

# Shape resonances as poles of the semiclassical Green's function obtained from path-integral theory: Application to the autodissociation of the $\text{He}_2^{++} \ ^1\Sigma_g^+$ state

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It is known that one-dimensional potentials,  $V(R)$ , with a local minimum and a finite barrier towards tunneling to a free particle continuum, can support a finite number of shape resonance states. Recently, we reported a formal derivation of the semiclassical Green's function,  $G_{\text{SC}}(E)$ , for such  $V(R)$ , with one and two local minima, which was carried out in the framework of the theory of path integrals [Th. G. Douvropoulos and C. A. Nicolaides, *J. Phys. B* **35**, 4453 (2002); *J. Chem. Phys.* **119**, 8235 (2003)]. The complex poles of  $G_{\text{SC}}(E)$  represent the energies and the tunneling rates of the unstable states of  $V(R)$ . By analyzing the structure of  $G_{\text{SC}}(E)$ , here it is shown how one can compute the energy,  $E_\nu$ , and the radiationless width,  $\Gamma_\nu$ , of each resonance state beyond the Wentzel-Kramers-Brillouin approximation. In addition, the energy shift,  $\Delta_\nu$ , due to the interaction with the continuum, is given explicitly and computed numerically. The dependence of the accuracy of the semiclassical calculation of  $E_\nu$  and of  $\Gamma_\nu$  on the distance from the top of the barrier is demonstrated explicitly. As an application to a real system, we computed the vibrational energies,  $E_\nu$ , and the lifetimes,  $\tau_\nu$ , of the  ${}^4\text{He}_2^{++}$ ,  $\nu=0, 1, 2, 3, 4$ , and  ${}^4\text{He}^3\text{He}^{++}$   $\nu=0, 1, 2, 3$ ,  ${}^1\Sigma_g^+$  states, which autodissociate to the  $\text{He}^+ + \text{He}^+$  continuum. We employed the  $V(R)$  that was computed by Wolniewicz [J. Phys. B **32**, 2257 (1999)], which was reported as being accurate, over a large range of values of  $R$ , to a fraction of  $\text{cm}^{-1}$ . For example, for  $J=0$ , the results for the lowest and highest vibrational levels for the  ${}^4\text{He}_2^{++} \ ^1\Sigma_g^+$  state are  $\nu=0$  level,  $E_0=10\,309 \text{ cm}^{-1}$  below the barrier top,  $\tau_0=6400 \text{ s}$ ;  $\nu=4$  level,  $E_4=96.6 \text{ cm}^{-1}$  below the barrier top,  $\tau_4=31 \times 10^{-11} \text{ s}$ . A brief presentation is also given of the quantal methods (and their results) that were applied previously for these shape resonances, such as the amplitude, the exterior complex scaling, and the lifetime matrix methods. © 2005 American Institute of Physics. [DOI: 10.1063/1.1961487]

## I. MOLECULES WITH AUTODISSOCIATING GROUND STATES

There are unusual ground molecular states whose geometrical equilibrium corresponds to a local minimum of the potential-energy surface (PES) that lies higher than the energy of the asymptotic region, which is repulsive. This fact implies that the vibrational energy spectrum consists of only a small number of quasidiscrete levels. Depending on the system, all or some of these levels have a finite lifetime (in a practical sense) towards autodissociation, i.e., they are vibrational shape resonances.

In our opinion, the two-electron  $\text{He}_2^{++} \ ^1\Sigma_g^+$  state constitutes the characteristic example of such systems. Its potential,  $V(R)$ , and five vibrational levels for the  ${}^4\text{He}$  isotope are shown in Fig. 1.

This figure shows clearly that the  $\text{He}_2^{++} \ ^1\Sigma_g^+$  state must autodissociate via tunneling into the  $\text{He}^{+2}S + \text{He}^{+2}S$  con-

tinuum. The volcanolike shape was first computed and explained by Pauling<sup>1</sup> in terms of covalent-ionic wave-function mixing. Energetically, this  $V(R)$  is the ionization threshold of the  $1\sigma_g^2 n\sigma_g$ ,  $n=2,3,\dots$ , Rydberg series of the  $\text{He}_2^{+2} \ ^2\Sigma_g^+$  spectrum.<sup>2</sup>

The first observation of this molecule was achieved in 1984 via charge stripping of  $\text{He}_2^+$ .<sup>3</sup> In 1989, as part of the proposal of using such ground states for the storage and the release of considerable amounts of energy per molecule,<sup>4</sup> the  $\text{He}_2^{++} \ ^1\Sigma_g^+$  system ( ${}^4\text{He}_2^{++}$  and  ${}^4\text{He}^3\text{He}^{++} \ ^1\Sigma_g^+$  states) was identified and studied<sup>4</sup> as a favorable, in principle, case of a possible propulsion fuel, due to its small mass. [See subsequent work on such metastable states, whose interesting property relates to the possibility of storing and releasing an amount of energy,  $\Delta E_D$ , which is larger than the amount stored ( $\approx \Delta E_B$ ), see Fig. 1.]

Crucial to this proposal<sup>4,5</sup> is the degree of stability of the intrinsically unstable (due to tunneling) ground state. Hence, the analysis and calculations of Ref. 4 focused on establishing accurate energies and autodissociation lifetimes for the

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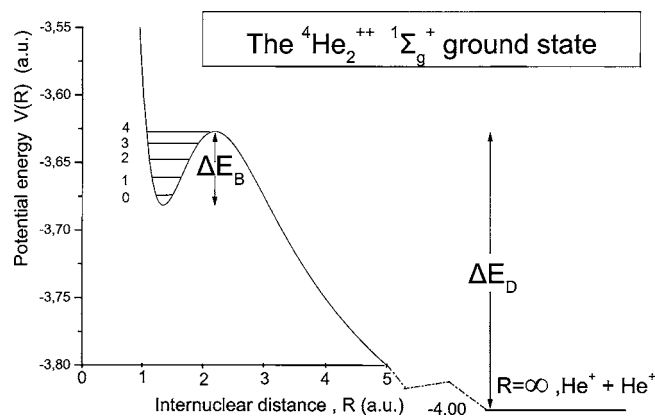


FIG. 1. The potential-energy curve,  $V(R)$ , of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state, in a.u., with the five vibrational levels computed in this work for the  $^4\text{He}$  isotope, see text. The accurate calculations of Wolniewicz (see Ref. 12) produced  $\Delta E_B = 1.486\ 06\ \text{eV}$  and  $\Delta E_D = 8.667\ 90\ \text{eV}$ .

vibrational levels—assuming cold molecules with zero rotational energy—which at the time were not known.

The calculations of the lifetimes in Ref. 4 employed the Wentzel-Kramers-Brillouin (WKB) formula of Eq. (1), which, as derived by Connor and Smith,<sup>6</sup> includes a correction valid for narrow levels [this correction is not significant quantitatively for the  $V(R)$  of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state]. The WKB calculation of the widths is economic and, as it turns out, rather reliable for relatively narrow levels, if the vibrational energies that are employed are accurate.

Subsequent to the publication of Ref. 4, a number of calculations of the energies and widths of the vibrational resonance levels were published, using either the formula of the WKB approximation<sup>7</sup> or various quantal methods.<sup>8–11</sup> A short discussion on their results is given in Sec. II.

For the purpose of computing accurate tunneling rates, it is imperative that the volcanolike PESs (of one or of many dimensions) are known precisely over a large geometrical domain. This is evident from the WKB one-dimensional formula, where the dependence of the tunneling rate on the  $V(R)$  and on the energy of the unstable level appears in the exponential. In the case of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state, its  $V(R)$  was recently computed to a very high level of accuracy, for many values of  $R$  up to 5 a.u., by Wolniewicz<sup>12</sup> who carried out a

thorough configuration-interaction (CI) calculation with 372 explicitly correlated variational functions. It is this  $V(R)$  that we have used in this work.

From the form of this  $V(R)$  and from the corresponding theory of tunneling it follows that as energy increases, the lifetime decreases rapidly. This was determined numerically in Ref. 4, for four vibrational levels of the  $^4\text{He}_2^{++}$  and  $^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  ground states (Table I).

(Due to the different reduced masses, 3647.15 a.u. for  $^4\text{He}_2^{++}$  and 3134.33 a.u. for  $^4\text{He}^3\text{He}^{++}$ , the vibrational spectra of the  $^4\text{He}_2^{++}$  and  $^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  ground states are different. In fact, there are five levels for the  $^4\text{He}_2^{++}$  state and only four for the  $^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  state.)

In the quantum-mechanical stationary-state formalism, the tunneling process is described in terms of mixing between bound and scattering components in the vibrational wave functions, whose magnitude and consequences depend on the level of excitation. As the top of the barrier is approached, the vibrational eigenfunction leaks into the adjacent continuum more easily. For example, this characteristic can be seen explicitly in the results of quantal calculations of the eight vibrational quasidecrete wave functions of the  $\text{BeH}^{++} \ 2\Sigma^+$  ground state, and in the concomitant phenomenon of multiphoton molecular dissociation *below* threshold.<sup>13</sup> (Given the nature of the problem in Ref. 13, rather than separating the full space into bound and scattering components and then computing the results of their interaction, the system was placed in a large box and the levels were obtained by diagonalization in a basis of trigonometric functions.)

Regarding volcanolike potentials, the intrinsic parameters that both theory and experiment aim at determining (as for any unstable state) are the energies and widths of the quasidecrete levels supported by such potentials. In the case of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  ground state, the widths are due to one-dimensional tunneling. It is the purpose of this paper to present new results on these properties, as an application of a semiclassical path-integral theory that goes beyond the WKB approximation.

Specifically, we have implemented the theory of path integrals to obtain the semiclassical Green's function,  $G_{\text{SC}}(E)$ , of the system defined by a potential of the form of

TABLE I. Comparison of the calculated tunneling widths,  $\Gamma_\nu$ , in a.u., for the vibrational shape resonances of the  $^4\text{He}_2^{++}$  (first line) and  $^4\text{He}^3\text{He}^{++}$  (second line)  $1\Sigma_g^+$  ground states, published since 1989. In a.u.,  $\Gamma_\nu = 1/\tau_\nu$ , where  $\tau_\nu$  is the lifetime. 1 a.u. of time =  $2.4189 \times 10^{-17}$  s.

$\nu$	Ref. 4 (1989)	Ref. 9 (1990)	Ref. 8 (1990)	Ref. 7 (1992)	Ref. 10 (1999)	Ref. 11 (2002)
0	0.182 (–20)		0.157 (–20)	0.134 (–20)		0.279 (–20)
0	0.672 (–19)		0.618 (–19)	0.896 (–19)	0.640 (–19)	
1	0.899 (–15)	0.24 (–14)	0.895 (–15)			0.143 (–14)
1	0.281 (–13)		0.288 (–13)		0.286 (–13)	
2	0.600 (–10)	0.128 (–09)	0.631 (–10)			0.889 (–10)
2	0.142 (–08)		0.149 (–08)		0.149 (–08)	
3	0.699 (–06)	1.18 (–06)	0.662 (–06)			0.841 (–06)
3	0.967 (–05)		0.925 (–05)		0.922 (–05)	
4	...		0.473 (–03)			0.423 (–03)
4	...			...		

Fig. 1. Given an accurate  $V(R)$ , as is the case of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state, a first-principles reliable calculation of the energies and of the lifetimes towards autodissociation of the unstable vibrational levels of the  ${}^4\text{He}_2^{++}$  and  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  states is possible. The energy-dependent  $G_{\text{SC}}(E)$  contains the contribution from the complete set of states to the decay dynamics of each level. Its analysis shows how the basic WKB approximation loses accuracy as one moves upwards toward the top of the barrier. The essentials of the formalism leading to the  $G_{\text{SC}}(E)$  that was computed and analyzed here have been published and justified in Ref. 14.

Since the results of the theory are in an analytic form, calculations of energies and tunneling rates such as the ones reported here can be carried out for resonances of all states, ground or excited, whose  $V(R)$  along a reaction coordinate is volcanolike.

## II. PREVIOUS RESULTS ON THE AUTODISSOCIATION LIFETIMES OF THE VIBRATIONAL LEVELS OF THE ${}^4\text{He}_2^{++}$ AND ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$ GROUND STATES

To the best of our knowledge, the only piece of experimental information regarding the stability of the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state comes from the 1989 work of Belkacem *et al.*,<sup>15</sup> who applied the method of ‘‘Coulomb-explosion imaging.’’ They ‘‘determined the lifetime to be longer than 5  $\mu\text{s}$ .’’ However, no identification was reported as to the vibrational level corresponding to this lifetime estimate. It is clear that the experimental spectroscopic information on this simple system is hard to obtain.

Also in 1989, the first systematic calculations of the lifetimes of the  $J=0$  and  $\nu=0, 1, 2, 3$  vibrational levels of the  ${}^4\text{He}_2^{++}$  and  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  ground states were published.<sup>4</sup> For example, it was reported that the metastable  $\nu=0$  level of  ${}^4\text{He}_2^{++}$  has a lifetime of about 220 min, while the lifetime of the  $\nu=1$  level is about six orders of magnitude shorter (0.027 s). Levels with rotational energy were of no immediate interest since the aim of the study was to establish magnitudes of lifetimes under optimal conditions for stability.

The problem was tackled in the following way. First, using the simple WKB tunneling formula, an understanding was pursued of the sensitivity of the lifetimes to the accuracy of the  $V(R)$  and to the corresponding vibrational energies,  $E_\nu$ ,  $\nu=0, 1, 2, 3$ , by examining five different  $V(R)$ , from earlier calculations<sup>16,17</sup> or from large linear combination of atomic orbitals molecular-orbital (LCAO-MO) CI ones carried out for this purpose.<sup>4</sup> In this respect, the smallness of the  $\text{He}_2^{++}$  molecule is favorable to systematic computational treatments of high to very high accuracy.

The results of the LCAO-MO CI calculation of Ref. 4 with normally used atomic-orbital basis sets had a sufficiently uniform accuracy out to the large  $R$  region. Nevertheless, since Yagisawa, Sato, and Watanabe<sup>16</sup> (YSW) used  $r_{12}$ -dependent basis sets that are expected to provide higher accuracy at small distances, it was decided that the YSW potential is more appropriate for the accuracy requirements of the project, which had to do with the reliable determination of the stability of cold ( $J=0$ ,  $\nu=0$ , or  $\nu=1$  levels)  $\text{He}_2^{++}$

$1\Sigma_g^+$ . [The energy difference from the bottom of the well to the top of the barrier was found to be 0.055 15 a.u. (1.5007 eV), in Ref. 16 and 0.054 03 a.u. (1.4702 eV) in Ref. 4, and, consequently, the lifetime of the  $\nu=0$  level when using the YSW  $V(R)$  was longer by an order of magnitude.]

The second important choice in the work of Ref. 4 had to do with the method for computing the sought-after widths,  $\Gamma_\nu$ . It was decided that, for this  $V(R)$ , the single-level WKB approach was both economic and pertinent. Furthermore, in the final computations, instead of the standard Gamow expression, the WKB formula with a correction that was proposed by Connor and Smith<sup>6</sup> for resonances of small widths was implemented:

$$\Gamma_\nu = \frac{\hbar}{2\pi} \omega(E_\nu) \exp \left[ 2\pi\alpha_\nu(E_\nu) + X_\nu \left( \frac{\beta(E_\nu)}{\pi} \right) \right]. \quad (1)$$

$\omega(E_\nu)$  is the frequency of vibration,  $\pi\alpha_\nu(E_\nu)$  is the phase integral for the barrier, and  $X_\nu(\beta(E_\nu)/\pi)$  is a *quantum correction* which depends on the phase integral for the well,  $\beta(E_\nu)$ .<sup>6</sup> (Because of the relatively large distance between the turning points of this  $V(R)$ , this correction is small—see Table III.)

Following the initial calculations of  $\Gamma_\nu$ ,<sup>4</sup> a number of studies by various groups were devoted to the calculation of these quantities, and of the corresponding  $E_\nu$ , with publications beginning in 1990.<sup>7-11</sup> Their results are collected in Table I, together with those of Ref. 4. In the next few paragraphs, we comment on each one of them.

Babb and Du<sup>8</sup> implemented a real-space amplitude method, whose foundations can be found in the work of Breit and Wigner.<sup>18</sup> Accordingly, by choosing two points,  $x_o$  and  $x_u$ , inside the classically allowed region, the energy distribution of each resonance [we write their Eqs. (5) and (6)],

$$p(E) = \int_{x_o}^{x_u} \psi_E^2(x) dx, \quad (2)$$

is fitted to a Lorentzian form

$$p(E) = \frac{\alpha}{\pi} \frac{\Gamma/2}{(\Gamma/2)^2 + (E - E_r)^2}. \quad (3)$$

The issues about the choice of the constant  $\alpha$  and of the limits of integration in (2), and about the search for the resonance energy,  $E_r$ , are discussed by the authors.<sup>8</sup> The assumptions (2) and (3) are reliable for narrow resonances, as demonstrated by the calculations of Ref. 8 on the  $\text{He}_2^{++} \ 1\Sigma_g^+$  state. They probably require additional justification when the resonance state is broad, with an energy-dependent width function.

Babb and Du<sup>8</sup> published energies and widths for two potential-energy curves. One was the  $V(R)$  of Ref. 16 and another one was a hybrid potential that was constructed from the values of Ref. 16 inside the well and of Ref. 17 for large  $R$ . The results of these quantal calculations are in harmony with the semiclassical ones.<sup>4</sup>

Also in 1990, another quantum-mechanical method was implemented. Nicolaides *et al.*<sup>9</sup> treated the quasidiscrete vibrational levels as isolated resonance states with complex

energies, satisfying the complex eigenvalue Schrödinger equation (CESE) for each rovibrational resonance level,  $m \equiv (\nu, J)$ ,

$$\frac{d^2\Psi_m}{dR^2} + \frac{2\mu}{\hbar^2} \left[ W_m - \left( V(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right) \right] \Psi_m = 0. \quad (4)$$

$$\text{For } J=0, \quad \Psi_\nu(0) = 0, \quad \Psi_\nu(R)_{R \rightarrow \infty} = e^{i\sqrt{2W_\nu}R}, \quad (4a)$$

$$W_\nu = E_\nu - \frac{i}{2}\Gamma_\nu.$$

The integration of Eq. (4) under proper boundary conditions was achieved numerically, by implementing the *exterior complex scaling* (ECS) procedure proposed in Ref. 19, whereby, for practical reasons, integration in the interaction (inner) region is done on the real coordinate axis and the regularization of the resonance eigenfunction is effected by following a contour path,  $C$ , for a complex coordinate of the free particle in the asymptotic region. Thus, the norm is defined by<sup>19</sup>

$$\int_{\text{all space}} \Psi_m^2 d\tau = \int_0^{R_{\text{ex}}} \Psi_m^2 dR + \int_C \Psi_m^2 ds. \quad (5)$$

According to Ref. 19,  $R_{\text{ex}}$  is a point on the real axis at the edge of the inner region and  $R < \text{Re } s < \infty$ . In the case of the  $\text{He}_2^{++} 1\Sigma_g^+$  calculation,  $J$  was zero and  $R_{\text{ex}}$  was chosen as 10 a.u. (Ref. 9).

As was already stated in Ref. 4, the approach of constructing and solving the problem in terms of the CESE is numerically extremely demanding for the accurate computation of very narrow widths. (Widths as small as  $10^{-14}$ – $10^{-15}$  a.u. were computed in Ref. 9, but the accuracy deteriorates around this limit. Improvement of the accuracy could, in principle, be achieved by extending the order of the Numerov integration scheme implemented in Ref. 9.) Therefore, only three  $\Gamma_\nu$ ,  $\nu=1, 2$ , and 3, were obtained,<sup>9</sup> with the  $V(R)$  that was computed in Ref. 4 in order to include more points for large values of  $R$ . Those results are also collected in Table I.

The results of the 1990 papers<sup>8,9</sup> indicated that, for this problem, the predictions of the work of Ref. 4, which implemented the WKB approximation, were physically meaningful. The WKB approach was soon after employed by Ackermann and Hogreve<sup>7</sup> in conjunction with a  $V(R)$  computed by them via LCAO-MO CI with large basis sets and special corrections. Given the use of different  $V(R)$ , the results of Ref. 7 are in essential agreement with those of the previous calculations<sup>4,8,9</sup> (Table I).

More recently, Sidky and Ben-Itzhak<sup>10</sup> implemented a phase-amplitude method,<sup>20–23</sup> modified so as to account for barrier penetration. Accordingly, they computed numerically the *Milne phase*,  $\phi(r_{\text{out}}, E)$ , and its energy derivative,  $\partial\phi(r_{\text{out}}, E)/\partial E$ , for the resonance wave functions of  ${}^3\text{He}^4\text{He}^{++}$ , using the  $V(R)$  of Refs. 7 and 16. The determination of the widths in Ref. 10 was done by fitting  $\partial\phi(r_{\text{out}}, E)/\partial E$  to a Lorentzian form plus a constant [we write their Eq. (12)],

$$\frac{\partial\phi(r_{\text{out}}, E)}{\partial E} = \frac{\Gamma/2}{(\Gamma/2)^2 + (E - E_r)^2} + C. \quad (6)$$

The results of Ref. 10 (from their list of Table Ia) are included in Table I.

Finally, Orlikowski<sup>11</sup> carried out scattering calculations and applied the lifetime matrix method of Smith,<sup>24</sup> in conjunction with the  $V(R)$  computed by Wolniewicz.<sup>12</sup> He concluded that the agreement with the results of Babb and Du<sup>8</sup> and of Nicolaides<sup>4</sup> is *only fair* and attributed this discrepancy to the different potentials with different zero-point energies that were used in the calculations (p. 1190 of Ref. 11). Although it is a fact that such widths are sensitive to small changes in the potential, it is also useful to have information as to the possible differences that are due exclusively to different approaches to the calculation of such shape resonances. Since the present calculations are also based on the Wolniewicz  $V(R)$ , any discrepancies between the results of Ref. 11 and of this work can be attributed to the differences in the two theories and their methodologies.

### III. THE $\text{He}_2^{++} 1\Sigma_g^+$ MOLECULE AS A MULTILEVEL SYSTEM OF SHAPE RESONANCES

Even if the nonadiabatic coupling to the excited  $1\Sigma_g^+$  states is neglected, the solution to the problem of computing the intrinsic properties of the shape resonances of the  $\text{He}_2^{++} 1\Sigma_g^+$  ground state must, in principle, account for the multilevel nature of the vibrational ( $J=0$ ) spectrum. This means that any isolated level approach must carry a certain inaccuracy, caused by the neglect of indirect interlevel coupling via the continuum. In other words, the position and width of each level are, from a rigorous point of view, a product of a collective spectral contribution, even though the vibrational levels are well separated. Such coupling is expected to show certain differences from the isolated resonance methodology, especially when the levels are near the top of the barrier. Therefore, it is worth implementing methods that incorporate the information from the whole spectrum. For example, for systems with coupling among electronic states, *ab initio* results from close-coupling scattering calculations on the predissociation partial and total widths of rovibrational levels of the  $C$  and  $D 2\Sigma^+$  states indicate significant deviations from the two-state level approximation.<sup>25</sup>

Also, as regards the properties of dications with volcano-like potentials, an alternative possibility exists for multi-state couplings. For example, this is represented by the spectrum of  $\text{NO}^{++}$ , where the lowest two electronic states, the  $X 2\Sigma^+$  and the  $A 2\Pi$ , exist in the local minima with their vibrational levels embedded into each other.<sup>26</sup> *Ab initio* calculations of multiphoton dissociation probabilities showed that the coupling of the two states enhances the dissociation through the  $X 2\Sigma^+$  channel by six orders of magnitude.<sup>27</sup>

For the case of interest here, which is concerned with an isolated ground-state  $V(R)$ , the  $S$ -matrix formalism applied in Ref. 11 is certainly general enough to account for the multilevel problem. The same is true of the present semiclassical theory and computations. Their fundamental objective is the analytic derivation and use of a practical form of the semi-



classical Green's function,  $G_{\text{SC}}(E)$ , from which the sought after resonance energies (including energy shifts) and widths is obtained. These quantities, for each level, then contain the collective effects of the whole spectrum.

#### IV. SEMICLASSICAL PATH-INTEGRAL CALCULATION OF $G_{\text{SC}}(E)$ FOR THE POTENTIAL OF FIG. 1

From the general theory of spectra, given a Hamiltonian,  $H$ , the resolvent operator is defined by  $R(z)=1/(z-H)$ , with  $z$  complex,  $z=E\pm i\eta$ ,  $\eta\rightarrow 0$ . The time evolution operator,  $e^{(i/\hbar)Ht}$ , is related via Fourier transform with  $R(z)$ , and inversely. In the space of the complete set of states of  $H$ ,  $R(z)$  turns into the Green's function of the system. Its poles and residues on the real energy axis correspond to the discrete stationary states for  $E<0$ , while its cut for  $E>0$  corresponds to the continuous spectrum of scattering stationary states. There are also complex poles for  $E>0$ , which, for  $t>0$ , decaying states must be placed on the second Riemann sheet below the real energy axis, since  $R(z)$  is analytic on the first sheet. For physical potentials, these poles represent the resonance states of the system, e.g., Ref. 28.

When, instead of the wave-function formalism, the Feynman theory of path integrals is adopted in its semiclassical version, corresponding to the quantum-mechanical retarded Green's function, ( $t>0$ ), there is also a semiclassical one,  $G_{\text{SC}}(E)$ , which, for certain potentials, can be obtained either numerically, as a Fourier transform of the propagator, or directly. Out of the large number of articles which have been published on path integrals and on semiclassical theory, covering topics such as imaginary quantities associated with tunneling, Morse and Maslov indices, WKB and higher approximations, etc. (e.g., see papers and books cited in Ref. 14), we have found the ones by Holstein and Swift<sup>29,30</sup> and by Holstein<sup>31</sup> on barrier penetration and on the connection to the WKB approximation, very lucid and instructive in developing a formalism with practical analytic formulas suitable for general one-dimensional volcanolike potentials and for double wells with and without a finite barrier.<sup>14</sup> The present discussion and computational implementation is a follow-up of the work in Ref. 14.

In the framework of path integrals, given two points in configuration space,  $x_1$  and  $x_2$ , the Green's function is written as

$$\begin{aligned} G(x_2, x_1; E) &= \frac{1}{2\pi\hbar} \int_0^\infty dt e^{iEt} \langle x_2 | e^{-(i/\hbar)Ht} | x_1 \rangle \\ &= \frac{1}{2\pi} \langle x_2 | \frac{i}{E - H + i\varepsilon} | x_1 \rangle. \end{aligned} \quad (7)$$

The plus sign in front of  $i\varepsilon$  relates to the fact that  $t>0$ . In semiclassical mechanics, the  $G(x_2, x_1; E)$  is obtained in the stationary phase approximation, i.e., the approximation whereby the quantity  $(i/\hbar)S$  ( $S$  is the action) is expanded about the extrema of  $S$  up to quadratic terms. (The action is

stationary on classical paths.) Following Refs. 29–31, we write  $G_{\text{SC}}(E)$  in the form,

$$G_{\text{SC}}(x_2, x_1; E) = \frac{1}{2\pi\sqrt{k(x_1)k(x_2)}} \sum_{j=1}^{\infty} \left\{ \prod_{i=1}^{N(j)} f_{ij} \right\}, \quad (8)$$

where  $x_1(t_1)$  and  $x_2(t_2)$ ,  $t_2>t_1$ , are two points in the allowed region, and

$$k(x) = \sqrt{2(E - V(x))} \quad (\text{in a.u., } \hbar = m = e = 1). \quad (9)$$

The index  $j$  refers to a particular path, which consists of  $N(j)$   $i$  events, each of which contributes the amplitude  $f_{ij}$  to the total propagation between the time-space points  $x_1$  and  $x_2$ . The form of each  $f_{ij}$  depends on the kind of event, namely, propagation or reflection, as well as on the nature of the region of motion, namely, allowed or forbidden. Thus, if propagation is in an allowed region, this factor is given by  $\exp[i\int_a^b k(x)dx]$ , while if propagation is in a forbidden region, it is given by  $\exp[-|\int_a^b u(x)dx|]$ , where  $u(x) = \sqrt{2(V(x) - E)}$ .

In Refs. 29–31 it is shown that the results from the normal WKB techniques of connection formulas can be replaced by simple rules expressing the phase changes of the wave function at turning points. By applying these rules to the potential of the form of Fig. 1, we showed that the corresponding  $G_{\text{SC}}(E)$  has the transparent form<sup>14</sup>

$$G_{\text{SC}}(E) = C(x_1, x_2; E) [S_{\text{regular}}(E) + S_{\text{pole}}(E)]. \quad (10)$$

$S_{\text{regular}}$  represents a smooth background for propagation and  $S_{\text{pole}}$  represents the energy-dependent presence of poles dominating propagation. The quantities in (10) are given by

$$C(x_1, x_2) = -\frac{i}{\sqrt{2\pi}} \frac{\sin[\Lambda(x_1) + \pi/4]}{(E - V(x_1))^{1/4} (E - V(x_2))^{1/4}}, \quad (11)$$

$$S_{\text{regular}} = \cos \left[ \Lambda(x_2) + \frac{\pi}{4} \right], \quad (12)$$

$$\begin{aligned} S_{\text{pole}} &= \sin \left[ \Lambda(x_2) + \frac{\pi}{4} \right] \\ &\times \frac{\sin \Lambda(\alpha) + i/4 \exp[-2\kappa] \cos \Lambda(\alpha)}{\cos \Lambda(\alpha) - i/4 \exp[-2\kappa] \sin \Lambda(\alpha)}, \end{aligned} \quad (13)$$

with

$$\Lambda(r) = \sqrt{2} \int_{\delta(E)}^r \sqrt{E - V(x)} dx, \quad (14)$$

$$\kappa = \sqrt{2} \int_{\alpha(E)}^{\beta(E)} \sqrt{V(x) - E} dx. \quad (15)$$

The above formulas allow the systematic computation of  $G_{\text{SC}}(E)$  for any system with a known  $V(x)$ , given either analytically or numerically. Obviously, the important information regarding the system's properties comes from the poles of  $S_{\text{pole}}(E)$ . Below we will proceed in two steps. In the first one, we will focus on the denominator of (13) and extract

from it forms for the energy width,  $\Gamma_n(E)$  and shift,  $\Delta_n(E)$ . In the second one, we will go further by examining the energy dependence of the numerator as well, thereby obtaining more accurate general formulas for  $\Gamma_n(E)$  and  $\Delta_n(E)$ .

The quantity  $\exp[-2\kappa]$  takes a very small value, and so the denominator of (13) becomes zero when

$$\cos \Lambda(\alpha(E)) = 0, \quad (16a)$$

or, equivalently, when

$$\Lambda(\alpha(E)) = n\pi + \frac{\pi}{2}, \quad n = 0, 1, 2, 3, \dots \quad (16b)$$

(Here we use the symbol  $n$  as the index for the quantized levels. In the other sections we use the symbol  $\nu$  for the vibrational levels.)  $\Lambda(\alpha(E))$  depends on energy not only through its direct connection to it [Eq. (14)], but also through its dependence on the limits of the integral. Therefore, by expanding the denominator of Eq. (13) around those values of energy,  $E_n$ , that satisfy Eq. (16), we obtain

$$\Pi \cong - \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} + i \left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right) \right) \times \left\{ E - \left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right) \frac{\exp[-2\kappa(E_n)]}{4} + \frac{i \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right) \exp[-2\kappa(E_n)]}{2 \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right)^2 + \left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right)^2} \right\}. \quad (17)$$

It follows from Eq. (17) that the width is given by the positive quantity

$$\Gamma(E_n) \equiv \Gamma_n = \frac{\left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right) \exp[-2\kappa(E_n)]}{2 \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right)^2 + \left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right)^2}. \quad (18)$$

At the same time, we also recognize the presence in (17) of the semiclassical version of the energy shift of a resonance state, which results from the interaction of the bound part with the continuum. It is given by

$$\Delta(E_n) \equiv \Delta_n = \frac{\left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right) \exp[-2\kappa(E_n)]}{\left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right)^2 + \left( \frac{\exp[-2\kappa(E_n)]}{2} \left( \frac{d\kappa}{dE} \right)_{E_n} \right)^2}. \quad (19)$$

Since the numerator is the product of two small quantities,  $\Delta_n$  is a very small quantity. In fact, it becomes zero if one assumes that  $(d\kappa/dE)_{E_n} = 0$ , which is a condition expected to hold to a very good approximation for the lowest-energy levels. At the same time, Eqs. (18) and (19) show that the magnitude of  $\Gamma_n(E)$  and  $\Delta_n(E)$  increases as the levels approach the barrier maximum, since the quantity  $\kappa$  is a decreasing function of the energy.

A further improvement toward accuracy is obtained when the numerator is expanded as well. The results are

$$\Gamma_n = \frac{\left[ \frac{\exp[-2\kappa(E_n)]}{1 + \exp[-2\kappa(E_n)]/4} \right] \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right)^{-1} \left[ 2 - \frac{\exp[-2\kappa(E_n)]}{1 - \exp[-2\kappa(E_n)]/4} \right]}{\frac{1}{4} \left( \left( \frac{d\Lambda}{dE} \right)_{E_n} \right)^{-2} \left\{ \frac{4 \left( \left( \frac{d\kappa}{dE} \right)_{E_n} \right)^2 \exp[-4\kappa(E_n)]}{(1 + \exp[-2\kappa(E_n)]/4)^4} \right\} + \left\{ 2 - \frac{\exp[-2\kappa(E_n)]}{1 + \exp[-2\kappa(E_n)]/4} \right\}^2}$$

$$\Delta_n = \frac{\left(\frac{d\kappa}{dE}\right)_{E_n} \exp[-2\kappa(E_n)](1 - \exp[-4\kappa(E_n)]/16)^{-1} \left[2 - \frac{\exp[-2\kappa(E_n)]}{1 + \exp[-2\kappa(E_n)]/4}\right]}{\frac{1}{4} \left(\left(\frac{d\Lambda}{dE}\right)_{E_n}\right)^{-2} \left\{ \frac{4 \left(\left(\frac{d\kappa}{dE}\right)_{E_n}\right)^2}{(1 + \exp[-2\kappa(E_n)]/4)^4} \right\} + \left\{ 2 - \frac{\exp[-2\kappa(E_n)]}{1 + \exp[-2\kappa(E_n)]/4} \right\}^2}. \quad (20)$$

Now we observe that, as regards the denominator of Eq. (13), the condition (16), namely,  $\cos \Lambda(\alpha(E))=0$ , does not secure that the denominator is nullified for those levels for which the quantity  $\exp[-2\kappa]$  is not negligible (i.e., the barrier is not relatively large). In order to correct systematically for this case, we start by assuming that the physically correct condition

$$\exp[-2\kappa_0] \ll 1 \quad (21)$$

holds for the lowest level,  $\nu=0$ . We then accept that for the following level, i.e., for  $\nu=1$ , the condition (21) does not hold, and proceed to compute the ratio  $\lambda=\kappa_0/\kappa_1$ . Evidently,  $\exp[-2\kappa_0]=\exp[-2\lambda\kappa_1]$ . We then let the quantity  $\exp[-m\kappa_1]$  be defined by

$$\exp[-m\kappa_1]\exp[-2\kappa_1]=\exp[-2\kappa_0]. \quad (22)$$

This means that

$$m=2(\lambda-1). \quad (23)$$

The above is applied as follows: By multiplying the denominator of  $S_{\text{pole}}$  with  $\exp[-m\kappa_1]$ , the imaginary part becomes proportional to  $\frac{1}{4}\exp[-2\kappa_0]$ . Therefore, because of (21), it can be set equal to zero.

The real part is  $\exp[-m\kappa_1]\cos[\Lambda_1(\alpha(E))]$ . This tends to zero more accurately for those values of energy which are close to the roots of the cosine. We now require that this term remain stationary for small variations of the energy around these values. Hence, we require

$$\frac{d}{dE}\{\exp[-m(E)\kappa_1(E)]\cos \Lambda_1(\alpha(E))\}=0. \quad (24)$$

The result of Eq. (24) is the condition

$$\tan \Lambda_1(\alpha(E)) = \frac{d[[2(\lambda(E)-1)\kappa_1]]}{d\Lambda_1}, \quad (25)$$

which contains a correction to the energy of the level.

Equation (25) connects the classically allowed with the forbidden region, via the derivative  $d\kappa_1/d\Lambda_1$  of the corresponding phase integrals. This connection is physically relevant to the case of resonance states, since these are products of motion in both regions. In other words, Eq. (25) takes into account motion in the allowed region via the term  $\cos \Lambda(\alpha(E))$  and in the forbidden region via the term  $\exp[-m(E)\kappa_1(E)]$ . This results in a correction to the WKB approximation which comes from the additional terms regarding the barrier as well as the energy corrections already discussed.

Therefore, with respect to the WKB formula

$$\Gamma_n(\text{WKB}) = \frac{\omega_n}{2\pi} \exp[-2\kappa(E_n)], \quad (26)$$

the relation (20) in conjunction with condition (25) provide a more accurate semiclassical description of the width. In fact, as the energy approaches the top of the barrier these corrections become more important. This is due to the presence of energy derivatives of quantities that relate to the barrier.

## V. RESULTS

As already stated in the Introduction, the  $V(R)$  that we used in this work is the one calculated by Wolniewicz.<sup>12</sup> Additional points were calculated by polynomial interpolation in the regions surrounding the vibrational energies. According to Wolniewicz, the calculated energies are accurate to a fraction of a wave number. The energy features of this  $V(R)$  are the following:<sup>12</sup> The minimum energy is  $E_{\text{min}}=-3.681\,455\,875$  a.u. at  $R_{\text{min}}=1.3281$  a.u., and the maximum of the barrier is  $E_{\text{max}}=-3.626\,843\,250$  a.u. at  $R_{\text{max}}=2.172$  a.u. The barrier height,  $\Delta E_B$ , is 1.486 06 eV and the dissociation energy,  $\Delta E_D$ , is -8.667 90 eV. For easy comparison, we note that, for the potentials that were previously used in the calculations of the vibrational resonances,  $\Delta E_B$  (Yagisawa *et al.*<sup>16</sup>) =1.5007 eV,  $\Delta E_B$  (Nicolaidis<sup>4</sup> and Nicolaidis *et al.*<sup>9</sup>) =1.470 eV, and  $\Delta E_B$  (Ackermann and Hogreve<sup>7</sup>) =1.488 eV.

### A. Vibrational energies

Wolniewicz calculated vibrational energies by imposing Dirichlet boundary conditions on the solution of the real-eigenvalue Schrödinger equation. He reported that *only* the three lowest resonances could be determined unambiguously for both the  $^4\text{He}_2^{++}$  and the  $^4\text{He}_3\text{He}^{++}$  molecules (p. 2265 and Table VIII of Ref. 12). Using the same  $V(R)$ , Orlikowski<sup>11</sup> calculated five levels, with which our results are compared in Table II. The agreement for the energies is very good.

The energies computed in this work emerge basically from the satisfaction of the condition (16). To these solutions we then add the (important for better accuracy) correction of Eq. (25). The whole procedure was considered satisfactory when the convergence error in the iterative search was less than  $10^{-8}$ .

## B. Autodissociation widths and energy shifts

The autodissociation widths calculated via the present approach are presented in Table II. They are also contained in Table III, where they are compared with the WKB results and with those from formula (1), which was proposed by Connor and Smith.<sup>6</sup> The present WKB calculation obtained the energy from the satisfaction of Eqs. (16),  $\cos \Lambda(\alpha(E)) = 0$  and  $\Lambda(\alpha(E)) = \nu\pi + \pi/2$ ,  $\nu=0,1,2,3$ . Under this condition, there is no WKB solution for the  $\nu=4$  level, which, in fact, exists just  $96.6 \text{ cm}^{-1}$  below the top of the barrier, according to the full semiclassical path-integral calculation. As an example of the energy difference between the WKB and the full calculation, we refer to the  $\nu=3$  level of  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$ . The WKB energy is  $E_{\text{WKB}} = -3.63348 \text{ a.u.}$ , while the energy obtained from the semiclassical Green's-function method described above is  $E_G = -3.63207 \text{ a.u.}$

On the other hand, for the  $\nu=0$  level there is no difference between the results of the WKB approximation and the full Green's-function computation. A similar agreement is expected for other potentials in which the widths of the lowest levels are very narrow.

As regards the calculation of  $\Gamma_\nu$  in the WKB approximation, the relation (26) is used, which is the result of the following reduction from Eq. (20). The quantity  $\omega$  is equal to  $\omega = \pi E / \Lambda(\alpha(E))$ , i.e., it is the frequency of classical vibrations. Also, from the numerator of Eq. (20) we keep only the term  $[\exp[-2\kappa(E_n)]/1 + \dots]((d\Lambda/dE)_{E_n})^{-1}[2 - \dots]$ , and from the denominator we keep  $(2)^2 = 4$ . In this way, by omitting terms of magnitude much smaller than unity, as well as terms related to energy derivatives of quantities involving the barrier, we obtain the WKB approximation. As in the case of energies, for the  $\nu=0$  level the WKB approximation yields the same results with those of the semiclassical Green's function for both  ${}^4\text{He}_2^{++}$  and  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$ .

Finally, Table III also contains the energy shifts,  $\Delta_\nu$ , that are calculated from Eq. (20). It is seen that they are smaller by orders of magnitude than the widths, and negligible for this problem. On the other hand, it is clearly established that as the barrier top is approached, the magnitude of  $\Delta_\nu$  increases rapidly. It is noteworthy that this semiclassical for-

TABLE II. Energies and widths, in a.u., of the  ${}^4\text{He}_2^{++} \ 1\Sigma_g^+$ ,  $\nu=0,1,2,3,4$ , vibrational shape resonances. Comparison of the results of Orlikowski (see Ref. 11), who implemented the lifetime matrix method of Smith (see Ref. 24), with those of the present semiclassical path-integral theory for the calculation of the Green's function. The numbers in parentheses denote powers of ten. Both calculations used the  $V(R)$  computed by Wolniewicz (see Ref. 12). In a.u.,  $\Gamma_\nu = 1/\tau_\nu$ , where  $\tau_\nu$  is the lifetime. 1 a.u. of time =  $2.4189 \times 10^{-17} \text{ s}$ .

$\nu$	Ref. 11		This work	
	$E_\nu$	$\Gamma_\nu$	$E_\nu$	$\Gamma_\nu$
0	-3.673 65	0.2790 (-20)	-3.673 81	0.3785 (-20)
1	-3.659 74	0.1434 (-14)	-3.660 68	0.1113 (-14)
2	-3.647 05	0.8889 (-10)	-3.647 74	0.7323 (-10)
3	-3.635 87	0.8408 (-06)	-3.635 46	0.3227 (-06)
4	-3.627 09	0.4228 (-03)	-3.627 28	0.2246 (-03)

TABLE III. Results for tunneling widths,  $\Gamma_\nu$ , and energy shifts,  $\Delta_\nu$ , of the shape resonances of the  ${}^4\text{He}_2^{++} \ 1\Sigma_g^+$ ,  $\nu=0,1,2,3,4$ , and  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$ ,  $\nu=0,1,2,3$  vibrational shape resonances, in a.u., from the present work. The  $V(R)$  is that computed by Wolniewicz (see Ref. 12). The  $\nu=4$  level does not exist for the  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  state. Also, the WKB approximation does not predict a fifth vibrational level ( $\nu=4$ ) for either system. The numbers in parentheses denote powers of ten.

$\nu$	WKB $\Gamma_\nu$	WKB+ Correction [Eq. (1)] $\Gamma_\nu$	Semiclassical Green's function Eq. (20), see text	
			$\Gamma_\nu$	$\Delta_\nu$
0	0.378 (-20)	0.407 (-20)	0.378 (-20)	0.933 (-38)
0	1.551 (-19)	1.6667 (-19)	1.551 (-19)	0.580 (-35)
1	0.651 (-14)		0.111 (-14)	0.353 (-27)
1	0.709 (-12)		0.735 (-13)	0.870 (-24)
2	1.674 (-10)		0.732 (-10)	0.133 (-17)
2	0.989 (-08)		0.549 (-08)	0.183 (-13)
3	0.490 (-06)		0.323 (-06)	0.194 (-09)
3	1.973 (-05)		0.600 (-04)	0.470 (-06)
4	—		0.225 (-03)	0.140 (-04)
4	—		—	—

malism leads to formulas that can be computed numerically very accurately, for values of  $\Delta_\nu$  or of  $\Gamma_\nu$  ranging over very many orders of magnitude.

## VI. CONCLUSION

The object of this work was the computation of the intrinsic properties of the shape resonances of one-dimensional volcanolike potentials, as in Fig. 1, in the framework of semiclassical mechanics.

In our previous work,<sup>14</sup> using a methodology of path integrals, we obtained the semiclassical Green's function for the  $V(R)$  of Fig. 1 in the general form of Eq. (10). Here, by analyzing the term  $S_{\text{pole}}(E)$ , whose complex poles represent the energies and widths of the shape resonances of Fig. 1, we obtained the results for the energies and the widths,  $\Gamma_\nu$  [Eq. (20)], which were applied, in conjunction with the very accurate  $V(R)$  of Wolniewicz,<sup>12</sup> for the *ab initio* calculation of the energies and autodissociation widths of the vibrational levels of the  ${}^4\text{He}_2^{++}$  and the  ${}^4\text{He}^3\text{He}^{++} \ 1\Sigma_g^+$  ground states. For  ${}^4\text{He}_2^{++}$ , these results were compared with those reported by Orlikowski,<sup>11</sup> who used the same  $V(R)$  and implemented the quantum-mechanical scattering method of the lifetime matrix (Table II). The energies are in very good agreement. However, for the widths a certain discrepancy is observed, up to factors of 2–3 for the two levels near the top of the barrier.

The formal results for  $E_\nu$ ,  $\Gamma_\nu$ , and  $\Delta_\nu$  that were derived and discussed in this paper go beyond the WKB approximation, while they are computationally practical and allow very accurate numerical implementation. A useful numerical result is the fact that, for the  $V(R)$  of  ${}^4\text{He}_2^{++} \ 1\Sigma_g^+$ , for the  $\nu=0$  level the values of the energy and the width from the WKB approximation are the same as those from the more advanced Green's-function treatment (Table III). This results from the narrowness of the resonance, which eliminates the corrections to the WKB treatment, and may characterize other potentials as well.



We suggest that there are at least two challenging open issues for such semiclassical methodologies. First is the question of handling the multichannel problem when more than one electronic states are involved, as in the case of  $\text{NO}^{++}$ .<sup>27</sup> Second is the question of the determination of shape resonances of multidimensional potentials.

In any case, we emphasize that the accurate computation of the properties of rovibrational resonance states in real molecules (i.e., not in model potentials) is very sensitive to the degree of precision with which the potential-energy surface is known. Otherwise, the computed tunneling widths may be wrong by orders of magnitude. The physically relevant fact concerning ground-state diatomics with a  $V(R)$  of Fig. 1 is that they offer a concrete opportunity for the interaction between experiment and the theory of structure and of tunneling dynamics, since the autodissociation lifetimes, i.e., the inverse of the rates of tunneling through the barrier, are, in principle, measurable, e.g., Refs. 15 and 32–34.

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