

## Autoionizing states of $H_2$ and $H_2^-$ using the complex-scaling method

Nimrod Moiseyev and Chris Corcoran

*Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706*

(Received 14 May 1979)

The complex-scaling method is applied to the study of molecular resonances within the framework of the Born-Oppenheimer approximation. In this procedure only the electronic coordinates of the Born-Oppenheimer Hamiltonian are scaled, and thus only the electron-nuclear attraction integrals need be recalculated with explicit complex arguments for each value of the scaling parameter. This method is applied to the study of resonances of  $H_2$  and  $H_2^-$ . This represents the first successful application of a complex-scaling procedure to the study of a molecular resonance.

The complex-scaling method<sup>1</sup> has been applied successfully in a number of studies of resonance states in atoms.<sup>2</sup> In this method the internal coordinates of the Hamiltonian are dilated by a complex factor  $\eta = \alpha e^{-i\theta}$  such that

$$H(r) \rightarrow H(r/\eta) \equiv H_\eta(r). \quad (1)$$

The spectrum of the Hamiltonian is affected in such a way that the resonance states become isolated in the complex energy plane with the imaginary part of the energy equal to half the resonance width  $\Gamma$ :

$$W_{\text{res}} = E_r + iE_i = E_r - \frac{1}{2}i\Gamma. \quad (2)$$

The success of this method in describing resonances of few electron atoms has spurred interest in extending its application to molecules<sup>3</sup> and many-electron systems.<sup>4</sup> In this work we will be primarily concerned with the extension of the complex-scaling method to molecular problems.

To date, the complex-scaling method has not been used to study molecular resonances. The reasons for this are twofold. First, it has not been clear exactly how the Balslev-Combes theorem,<sup>5</sup> which is the foundation for the use of this procedure in atoms, may be applied in conjunction with the Born-Oppenheimer approximation to provide a tractable method for molecular calculations. Secondly, the use of "trajectory"<sup>6</sup> and iterative<sup>7</sup> methods for the determination of resonance positions frequently requires the solution of variational problems for a large number of scale factors. This is potentially a severe handicap in molecular calculations where a large number of two-electron integrals may have to be recalculated and transformed for each value of the scaling parameter. In this work we apply a complex-scaling procedure within the Born-Oppenheimer approximation in such a way as to avoid the necessity of recalculating and retransforming

the two-electron integrals for each scaling factor. While the Balslev-Combes theorem does not directly apply in this procedure, the method is shown to be plausible on other grounds.

The complex-scaling method, as developed by Aguilar, Balslev, Combes,<sup>5</sup> and Simon,<sup>1</sup> is restricted to a class of potentials described as dilation analytic. Since the forces of chemical interest which act within molecules are Coulombic, it is clear that the molecular potential, considered as a function of nuclear as well as electronic coordinates, is dilation analytic. The application of the complex-scaling method to this potential (applying the Born-Oppenheimer approximation after dilation) would, however, result in the determination of electronic spectra for unphysical complex internuclear separations. We choose to examine the alternative, which is to first apply the Born-Oppenheimer approximation then the complex-scaling method. In this method the electronic coordinates are dilated independent of the nuclear coordinates.

The equivalence between dilation of the Hamiltonian and scaling the basis is easily seen by the following relation:

$$W_\eta = \frac{(\phi(r, R) | H(r/\eta, R) | \phi(r, R))_r}{(\phi(r, R) | \phi(r, R))_r} \\ = \frac{(\phi(\eta r, R) | H(r, R) | \phi(\eta r, R))_r}{(\phi(\eta r, R) | \phi(\eta r, R))_r} \quad (3)$$

where the bold-face parentheses denote integration over the electronic coordinates only. Here  $r$  and  $R$  represent the set of electronic coordinates and the set of nuclear coordinates, respectively, and  $H(r, R)$  is the Born-Oppenheimer Hamiltonian. For a complete basis, the stationary value of the variational integral on the right-hand side of Eq. (3) must be independent of the real scaling parameter, whereas the variational energy calculated

in a finite basis will generally be a function of the scale. The invariance of the eigenvalues to the scaling of the basis is of course valid only for real scaling parameters; unlike the case for atomic problems, we cannot directly invoke the Balslev-Combes theorem to justify continuing the scaling to complex values. However, introduction of a complex scaled Hamiltonian, in both the atomic and molecular case, is equivalent to the analytic continuation of the basis, to yield a basis which is more suitable for the description of resonance wave functions. It is expected that variational eigenvalues corresponding to molecular resonance will converge to stationary complex values as in the atomic case.

The application of complex-scaling methods to potentials which are not dilation analytic is not without successful precedent. The application of this procedure to the Stark effect in H and H<sup>-</sup> by Reinhardt *et al.*<sup>8</sup> proved profitable not only in the results obtained, but also in that it fostered an advance in the theory as well.<sup>9</sup> These methods have also been applied to a simple model Hamiltonian for predissociative processes.<sup>10</sup>

There is a significant computational advantage to be gained by scaling only the electronic coordinates. Since the kinetic energy and electron repulsion are homogeneous functions of the electronic coordinates, the scaled Hamiltonian matrix elements are given by

$$H_{ij} = (i|T(r/\eta)|j) + (i|V_{ee}(r/\eta)|j) + (i|V_{ne}(r/\eta, R)|j) \quad (4a)$$

$$= \eta^2(i|T(r)|j) + \eta(i|V_{ee}(r)|j) + \eta(i|V_{ne}(r, \eta R)|j) \quad (4b)$$

and only the electron-nuclear attraction integrals need be recalculated for each value of  $\eta$ . There has apparently been some question as to the convergence of this nuclear attraction integral:

$$(i|V_{ne}(\vec{r}, \vec{\eta R})|j) = \sum_n \int \frac{\varphi_i(\vec{r})\varphi_j(\vec{r})}{|\vec{r} - \vec{\eta R}|} d\vec{r} \quad (5)$$

for complex scale factors  $\eta = \alpha e^{-i\theta}$ ,<sup>11</sup> since the integrand has a circle of square-root branch points. This is only a conceptual problem, however, since this behavior disappears if one simply rotates the radial path of integration by  $-\theta$ . This is independent of the potential numerical problem which arises in the evaluation of this integral.<sup>12</sup>

Despite this computational advantage, we must be aware that scaling the electronic coordinates independent of the nuclear coordinates is to effectively move the basis function off the nuclear centers. In a complete basis this presents no problem, but in a finite basis this may signifi-

cantly affect the quality of the results if the magnitude of the scale factor differs greatly from unity. The diffuse nature of resonance wave functions minimizes this effect somewhat.

In a finite basis the identification of a resonance eigenvalue is made by requiring that the eigenvalue satisfy the complex virial theorem<sup>13</sup>

$$\left. \frac{dW}{d\eta} \right|_{\eta_{opt}} = 2\eta_{opt}T + V_{ee} + V_{ne}(\eta_{opt}R) + \eta_{opt} \left. \frac{\partial V_{ne}(\eta R)}{\partial \eta} \right|_{\eta_{opt}} \quad (6)$$

( $\eta_{opt} = \alpha_{opt} e^{-i\theta_{opt}}$ ) as nearly as possible. In practice, the approximate locations of such resonances are identified by examining several trajectories of complex eigenvalues (variation of  $\theta$  for fixed  $\alpha$  in the factor  $\eta = \alpha e^{-i\theta}$ ). Pathological behavior such as loops, cusps, or even inflections in these trajectories may indicate the proximity of a stationary point. This point is further isolated by minimizing  $|dW/d\eta|$  by a direct search algorithm.<sup>14</sup>

The molecules H<sub>2</sub> and H<sub>2</sub><sup>-</sup> represent the simplest molecules exhibiting resonance behavior. Each has been the subject of a number of theoretical and experimental investigations. The resonance positions and widths of H<sub>2</sub><sup>-</sup> are of particular current interest since they are involved in the determination of the dissociative attachment cross section of  $e^- + H_2 \rightarrow H + H^-$ .<sup>15</sup> For both H<sub>2</sub> and H<sub>2</sub><sup>-</sup> the resonance positions and widths were determined at the near equilibrium (ground-state) geometry of  $R = 1.4$  a.u. using a (5s, 3p, 1d/3s, 2p, 1d) contracted Gaussian atomic basis.<sup>16</sup> Approximately 45 configurations of natural orbitals were used as the final basis for the complex-scaling procedure in each case. In Fig. 1 the variation of several eigenvalues of H<sub>2</sub> as a function of  $\theta$  for  $\alpha = 1.0$  is shown to demonstrate the characteristic behavior of bound states, resonance states, and scattering states in the molecular calculations. The fact that the bound-state eigenvalue moves from the real axis is due to the limited nature of the basis and the fact that this basis was optimized (in the choice of natural orbitals) for the resonance state. There are, however, no stationary points with respect to variation of  $\eta$  off the real axis for the bound-state eigenvalue. In Fig. 2, a  $\theta$  trajectory for near optimal value of  $\alpha$  is shown for the  $^2\Sigma(\sigma_u^2\sigma_g)$  resonance of H<sub>2</sub><sup>-</sup>. In Table I the numerical results we have obtained using the complex virial theorem are compared with the resonance position and width for H<sub>2</sub> obtained by Bottcher and Docken<sup>17</sup> using projection operator techniques, and the resonance position for H<sub>2</sub><sup>-</sup> obtained by Eliezer, Taylor, and Williams<sup>18</sup>

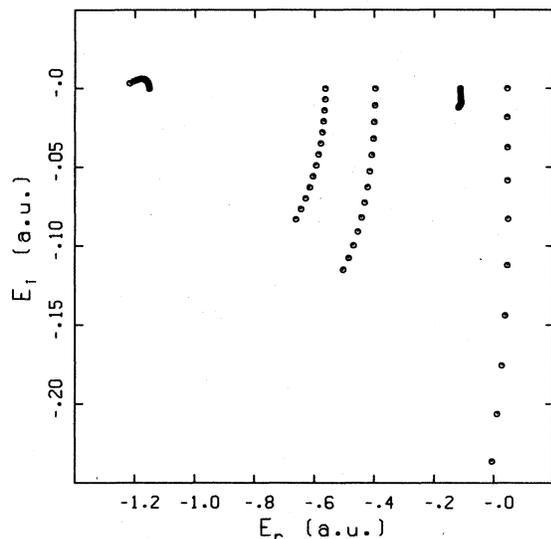


FIG. 1. Variation of the  $H_2^+ 1\Sigma_g^+$  eigenvalues as a function of  $\theta$  with  $\alpha = 1.0$ .  $\theta$  ranges from 0 to 0.24 radians in steps of 0.02.

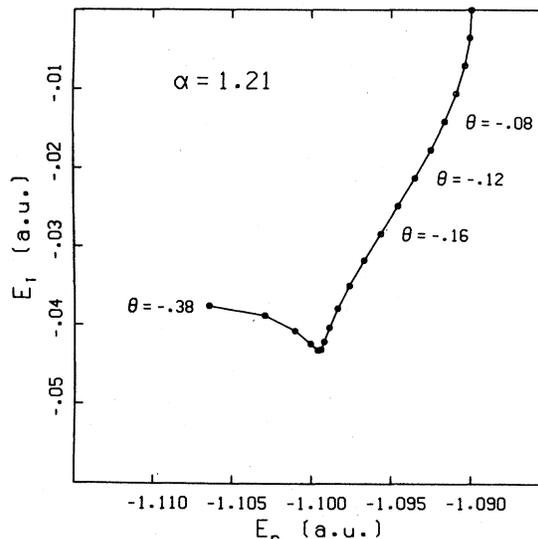


FIG. 2.  $\theta$  trajectory with  $\alpha = 1.21$  for  $H_2^- 2\Sigma_u^+(\sigma_g^2\sigma_u)$  resonance.

using the quasivariational method.

These numerical results represent the first applications of a complex-scaling procedure to true molecular electronic resonance states. As we have stressed, there is as yet no assurance that the complex-scaling procedure we have implemented is a formal extension of the original complex-scaling method as developed by Balslev, Combes, and Simon. However, we state our results for  $H_2$  and  $H_2^-$  as a demonstration that this method can provide useful information about the positions and widths of molecular resonances, while remaining economically feasible. In particular, our procedure avoids the recalculation of two-electron integrals which seems to be required in the Rescigno-McCurdy procedure.<sup>3</sup> We

feel that the method presented here, as well as other methods which extend the complex scaling procedures to molecules, should be further investigated, and that the numerical results we have obtained offer strong encouragement to this pursuit.

#### ACKNOWLEDGMENT

We would like to express our gratitude to Dr. Phil Certain and Dr. Frank Weinhold for many helpful discussions, remarks, and much encouragement during this work. We would also like to thank Dr. Saul Epstein for a discussion of the different possibilities of scaling of the Born-Oppenheimer Hamiltonian. This research was supported by NSF Grants No. CHE77-19941 and CHE76-22760.

TABLE I. Resonances of  $H_2$  and  $H_2^-$  at  $R = 1.4$  a.u.

	$-E_r$ (a.u.)	$-E_i$ (a.u.)	$\alpha_{opt}$	$\theta_{opt}$ (rad)	$E_{res}$ (eV) <sup>a</sup>	$\Gamma$ (eV)
$H_2^+ 1\Sigma_g^+(\sigma_u^2)$	0.0967	0.0222	1.263	0.281	29.04	1.21
		Previous estimate <sup>b</sup>			28.96	0.97
$H_2^- 2\Sigma_u^+(\sigma_g^2\sigma_u)$	1.0995	0.0432	1.205	0.291	1.76	2.35
		Previous estimate <sup>c</sup>			2.00	...

<sup>a</sup> Results in eV relative to ground vibrational level of  $H_2 X^1\Sigma_g^+$ . [For conversion factors see T. E. Sharp, *At. Data* **2**, 119 (1971)].

<sup>b</sup> C. Bottcher and K. Docken, *J. Phys. B* **7**, L5 (1974).

<sup>c</sup> I. Eliezer, H. S. Taylor, and J. K. Williams, *J. Chem. Phys.* **47**, 2165 (1967).

- <sup>1</sup>B. Simon, *Phys. Lett. A* **36**, 23 (1971); *Ann. Math.* **97**, 247 (1973).
- <sup>2</sup>See, for example, W. P. Reinhardt, *Int. J. Quantum Chem.* **S10**, 359 (1976); P. Winkler and R. Yaris, *J. Phys. B* **11**, 1 (1978); N. Moiseyev, P. R. Certain, and F. Weinhold, *Int. J. Quantum Chem.* **14**, 727 (1978); see also the special complex-scaling issue of *Int. J. Quantum Chem.* **14**, 4 (1978).
- <sup>3</sup>See, for example, C. W. McCurdy and T. N. Rescigno, *Phys. Rev. Lett.* **41**, 1364 (1978); B. Simon (unpublished); C. A. Nicolaides and D. R. Beck, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Boston, 1978).
- <sup>4</sup>See, for example, T. N. Rescigno, C. W. McCurdy, and A. E. Orel, *Phys. Rev. A* **17**, 1931 (1978).
- <sup>5</sup>E. Balslev and J. M. Combes, *Commun. Math. Phys.* **22**, 280 (1971); see also J. Aguilar and J. M. Combes, *ibid.* **22**, 269 (1971); B. Simon, *ibid.* **27**, 1 (1972).
- <sup>6</sup>See, for example, G. D. Doolen, *J. Phys. B* **8**, 525 (1975) or W. P. Reinhardt (1976) in Ref. 2.
- <sup>7</sup>E. Brändas and P. Froelich, *Phys. Rev. A* **16**, 2207 (1977); N. Moiseyev, P. R. Certain, and F. Weinhold, *Mol. Phys.* **36**, 1613 (1978); P. Winkler, *Z. Phys. A* **283**, 140 (1977).
- <sup>8</sup>See W. P. Reinhardt (1976) in Ref. 2; J. J. Wendoloski and W. P. Reinhardt, *Phys. Rev. A* **17**, 195 (1978).
- <sup>9</sup>I. Herbst and B. Simon, *Phys. Rev. Lett.* **41**, 67 (1978).
- <sup>10</sup>See N. Moiseyev, P. R. Certain, and F. Weinhold, (1978) in Ref. 7.
- <sup>11</sup>Private communication from a number of sources. This is also alluded to in the first two references in Ref. 3.
- <sup>12</sup>The potential numerical problem associated with the electron-nuclear attraction may be outlined as follows: The matrix element for *s*-type Gaussians is of the form [I. Shavitt, *Methods in Computational Physics*, (Academic, New York, 1963), Vol. 2]:

$$V_{ij}(\eta R) \sim F_0 [(\gamma_i + \gamma_j)(\vec{P} - \eta \vec{R})^2] \\ \times \exp[-(\gamma_i \gamma_j / \gamma_i + \gamma_j)(\vec{R}_i - \vec{R}_j)^2],$$

where  $\vec{P}$  is the weighted center of the two functions with orbital exponents  $\gamma_i$  and  $\gamma_j$  and positions  $\vec{R}_i$  and  $\vec{R}_j$ , respectively,  $\vec{R}$  is the position of the nucleus, and  $F_0$  is the incomplete  $\gamma$  function. The simplest example of the problem occurs for  $\gamma_i = \gamma_j \equiv \gamma$  and  $R_i = R_j = R \neq 0$ . In this case we have

$$\tilde{V}_{ij}(\eta R) \sim F_0 [2\gamma R^2(1 - \eta)^2] \equiv F_0(t).$$

The series expansion for  $F_0(t)$  has a prefactor of  $\exp(-t)$ . Near  $|\eta| = 1$  one may have  $\text{Re}(1 - \eta)^2 < 0$ , and therefore  $V_{ij}$  may become large for large values of the nonlinear parameter  $\gamma$ . In our calculations we do not restrict ourselves to  $|\eta| = 1$ , and though we have encountered numerical instability for large values of  $\theta$  (in  $\eta = \alpha e^{-i\theta}$ ), the stationary points we look for have all occurred with sufficiently small  $\theta$  that this does not appear to be a problem.

- <sup>13</sup>P. Froelich, M. Hehenberger, and E. Brändas, *Int. J. Quantum Chem.* **11**, 295 (1977); N. Moiseyev, P. R. Certain, and F. Weinhold (1978), in Refs. 1 and 7.
- <sup>14</sup>M. J. D. Powell, *Computer J.* **7**, 155 (1964).
- <sup>15</sup>M. Allan and S. F. Wong, *Phys. Rev. Lett.* **41**, 1791 (1978); J. M. Wadehra and J. N. Bardsley, *ibid.* **41**, 1795 (1978).
- <sup>16</sup>S. Huzinga, *J. Chem. Phys.* **42**, 1293 (1965). The Huzinga *s* and *p* functions were augmented with a set of *d* functions with orbital exponents of 0.3. A more detailed discussion of basis set effects will be presented later.
- <sup>17</sup>C. Bottcher and K. Docken, *J. Phys. B* **7**, L5 (1974).
- <sup>18</sup>I. Eliezer, H. S. Taylor, and J. K. Williams, *J. Chem. Phys.* **47**, 2165 (1967).