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Direct calculation of resonance energies and widths using an *R*-matrix approach

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A modified *R*-matrix technique is presented which determines the eigenvalues and widths of resonant states by the direct diagonalization of a complex, non-Hermitian matrix. The method utilizes only real basis sets and requires a minimum of complex arithmetic. The method is applied to two problems, a set of coupled square wells and the Π_g resonance of N₂ in the static-exchange approximation. The results of the calculation are in good agreement with other methods and converge very quickly with basis-set size.

I. INTRODUCTION

The *R*-matrix method has been used successfully to study the electron scattering from both atomic and molecular systems.¹ In all of these applications the internal wave function is matched at the *R*-matrix surface to proper asymptotic forms obtained by numerical integration of appropriate differential equations in the external region. When resonances are present in the scattering cross section they appear quite naturally by eigenphase sums increasing by Π over some range of incident electron energy. By fitting the eigenphase sums to appropriate analytic forms (e.g., Breit-Wigner plus background) it is possible to extract the resonance energy and width from the scattering calculation.

In recent years there have been efforts to develop methods which calculate the resonant energy and width directly. These new techniques reduce the full scattering problem to the diagonalization of a complex, non-Hermitian matrix.² The real part of the eigenvalue gives the resonance position while the imaginary part gives the total width. Two of these approaches, the complex coordinate technique and the Siegert method, have met with considerable success.²⁻⁴ The purpose of this paper is to show how the *R*-matrix method may be easily modified to compute these complex eigenvalues directly. Just as with the complex coordinate and Siegert method we diagonalize a complex non-Hermitian matrix. In fact it is easy to demon-

strate that we are solving the Siegert eigenvalue problem using a modified Hamiltonian which incorporates the boundary conditions required of a resonant state directly in the definition of the operator. This approach has several practical advantages. By imposing the outgoing wave boundary conditions in the modified Hamiltonian we avoid the need to introduce complex basis functions in the variational trial function. This in turn obviates the calculation of complex matrix elements involving the interelectronic interaction. In our approach the complex part of the matrix arises from a singular boundary value operator, first introduced by $Bloch^5$ in nuclear physics, which involves the unknown logarithmic derivative of the resonant wave function on the *R*-matrix surface. When the resonant condition is satisfied there is a self-consistency condition between the logarithmic derivative of the wave function on the surface and the resonance eigenvalue. By diagonalizing the modified Hamiltonian for a few values of the complex momentum it is possible to locate the resonant eigenvalue and fit it to a simple power series. The Newton-Raphson method may then be used to find the precise location of the resonance eigenvalue in the complex plane. In practice we have found that it is possible to determine the position and width of the resonance with three or four diagonalizations of the modified Hamiltonian if the complex momenta are chosen reasonably.

1

24

II. THEORY

Following Bloch⁵ we write the Schrödinger equation in the internal region as

$$(H + L - E | \Psi) = L | \Psi), \qquad (1a)$$

where

$$L = \frac{1}{2} \sum_{C} |C| \delta(r - a) \left(\frac{\partial}{\partial r} - L_{c} \right) (C|.$$
 (1b)

The L operator is defined here with the true logarithmic boundary condition L_c of the outgoing wave, rather than b as in the R-matrix method. Since L_c depends implicitly on the channel momentum, the eigenvalue problem

$$(H+L)|\Psi_i\rangle = E_i(E)|\Psi_i\rangle \tag{2}$$

is energy dependent. These eigenfunctions, first defined by Kapur and Peierls, ⁶ can be used to solve the full scattering problem. Resonances appear when some particular eigenvalue $E_i(E)$ lies near the real axis with a small negative imaginary part. However, true resonances are poles of the S matrix and do not depend on the incident energy. Siegert⁶ demonstrated that the resonance energies satisfy the same eigenvalue problem as Eq. (2) but with the additional condition that

$$(k_c^2)_{\rm res} = 2(E_{\rm res} - \epsilon_c), \qquad (3a)$$

TABLE I. Results for the coupled-square-well problem.

| | Model B E _{res} | Г | | |
|---|-----------------------------|-----------------|--|--|
| Exact | 45.6347 | 0.0729 | | |
| N = 10 | 45.6347 | 0.0729 | | |
| $N = 10^{a}$ | 45.6656 | 0.0718 | | |
| $N = 20^{a}$ | 45.6358 | 0.0729 | | |
| $N = 25^{a}$ | 45.6351 | 0.0729 | | |
| Model D | | | | |
| Exact | 46.8517 | 0.5562 | | |
| N = 10 | 46.8511 | 0.5577 | | |
| $N=10^{a}$ | 46.9005 | 0.5673 | | |
| $N=20^{a}$ | 46.8534 | 0.5567 | | |
| $N=25^{a}$ | 46.8521 | 0.5561 | | |
| Square-well energies and coupling potentials Model B | | | | |
| $E_1 = 0.0$ | $E_2 = 37.5$ | $E_3 = 50.0$ | | |
| $V_{11} = -5.0$ | $V_{22} = -1.0$ | $V_{33} = 8.0$ | | |
| $V_{12} = V_{32} = -0.05$ | | $V_{13} = -5.0$ | | |

| $v_{12} = v_{32} = -0.05$ | | $V_{13} = -5.0$ |
|---------------------------|-----------------|-----------------|
| | Model D | |
| $E_1 = 0.0$ | $E_2 = 37.5$ | $E_3 = 50.0$ |
| $V_{11} = -5.0$ | $V_{22} = -1.0$ | $V_{33} = 8.0$ |
| $V_{12} = 0.05$ | $V_{13} = -5.0$ | $V_{23} = -2.5$ |

^a Reference 2.

 $\epsilon_c = \text{channel energy},$ (3b)

$$k_c$$
 = resonance channel momentum, (3c)

 $E_{\rm res}$ = resonance energy. (3d)

III. NUMERICAL RESULTS

To test the numerical efficiency of the method we have examined two problems. The first consists of three square wells coupled by a constant potential matrix. This problem has been treated by McCurdy and Rescigno² using the conventional Siegert approach as well as by Hazi and Fels⁷ using the stabilization method. It is particularly interesting in that one can compare the convergence patterns of the two numerical procedures and draw some interesting conclusions. In order to keep the calculation extremely simple we have used polynomials as a basis for the expansion of the internal wave function. The required matrix elements of the modified Hamiltonian are absolutely trivial to compute and no complex arithmetic is required until the last step when we assemble the Bloch operator from the surface projections of the elementary polynomial integrals. The second problem we consider is that of $e + N_2$ scattering in the static-exchange approximation. This system is known to have a resonance in $\Pi_{\mathbf{F}}$ symmetry at $E \sim 3.70$ eV when using the Nesbet target wave function.⁸ To carry out the calculation we used our newly developed R-matrix integral program for diatomic molecules modified to account for the complex logarithmic derivative condition of the Siegert eigenvalue problem. In this calculation all one and two electron integrals are computed inside a finite radius in spheroidal coordinates. Just as with the square well no complex arithmetic is required until the last step when we assemble the Bloch matrix elements from the primitive integrals. To facilitate a comparison we have calculated the resonance position and width by a conventional R-matrix calculation using the same basis set.

The results for the coupled-square-well problem are given in Table I. We include the results of McCurdy and Rescigno as a function of basis-set

TABLE II. Position and width of the *d*-wave $e + N_2$ resonance in the static-exchange approximation.

| Method | $E_{\rm res}$ (eV) | Γ (eV) |
|------------------------------|--------------------|--------|
| R matrix ^a | 3.70 | 1.16 |
| Iterative close coupling | 3.77 | 1.20 |
| This work ^a | 3.62 | 1.11 |

^a The *R*-matrix radius was at r=10.

size for comparison. Although the basis sets used in the two calculations were not the same there is no reason to expect that one is substantially better than the other for this particular problem. Given that assumption it is clear that the convergence of our method with basis-set size is better than the standard Siegert technique. One may speculate about the reasons for this since a similar behavior has been observed in a comparison of the Schwinger and Kohn variational methods.⁹ Both the standard Siegert method and the Kohn variational technique employ basis functions in the variational trial function which are required to satisfy certain asymptotic conditions. These functions do not behave correctly for small r and must be multiplied by an arbitrary cutoff to ensure proper behavior near the origin. We argue that this cutoff basis function behaves very poorly in the internal region, causing the other members of the basis set to work very hard to correct the difficulty. The Bloch operator allows us to avoid these irregular solutions and converges much more quickly with basis-set size.

In Table II we present the results of our calculation of the position and width of the *d*-wave $e + N_2$ resonance in the static-exchange approximation. The *R* matrix, and iterative close coupling calculations are shown for comparison. The results of all three methods are in good agreement. One reason for the discrepancy between the Siegert and R-matrix calculations, which were done with the same basis set, lies in the procedure for computing the logarithmic derivatives on the R-matrix surface. In the R-matrix calculation the full zeropotential Schrödinger equation was integrated in spheroidal coordinates from infinity to the R-matrix surface. In the Siegert calculation it was assumed that the angular functions could be treated as Legendre polynomials and the radial functions as Bessel functions. This is an approximation which could easily account for the few-percent difference in the numerical results.

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3

24