p$ orbital which describes the outgoing electron, i.e., the $\varepsilon p$ orbital involved in the "continuum" wave function $\tilde{X}_n = \|1s\varepsilon p\|$ satisfying the resonance condition $\tilde{E}_n \simeq E_1^d$. Figure 6 shows that, as $R$ increases, the average wavelength of the oscillations of this orbital increases; this is an obvious consequence of the fact that, as $R$ increases, the energy difference between the resonance and the ionization limit decreases rapidly (see Fig. 7), and accordingly, the kinetic energy of the outgoing electron becomes smaller, so that the corresponding orbital, $\varepsilon p$, presents less oscillations in the molecular region. Then one can expect the interaction $V$ [Eq. (7)] between the open-channel and the discrete wave functions to be the larger the less oscillatory the orbital that make up the former.

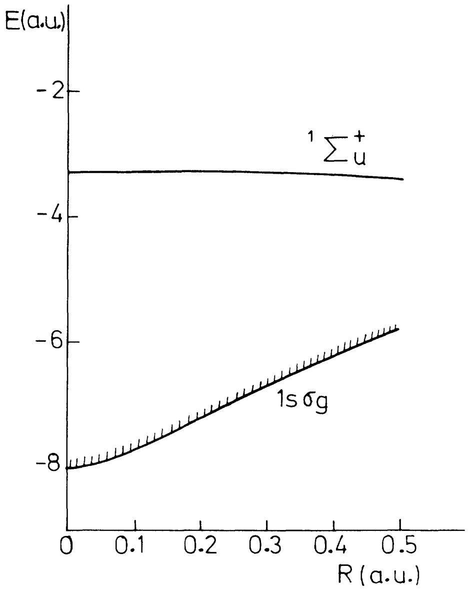

FIG. 7. Variation of the energy of the first $^1\Sigma_u^+$ resonant state of $He_2{}^{2+}$ and of $He_2{}^{3+}$ ($1s\sigma_g$) ionization limit as functions of the internuclear distance.

### B. Heteronuclear case

While in the homonuclear case, discussed above, the $^1\Sigma_u^+$ resonant state correlated to $^1P$ $(2s2p)$ in the UA limit presents no avoided crossings, because the next resonant state of the same symmetry is well separate in energy, in the heteronuclear case the absence of exact $g$-$u$ symmetry implies that, just as for ordinary bound states, the first four $^1\Sigma$ resonance positions that are correlated to the quasidegenerate UA ones—$^1S$ $(2s^2)$, $^1S$ $(2p^2)$, $^1D$ $(2p^2)$, and $^1P$ $(2s2p)$—pseudocross at small internuclear distances (see illustration for the $LiHe^{3+}$ quasimolecule in Ref. 54). Therefore, and following the reasoning developed in Sec. II, we have obtained the positions and widths of the *diabatic* $^1\Sigma$ resonant state of $HeH^+$ and $LiHe^{3+}$ which correlates, in the UA limit, to $^1P$ $(2s2p)$, using block-diagonalization techniques.[45,46] In this case, these techniques are easily implemented by enforcing $u$ symmetry, i.e., from all possible configurations of $\Sigma$ symmetry built up from $s$, $p$, $d$, and $f$ atomic orbitals only configurations of $sp_\sigma$, $p_\sigma d_\sigma$, and $d_\sigma f_\sigma$ type have been included.

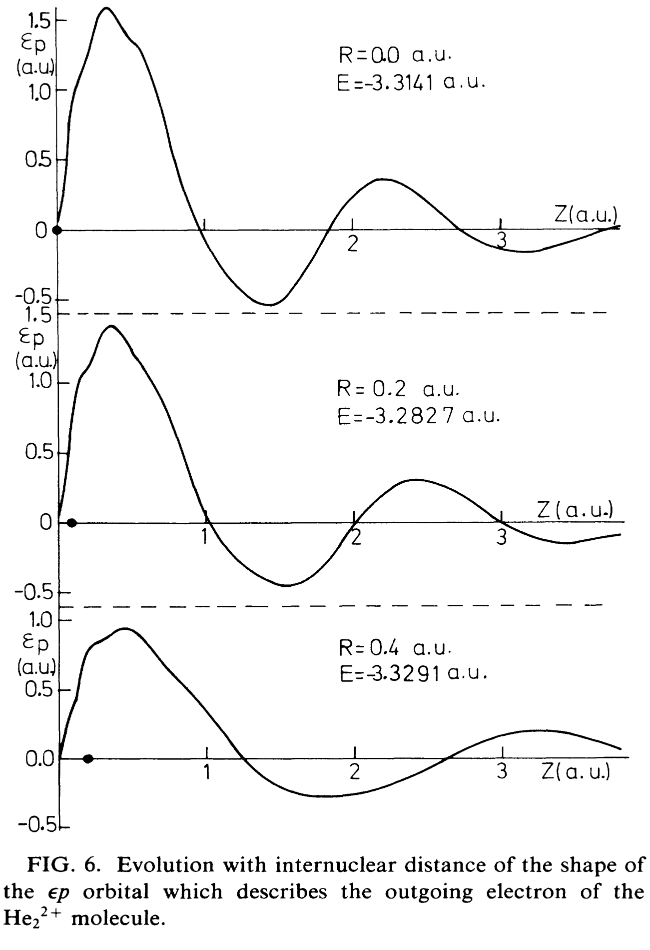

FIG. 6. Evolution with internuclear distance of the shape of the $\epsilon p$ orbital which describes the outgoing electron of the $He_2{}^{2+}$ molecule.

TABLE III. Energies and widths for the first resonant diabatic $^1\Sigma$ state of (a) $HeH^+$ and (b) $LiHe^{3+}$ molecules correlated in the UA limit to $^1P$ $(2s2p)$ in the region of small internuclear distances.

| $R$ (a.u.) | $E$ (a.u.) | $\Gamma$ (eV) |
|---|---|---|
| | (a) $HeH^+$ | |
| 0.0 | −1.753 999 | 0.060 00 |
| 0.1 | −1.749 146 | 0.066 48 |
| 0.2 | −1.742 722 | 0.084 77 |
| 0.3 | −1.741 548 | 0.117 73 |
| 0.4 | −1.746 736 | 0.175 23 |
| 0.5 | −1.757 138 | 0.280 69 |
| | (b) $LiHe^{3+}$ | |
| 0.0 | −5.373 545 | 0.083 00 |
| 0.1 | −5.334 904 | 0.108 02 |
| 0.2 | −5.318 130 | 0.195 66 |
| 0.3 | −5.358 254 | 0.483 23 |
| 0.4 | −5.432 856 | 1.4027 |

The results obtained are presented in Table III, and the variation of the widths with the internuclear distance is plotted in Fig. 8(a) and 8(b) for $HeH^+$ and $LiHe^{3+}$, respectively. We have found no published results to compare ours with, and our values follow the same pattern as in the homonuclear case, i.e., a resonance width increasing with the internuclear separation.

It may be remarked that inspection of our intermediate data showed that for both homonuclear and heteronuclear systems, the contribution of *npn'd* and *ndn'f* configurations to both energy positions and widths is negligible, especially for the latter quantities. This agrees with our finding (see paper I) that for atomic $^1P$ resonances, *sp*-type configurations are the main contributors to $\Gamma$.

Finally, we report the conclusions of our tests on the influence of the origin of the electronic coordinates in the definition of $P_k$ in Eq. (9) and in the one-center basis sets used. To study this point, we have chosen the $LiHe^{3+}$ system because accurate calculations on the energy position of the same $^1\Sigma$ resonant state, using a *two-center* expansion and a stabilization method down to $R=0.8$ a.u., have been reported in the literature.[55] In Fig. 9 we present our calculated energies using one-center expansions for three different choices of the origin together with the stabilization results of Ref. 55. From this excellent agreement it seems clear that optimum choice corresponds to the center of nuclear charge which for $R<0.8$ a.u. provides even lower energies than the two-center expansions of Ref. 55.

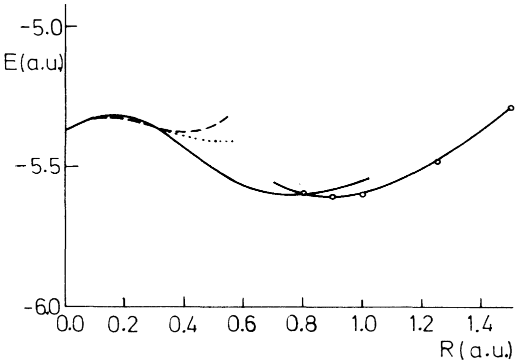

FIG. 9. Calculated energy positions for the $^1\Sigma$ state of $LiHe^{3+}$ correlated in the UA limit to $^1P$ $(2s2p)$. — — —, origin on Li nucleus; · · · ·, origin on $z=0.2R$ ($z$ axis coincides with the internuclear axis); ——, origin on the center of nuclear charge; ○, values obtained using a two-center expansion and a stabilization method taken from Ref. 55.

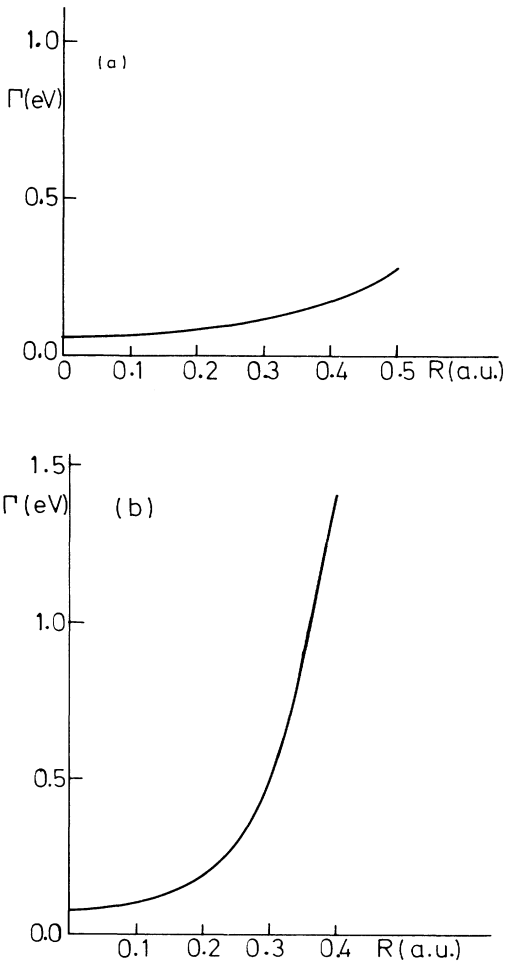

FIG. 8. Variation of the width of the *diabatic* $^1\Sigma$ resonant state correlated in the UA limit to $^1P$ $(2s2p)$. (a) $HeH^+$ system, (b) $LiHe^{3+}$ system.

## V. CONCLUSIONS

The third paper in this series closes what may be regarded as a formal presentation of a new method to calculate autoionization widths for two-electron Feshbach resonances (for shape resonances, which play a more important role in the molecular than in the atomic case, see our remarks in Sec. III of paper I). This method, which was briefly proposed by Macías and Riera in a recent publication,[31] consists of an implementation of the well-known Feshbach formalism, involving a discretization of the open-channel spectrum, together with specific techniques to achieve closed-open channel degeneracy and to evaluate the density of states. In this series we have presented the method in full detail.

(1) In paper I we have explained the steps involved in our approach, the fundamentals behind each one of its approximations, and the tests that can be performed to gauge their accuracy.

(2) In paper II an extensive application of our method to atomic benchmark cases yields very good agreement with published data. Additional information is provided, in the form of contributions to the widths from configurations of a given character, of compact fitted expressions for $Z>2$, and of illustrations on the use of different types of atomic bases to perform the continuum discretization.

(3) In the present paper we show that the method is applicable to molecular systems. For the sake of simpli-

city in the corresponding programming effort, we have restricted this illustration to the small-$R$ region where one-center expansions are sufficiently accurate to describe the wave functions, and we have treated two homonuclear and two heteronuclear molecular systems. From the point of view of testing our method, it is unfortunate that the (very few) published results of (quasi) molecular resonance widths refer to intermediate distances where one-center expansions are inaccurate[56] (see Fig. 9). In the absence of a direct comparison with other published results, we do not claim that our method's accuracy for the molecular case is as high as for atoms, and our data may be taken as predictive, to be confirmed (or not) by other authors. On the other hand, the fact that for $H_2$ our results merge so smoothly with those of Sato and Hara,[30] who use a completely different basis set and treatment of the continuum, is a very good indication that our method works at short $R$. As in the atomic case, we have performed, for both homonuclear and heteronuclear systems the tests proposed in paper I to check the validity of the method's assumptions. On the other hand, as could be expected, new features appear in the molecular case. The most conspicuous one is the possibility of avoided crossings between resonance positions, as functions of $R$, when an unmodified Feshbach approach is used; then the golden-rule expression may be meaningless when the corresponding resonances overlap. From the two possible solutions to this difficulty, which are the modification of the Feshbach approach (as proposed by Feshbach himself[37]), and the use of diabatic wave functions, we have opted for the simpler, second one, using block-diagonalization techniques.[45,46]

Once the usefulness of our approach has been demonstrated, besides applying it to more systems and states than those hitherto considered, the main practical challenge (which will be the object of future work) is the nontrivial extension of our techniques to the region of internuclear distances where a two-center basis set is needed to represent the wave functions.

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