

<sup>4</sup>L. L. Foldy, Phys. Rev. **83**, 688 (1951).

<sup>5</sup>It is worth noting that the Thomas factor of  $\frac{1}{2}$  which enters into the spin-orbit interaction for electrons is absent for neutrons.

<sup>6</sup>Of course the neutron experiences the electric field of the 82 protons. However, the resultant electromagnetic spin-orbit splitting is part of the energy of the normal  $\gamma$  ( $^{207}\text{Pb}$  without a muon), with respect to which we measure our shifts. Such electromagnetic spin-orbit splittings are important in evaluating Coulomb energies of isobaric analog states. See J. A. Nolen, Jr., and J. P. Schiffer, Ann. Rev. Nucl. Sci. **19**, 471 (1969).

<sup>7</sup>W. Bertozzi, J. Friar, J. Heisenberg, and J. W. Negele, Phys. Lett. **41B**, 408 (1972).

<sup>8</sup>D. Kessler, in *Proceedings of the Third International*

*Conference on High Energy Physics and Nuclear Structure*, edited by S. Devons (Plenum, New York, 1969).

<sup>9</sup>H. Backe *et al.*, Nucl. Phys. **A234**, 469 (1974).

<sup>10</sup>B. Budick, R. Anigstein, and J. W. Kast, to be published. A possible resonance due to the near degeneracy of the  $4f-3p_{3/2}$  muonic intervals with the  $\frac{3}{2}^- - \frac{1}{2}^-$  nuclear interval has been considered. It cannot account for the observed intensity of the nuclear  $\gamma$  ray.

<sup>11</sup>J. Speth, L. Zamick, and P. Ring, Nucl. Phys. **A232**, 1 (1974).

<sup>12</sup>R. Engfer *et al.*, At. Data Nucl. Data Tables **14**, 509 (1974); see also H. K. Walter, Nucl. Phys. **A234**, 504 (1974), p. 530.

<sup>13</sup>The Foldy term in the matrix element, Eq. (1), contributes only  $-10$  eV to the isomer shift.

## Complex Stabilization Method for Resonant Phenomena

B. R. Junker

U. S. Office of Naval Research, Arlington, Virginia 22217

(Received 14 January 1980)

A technique is presented which can be used to compute the complex poles of the resolvent (defined as resonances) directly by use of a square-integrable basis without a coordinate rotation and without explicitly imposing a boundary condition such as a Siegert resonant boundary condition. Such a technique is directly applicable to all phenomena which can be put in the form of a resonance such as photoionization, field ionization, and electron resonances in atoms and molecules.

PACS numbers: 31.15.+q, 34.80.Bm, 34.80.Dp

The description of many interesting phenomena, including field ionization, photoionization (in second quantization), electron resonances in atoms and molecules, and various combinations of these, can be formulated in a resonance picture. That is, the observed structure can be described in terms of the real and imaginary parts (position and width, respectively) of the complex energy,  $E^{\text{res}}$ , of a pole of the scattering matrix.<sup>1</sup>

A number of methods have been developed to try to determine these poles of the  $S$  matrix. Prior to the advent of the complex-coordinate method they all required an explicit boundary condition to extract the scattering information. These techniques could be very difficult to apply to phenomena such as field ionization, where the wave function goes asymptotically as an exponential containing fractional powers of the radial coordinate for just the simple case of a hydrogenic system in a constant electric field, and to molecular resonances.

On the other hand, the advantage of the complex-coordinate method<sup>2</sup> for computing the com-

plex poles of the resolvent operator<sup>3</sup> directly is that for a sufficiently large rotation angle,  $\theta$ , in the transformation

$$r \rightarrow r \exp(i\theta), \quad (1)$$

the resonant wave function  $\psi(\theta)$ , is square integrable. Thus an explicit boundary condition is not required to extract the complex resonant energy. The direct application of this method to molecules, however, results in complete internuclear separations. Although in principle complex internuclear separations are not a theoretical barrier, the retention of the Born-Oppenheimer approximation with real internuclear separations often offers a desirable picture both conceptually and computationally.<sup>4</sup>

A number of techniques have been suggested recently for applying the complex-coordinate method to molecular systems<sup>4,5</sup> while attempting to retain the concept of real internuclear separations. These involve external complex scaling or distorted integration contours. I will now present arguments based on previous complex-coor-

dinate calculations which indicate that one can compute directly the complex resonant energies with a square-integrable basis with the real unrotated Hamiltonian and without explicitly imposing a boundary condition.

In all previous complex-coordinate calculations the basis functions representing the unbound particle<sup>6,7</sup> or, more often, all particles<sup>8</sup> have been chosen to be functions of  $r$  only, i.e., independent of  $\theta$ . In all of these calculations the complex resonant eigenvalue is computed for a number of  $\theta$  values (this set of eigenvalues being called a  $\theta$  trajectory) by use of a variational principle. Although the exact resonant energy is independent of  $\theta$ , only regions of quasistability of the approximate eigenvalue,  $\tilde{E}^{\text{res}}$ , with respect to variations in  $\theta$  are obtained. It is assumed that these are the regions where the variational estimate best approximates the exact resonant energy.

On the other hand, it is clear that the exact resonant wave functions<sup>6</sup> depend on  $r$  and  $\theta$  only in the combination  $r \exp(i\theta)$ . This symmetry requirement implies that any variational wave function,  $\psi^{\theta_1}$ , evaluated at  $\theta = \theta_1$  has an *exactly equivalent* wave function yielding *exactly* the same complex eigenvalues at  $\theta = \theta_2$  (including  $\theta_2 = 0$ ) and that  $\psi^{\theta_2}$  is obtained from  $\psi^{\theta_1}$  by the transformation  $r \rightarrow r \exp[i(\theta_2 - \theta_1)]$ . For all previous complex-coordinate calculations the equivalent variational resonant wave functions at  $\theta_2 = 0$  are square integrable even though the exact resonant wave functions diverge exponentially. That is, in the exact wave function for the complex pole,  $E^{\text{res}}$ , of the resolvent associated with the resonance, the asymptotic form of the radial dependence obeys a Siegert boundary condition, i.e.,

$$\begin{aligned} \psi^S &\simeq \varphi r_j^{-1} \exp(ikr_j) S(k) \\ &= \varphi r_j^{-1} \exp(ik_R r_j) \exp(k_i r_j) S(k), \end{aligned} \quad (2)$$

where

$$E^{\text{res}} = \frac{1}{2} k^2 = \frac{1}{2} (k_R - ik_i)^2, \quad (3)$$

$S(k)$  corresponds to a pole of the  $S$  matrix, and  $\varphi$  is the wave function for all other particles. Since none of these previous approximate wave functions satisfy this boundary condition, explicit imposition of this boundary condition is unnecessary. Instead, the existence of a region in the complex coordinate plane where the resonant wave function is square integrable, and the analyticity of the Hamiltonian and the resonant wave

function, imply that one can compute the complex resonant eigenvalues using the unrotated Hamiltonian with a square-integrable basis without explicitly imposing a Siegert boundary condition.

In these previous calculations  $\theta$  is merely playing the role of a nonlinear variational parameter and the behavior of the  $\theta$  trajectories is merely a result of the use of a variational principle to locate an isolated complex pole of the resolvent.<sup>9</sup> Realizing this I propose the following complex stabilization method for computing the isolated complex poles of the resolvent. Using the unrotated Hamiltonian, one would simply compute nonlinear parameter trajectories instead of  $\theta$  trajectories and stabilize  $\tilde{E}^{\text{res}}$  with respect to variations in the various nonlinear parameters,  $\gamma$ , in the basis set. This stabilization could be performed with each parameter individually, with groups of parameters, or globally with all parameters at one time, including a complex scaling which is effectively what previous complex-coordinate calculations have done, i.e.,  $\gamma \rightarrow \gamma \times \exp(i\alpha)$ . In effect a complex boundary condition is being implicitly imposed on the wave function in the form of complex values over some finite radial range through the variational calculation itself, as opposed to forcing the wave function to have some explicit complex asymptotic functional form such as a Siegert boundary condition or explicitly forcing a matching at some boundary as in  $R$ -matrix theory. This results in a considerable simplification computationally, particularly in the case of phenomena such as field ionization and electron resonances in molecules where the boundary conditions can be complicated. Since I am using the unrotated Hamiltonian directly, I do not require dilation analyticity explicitly.<sup>10</sup> On the other hand, although dilation analyticity is probably overly restrictive, the arguments I have used to justify my method rely on the existence of the complex-coordinate theorems.

To illustrate how such a technique might be employed we will consider a model potential problem which has been previously discussed in the literature<sup>11</sup>:

$$H = T + 7.5r^2 \exp(-r). \quad (4)$$

The energy of the resonance is known to be  $3.42639 - 0.012775i$  a.u. from numerical integration of the Schrödinger equation. The generalization to the  $n$ -particle case is straightforward.<sup>6,12</sup>

Although many choices for the form of the variational wave function are conceivable I have used

the following:

$$\Psi_t = \sum_{i=1}^n c_i \varphi_i(\beta_i, r) + \exp(ikr) \{c_{n+1} \exp(-\alpha r) + c_{n+2} \exp[-(\alpha + \epsilon)r]\}, \quad (5)$$

where  $\beta_i$ ,  $\alpha$ ,  $\epsilon$ , and  $k$  are all real nonlinear parameters with respect to which  $\bar{E}^{\text{res}}$  is to be stabilized, and the  $\varphi_i$  are Slater-type orbitals. If  $\epsilon$  is a small parameter, the explicitly complex basis functions contribute in the region around  $r = \alpha^{-1}$ . The two most important properties of the complex basis functions are that they be square integrable and that a similarity transformation which could transform them to a real basis not exist.

Initially a variational wave function with  $n = 10$  was used and detailed calculations were performed in which  $\bar{E}^{\text{res}}$  was stabilized with respect to all nonlinear parameters individually except  $\alpha$  and  $\alpha + \epsilon$  which were stabilized together. The maximum for the most extended basis function in this wave function occurred around 4.0 a.u. and the resonant eigenvalue obtained was  $3.426\,37 - 0.012\,738i$ . Subsequently nine and then nineteen additional Slater orbitals were added to this core function. In each case all nonlinear parameters for the added Slater orbitals were stabilized together. In addition  $k$  and the pair  $\alpha + \epsilon$  were restabilized. The locations of the maxima of the most extended basis functions in each of these cases were 6.7 and 10.6 a.u., respectively, while the resonant eigenvalues obtained were  $3.426\,39 - 0.012\,779i$  and  $3.426\,39 - 0.012\,774i$  a.u., respectively.

TABLE I. Variation of resonant eigenvalue with respect to  $k$  for 21-term wave function.

$k$	$\Delta E_R$	$\Delta E_I$
1.8270	+7.4(-7)	+4.3(-6)
1.9575	+1.5(-6)	+2.6(-6)
2.0880	+8.9(-7)	+1.3(-6)
2.2185	-4.0(-8)	+2.8(-7)
2.3490	-7.2(-7)	-6.0(-7)
2.4795	-9.6(-7)	-1.4(-6)
2.6100	-6.5(-7)	-2.3(-6)
2.7405	-6.2(-8)	-3.3(-6)
2.8710		

Table I illustrates a typical variation of the complex resonant eigenvalue with respect to variation of a nonlinear parameter which in this case is  $k$ .  $\Delta E_R$  and  $\Delta E_I$  are the changes in the real and imaginary parts of the complex eigenvalue for an incremental change in  $k$ . The eigenvalue of the italicized value of  $k$  is  $3.426\,39 - 0.012779i$ .

Additional details concerning the calculation will be elaborated later.<sup>12</sup> However, several points should be noted. First the complex eigenvalues are a multiparameter function of the nonlinear orbital parameters. As such there is no reason to expect that there is necessarily a single unique set of "optimized values" for the nonlinear parameters. This is well known in large configuration-interaction calculations for bound states. In these calculations we required simultaneous stability of both the real and imaginary parts of the resonant eigenvalue with respect to variations in the nonlinear parameters. Secondly, the magnitude of the variation of  $\bar{E}^{\text{res}}$  with respect to variation of any particular parameter will, of course, depend on the importance of that basis function to the representation of the resonant wave function. This can be estimated by computing the structure projections,  $S_j$ , for each configuration,  $\chi_j$ , where  $S_j$  is defined as

$$S_j = \langle \chi_j | \Psi_t \rangle. \quad (6)$$

In conclusion, I have shown that previous complex-coordinate calculations indicate that one need not describe the resonant wave function exactly asymptotically. In fact, one need not *explicitly* impose a boundary condition at all. This represents a considerable advantage over the Siegert, Kapur-Peierls, and  $R$ -matrix techniques since neither the explicit form nor the explicit location of the boundary condition need be denoted. In addition I have shown that one need not perform a coordinate rotation as in the complex-coordinate method even though one still uses a square-integrable basis. This method is thus directly applicable to molecular systems without the questions of complex internuclear separations, distorted integration contours, external complex scaling, or explicit Siegert boundary conditions ever arising. Successful preliminary calculations on atomic systems<sup>13</sup> and field ionization<sup>14</sup> have also been performed with this method.

<sup>1</sup>See, for example, J. Taylor, *Scattering Theory* (Wiley, New York, 1972), Chap. 12.

<sup>2</sup>The entire special issue of *Int. J. Quantum Chem.* **14**, No. 4 (1978), is devoted to the complex-coordinate method.

<sup>3</sup>In potential scattering the poles of the resolvent can be shown to correspond to the poles of the  $S$  matrix. This is assumed to be the case also in  $n$ -particle scattering.

<sup>4</sup>C. W. McCurdy, Jr., and T. N. Rescigno, *Phys. Rev. Lett.* **41**, 1364 (1978); B. Simon, *Phys. Lett.* **71A**, 211 (1979).

<sup>5</sup>N. Moiseyev and C. Corcoran, *Phys. Rev. A* **20**, 814 (1979).

<sup>6</sup>B. R. Junker, *Int. J. Quantum Chem.* **14**, 371 (1978). In their original paper E. Balslev and J. M. Combes [*Commun. Math. Phys.* **22**, 280 (1971)] showed that the domain of the bound states of the rotated Hamiltonian is the domain of the unrotated Hamiltonian with  $r$  replaced by  $r \exp(i\theta)$ . Here however, we are inter-

ested in the resonance states.

<sup>7</sup>B. R. Junker and C. L. Huang, *Phys. Rev. A* **18**, 313 (1978); B. R. Junker, *Phys. Rev. A* **18**, 2437 (1978); T. N. Rescigno, C. W. McCurdy, Jr., and A. E. Orel, *Phys. Rev. A* **17**, 1931 (1978).

<sup>8</sup>For example, G. D. Doolen, *J. Phys. B* **8**, 525 (1975); G. D. Doolen, J. Nuttall, and R. W. Stagat, *Phys. Rev. A* **10**, 1612 (1974); Y. K. Ho, *J. Phys. B* **10**, L373 (1977).

<sup>9</sup>The variation of a parameter in the Hamiltonian can be related in a straightforward manner to the variation of an equivalent parameter in the wave function.

<sup>10</sup>R. Yaris, J. Bendler, and R. Lovett, *Phys. Rev. A* **18**, 1816 (1978).

<sup>11</sup>R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukumar, *J. Phys. B* **7**, 2189 (1974).

<sup>12</sup>B. R. Junker, to be published.

<sup>13</sup>B. R. Junker, to be published.

<sup>14</sup>B. R. Junker, to be published.

## Observation by Neutron Correlation Spectroscopy of a Nonlinear Soft Mode at the Rayleigh-Bénard Instability in Para-Azoxyanisole

K. Otnes and T. Riste

*Institutt for Atomenergi, N-2007 Kjeller, Norway*

(Received 31 January 1980)

By use of neutron correlation spectroscopy a soft mode has been found for the Rayleigh-Bénard instability with frequency  $\omega \sim (R/R_c - 1)^{0.5}$ ,  $R$  denoting the Rayleigh number. The power spectrum shows periodic states split into a narrow band, and some low, perhaps solitary, states. Guided by the autocorrelation function the main features are modeled by phase modulation of the soft mode by the slower modes. A connection is made to the central-mode problem in structural phase transitions.

PACS numbers: 47.25.-c, 61.30.-v

Recently critical fluctuations near the convective instability in para-azoxyanisole (PAA) were reported.<sup>1</sup> The fluctuations manifested themselves as excursions from the time average of the intensity of scattered neutrons. In this paper we report on the dynamics of these fluctuations. For the experiment we used a slab-type aluminum vessel of dimensions  $38 \times 38 \times 5$  mm<sup>3</sup> filled with fully deuterated PAA. Of the long dimensions one is vertical; the other is horizontal and along the common direction of the scattering vector and a magnetic field. The temperature at midheight of the aluminum side walls was kept constant at 121°C. PAA is then a nematic liquid crystal susceptible to alignment by a magnetic field. A vertical temperature difference  $\Delta T$  is obtained by setting the difference of the power fed to the heating elements at the top and bottom of the vessel; positive  $\Delta T$  denotes a warmer bot-

tom than top. Convection sets in at a predictable value  $\Delta T_c$ , the Rayleigh-Bénard instability point.<sup>2</sup>  $\Delta T_c$  is proportional to  $R_c$ , the critical value of the dimensionless Rayleigh number  $R$ . In isotropic liquids  $R = \beta g l^3 \Delta T (\nu \kappa)^{-1}$ . Here  $\beta$  is coefficient of the thermal expansion,  $g$  the gravitational acceleration,  $l$  the vertical layer thickness,  $\nu$  the kinematic viscosity, and  $\kappa$  the heat diffusivity. For our cell only one convection roll is predicted<sup>3</sup> and observed,<sup>4</sup> but higher harmonics develop gradually at increasing  $R$ .<sup>5</sup> Neutron scattering can explore these phenomena in nematic liquid crystals.<sup>4</sup> This method rests on the coupling between molecular orientation and flow, and on the anisotropic scattering power of the molecules. In the absence of flow the molecules are aligned horizontally by the field. The convection makes molecules tilt towards the vertical direction, which in turn gives increased neutron intensity