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Search Procedure for Multichannel Resonances in Electron-Atom Scattering

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A general computational procedure is described for locating electron-atom scattering resonances and for computing accurate values of the resonance parameters (eigenchannel vector, energy, width, and background eigenphase). The procedure makes use of the anomaly-free multichannel variational method and of the hierarchical continuum Bethe-Goldstone formalism published previously. Eigenvalues of the electronic Hamiltonian in a variational Hilbert space are located by an accurate procedure that takes advantage of analytic properties of the matrices constructed in a variational phase shift calculation. Without computing the Hilbert space eigenvector, effective bound-free matrix elements for a resonance are computed from residues of matrix elements that have poles at the Hilbert space eigenvalues. Each eigenvalue associated with a resonance defines an initial approximation to the resonance parameters, which are then refined by an iterative process that uses variational calculations of the eigenphases. The proposed method combines the ability of stabilization methods to locate narrow resonances with an accurate computation of phase shifts in the resonant region. Calculations of electron-hydrogen resonances are given as examples of the method.

I. INTRODUCTION

In electron-atom scattering, a *resonance* occurs as a rapid increase through π radians of a partial-wave phase shift δ_l in a small energy interval of magnitude $2\Gamma_r$, where Γ_r is the *width* of the resonance. In multichannel scattering, all coupled open scattering channels experience this rapid variation of phase shift in the same energy interval. Reviews of theory and experimental data have been given recently by Burke[1] and by Taylor.[2]

For a single open channel, an isolated resonance can be parametrized by

$$\delta_l(E) = \delta^0_{l0} + \delta^0_{l1}(E - E_r) + \cdots + \tan^{-1}[\tfrac{1}{2}\Gamma_r/(E - E_r)], \tag{1}$$

where $\delta^0_l(E)$, the background or potential scattering phase shift, is a slowly varying function of E near E_r. Equation (1), a Breit-Wigner formula for an isolated resonance, follows from the general resonance theory of Feshbach.[3] For coupled channels, a resonance is described for n coupled channels by the n solutions $\delta_j(E)$ of the equation given by Macek,[3]

$$E - E_r = \tfrac{1}{2}\Gamma_r \sum_{i=1}^{n} y_i^2 \cot[\delta^0_i(E) - \delta(E)]. \tag{2}$$

In this equation, index i refers to an eigenchannel, obtained by diagonalizing the scattering matrix S, or equivalently, by diagonalizing the real symmetric reactance matrix R (or K) defined by[4]

$$S = (1 + iR)/(1 - iR).$$

The coefficients y_i^2, whose sum is unity, determine the partial widths of the resonance with respect to the eigenchannels. Partial widths with respect to physical channels can be obtained by the inverse of the orthogonal transformation that diagonalizes the R matrix.

Equation (2) defines n continuous functions $\delta_j(E)$ that connect the set of background phase shifts δ^0_i, for $E < E_r$, with the same set of asymptotes (modulo π) for $E > E_r$. The sum of eigenphases $\sum_j \delta_j(E)$ increases by π radians in passing through the resonance. If the resonance occurred in a single eigenchannel, the resonant eigenphase, increasing continuously through π radians, would become degenerate (modulo π) in turn with each of the nonresonant eigenphases in all other open channels. Since a noncrossing rule holds for the tangents of the eigenphases (eigenvalues of the R matrix), unless interactions between the eigenchannels are forbidden by symmetry selection rules, such a continuous increase of one eigenphase is not possible but must be broken up by avoided crossings.[3] If the background eigenphases δ^0_i are given as an ordered list in an interval of π radians, the noncrossing rule implies that in a multichannel resonance each function $\delta_j(E)$, which must increase monotonically with energy,[3] connects one of the δ^0_i with the next higher one in the given list, the greatest initial δ^0_i being connected to the least plus π. Since any one background phase δ^0_i could be taken to be the lowest member of the ordered list, the multichannel resonance could be described as a resonance in that eigenchannel (δ^0_i increasing by π radians), perturbed by the other eigenchannels through the effect of the noncrossing rule. The original eigenchannel can be traced through the resonance by the approximate continuity of the eigenchannel vector, jumping from one branch of the function $\delta_j(E)$ to another at each avoided crossing.

This description of the resonance will be most appropriate for the eigenchannel of maximum weight y_i^2 in Eq. (2). In the present method, the important simplifying assumption is made that a single *resonant eigenchannel*, defined in principle by maximum y_i^2, will dominate a given multichannel resonance. Under this assumption, the perturbing effects of avoided crossings with other interacting eigenchannels can be removed by considering the sum of eigenphases $\sum_j \delta_j(E)$, and this sum can be fitted to the single-channel resonance formula, Eq. (1).

Only isolated resonances, for which Γ_r is smaller than the spacing between successive resonances in the same eigenchannel, will be considered here. For such resonances the essential parameters to be determined are the normalized channel eigenvector components (the eigenchannel vector) and the values of $\delta_0 = \delta^0(E_r)$, E_r, and Γ_r to be used in Eq. (1).

The physical origin of scattering resonances is the occurrence of a metastable state that has a finite lifetime because of weak interaction with an adjacent continuum. The simplest example of such a resonance is given by a one-dimensional potential well enclosed by a barrier of finite height. Stationary eigenstates of a particle in the potential well, defined for infinite barrier height, become metastable as the barrier is reduced, interacting with the scattering continuum of states outside the barrier. Resonances of this kind are known as shape resonances. The resonant energy E_r is approximated by the unperturbed metastable energy level, and Γ_r is determined by the matrix element of the Hamiltonian connecting this unperturbed state with the adjacent scattering continuum.

In a system with several degrees of freedom, resonances can arise from the interaction between a nominally discreet excitation of one degree of freedom and an adjacent continuum of excitations of another degree of freedom. In electron-atom scattering, excited states of the target atom are degenerate with the kinetic energy continuum of an external electron incident on the target atom in its ground state. An attractive interaction between the excited target state and the external electron can lead to a metastable compound state with energy below the target atom excitation threshold. Because the adjacent scattering continuum arises from a lower state of the target atom the interaction matrix element is generally small, and the resulting width of the metastable state is small. Such narrow resonances immediately below an excitation threshold are referred to as closed channel resonances,[1] or as core-excited resonances of type 1 (CE1).[2]

If the incident electron has orbital angular momentum greater than zero, an effective rotational barrier can cause a compound state to be metastable even though it lies above the corresponding excitation threshold of the target atom. Because the adjacent scattering continuum contains states arising from the same target atom state, interaction matrix elements are greater than in the case of closed channel resonances (CE1), and the metastable state or resonance is broader. Such resonances, analogous to shape resonances, are referred to as core-excited resonances of type 2 (CE2).[2]

In the close-coupling calculations (including correlation functions in some cases) reviewed by Burke[1] a resonance is found essentially as it would be observed experimentally, by scanning a range of incident electron energy E or wave vector k and looking for characteristic resonant behavior of the phase shift. If no other information is available, in the case of a typically narrow CE1 resonance this may require a tedious search with very small increments of k. Once a resonance is spanned on a sufficiently small scale of k increments, the resonance parameters are obtained by a least-squares fit to Eq. (1) or to its generalization for multichannel resonances.

The formalism of Feshbach[3] can be used directly as a computational procedure by solving the Schrödinger equation in a truncated Hilbert space that excludes the scattering continuum. By suitable constraints, as in the work of O'Malley and Geltman on H and He$^+$, energy eigenvalues in this truncated Hilbert space are variational upper bounds for the energies of metastable states associated with CE1 resonances.[3] A more generally applicable approach, used in the stabilization method of Taylor and co-workers[2,5] is to diagonalize the $N+1$-electron Hamiltonian matrix (for an N-electron target atom or molecule) in the Hilbert space defined by a finite set of normalizable basis functions. Eigenvalues that lie above the threshold of the physical scattering continuum, but are found to be insensitive to improvements in the finite basis function set, correspond to metastable states and scattering resonances. Model calculations by this method[6] show that the eigenvectors represent the projection of scattering continuum wave functions in the variational Hilbert space. For a stabilized eigenvalue, the eigenvector is an accurate representation of a metastable state. The width of the corresponding resonance is related to the rate of change of a stabilized eigenvalue with respect to the dimension of the spatial region effectively spanned by the basis function set.[6] Thus narrow resonances lead to well-defined stabilized energy eigenvalues, unless the basis set is so large that individual eigenvalues cannot be distinguished.

The method used by Hazi and Taylor[6] to compute resonant widths cannot easily be generalized from their model problem. More recently, Hazi and Fels[7] have shown, for single-channel resonances in a two-level model problem, that two or more stabilized eigenvalues corresponding to the same resonance but obtained with different Hilbert space basis functions can be used to determine the parameters

Γ_r and δ_0. In this method, it is necessary to evaluate bound-free matrix elements of the Hamiltonian, connecting the variational Hilbert space to continuum functions.

In earlier papers[8,9] it has been shown how computational procedures similar to those used successfully for stationary states of many-electron atoms can be applied to electron-atom scattering. In the present paper this analysis is extended to include an automatic search procedure for locating multichannel resonances and for computing accurate values of the resonance parameters. Since a bound-bound matrix is constructed in this method, its eigenvalues can be used to locate possible resonances, as in the stabilization method. Then the bound-free and free-free matrices are computed and a version of the multichannel Kohn variational method,[4] modified to avoid spurious singularities characteristic of this method, is used to carry out accurate phase shift calculations near the eigenvalue. Limiting properties at the eigenvalue of matrices occurring in this formalism are used to estimate the range of k to be scanned for a resonance, and to determine the resonant eigenchannel vector. Resonance parameters are determined by fitting the resonant eigenphase to Eq. (1). Thus the present method combines the capability of stabilization methods to locate narrow resonances with the accurate determination of resonance parameters characteristic of the close-coupling method and of its generalizations that include correlation terms.

Details of the method proposed here are given in Secs. II–V. Computations of $^1S^e$ and $^3S^e$ resonances in e^-–H scattering are given in Sec. VI as an example of the method.

II. NOTATION AND DEFINITIONS

Scattering of an electron by an N-electron atom can be described by a stationary state wave function of the general form

$$\Psi = \sum\nolimits_p \mathcal{A}\,\Theta_p \psi_p + \sum\nolimits_\mu \Phi_\mu c_\mu \ . \tag{3}$$

Here Θ_p is a normalized N-electron wave function for the electronic stationary state of the target atom corresponding to scattering channel p; ψ_p is the one-electron *channel wave function* for an open channel with angular momentum l_p, wave-vector magnitude k_p (kinetic energy $\frac{1}{2}k_p^2$ in Hartree atomic units); Φ_μ is one of an assumed orthonormal set of $N+1$-particle Slater determinants that constitute the *Hilbert space component* of Ψ. The operator $\mathcal{A}$ antisymmetrizes $\Theta_p\psi_p$ and includes the factor $(N+1)^{-1/2}$ required to give the antisymmetrized function the same relative normalization as an $N+1$-electron Slater determinant.

The Slater determinants Φ_μ, defined in terms of an N-electron reference state determinant Φ_0, are exemplified by

$$\begin{aligned}
\Phi^a &= \det\phi_1(1)\ \cdots \phi_i(i)\ \cdots\ \phi_j(j)\ \cdots\ \phi_N(N)\phi_a(N+1),\\
\Phi_i^{ab} &= \det\phi_1(1)\ \cdots \phi_a(i)\ \cdots\ \phi_j(j)\ \cdots\ \phi_N(N)\phi_b(N+1),\\
\Phi_{ij}^{abc} &= \det\phi_1(1)\ \cdots\ \phi_a(i)\cdots\ \phi_b(j)\ \cdots\ \phi_N(N)\phi_c(N+1),\\
\cdots &\qquad\qquad \cdots
\end{aligned} \tag{4}$$

where an assumed denumerable orthonormal set of one-electron orbital functions is subdivided into orbitals $\phi_i, \phi_j, \ldots$ occupied in Φ_0, and orbitals $\phi_a, \phi_b, \ldots$ that are orthogonal to the occupied set. *det* implies antisymmetrization and normalization appropriate to the number of electrons. The orbitals are quadratically integrable functions of space and spin variables, normalized to unity. As assumed Hilbert space of orbitals and assumed reference state Φ_0 generate a uniquely defined $N+1$-electron Hilbert space $\{\Phi_\mu\}$ through Eqs. (4) if indices are ordered by the convention

$$i<j<\cdots\leq N<a<b<\cdots \ . \tag{5}$$

The general computational procedure of successive variational calculations using nested subspaces in a lattice decomposition of the Hilbert space $\{\phi_\mu\}$ has been described elsewhere,[8,10] and will not be discussed in detail here. This computational procedure is equivalent to variational solution of a hierarchy of continuum Bethe-Goldstone equations.[8]

The channel wave function is of the form

$$\psi_p = f_p(r)\,Y_{l_p m_{lp}}(\theta,\phi)\,v_{m_{sp}}, \tag{6}$$

where f_p satisfies the usual bound-state boundary condition at $r=0$, is orthogonal (by construction) to all radial functions for Hilbert space orbitals $\{\phi_i;\phi_a\}$ with the same angular and spin quantum numbers, and has the asymptotic form

$$f_p(r) \sim r^{-1}\sin(k_p r - \tfrac{1}{2}l_p\pi + \delta_p). \tag{7}$$

Here Y_{lm} is a normalized spherical harmonic and v is an elementary spin function. Equation (7) can be written in the form

$$f_p = \alpha_{0p}S_p + \alpha_{1p}C_p \tag{8}$$

where

$$S_p \sim r^{-1}\sin(k_p r - \tfrac{1}{2}l_p\pi), \quad C_p \sim r^{-1}\cos(k_p r - \tfrac{1}{2}l_p\pi). \tag{9}$$

These functions are constructed to satisfy the same boundary and orthogonality conditions as f_p.

The target atom wave function Θ_p is expressed as

$$\Theta_p = \sum\nolimits_\sigma \Phi_\sigma c_\sigma^p, \tag{10}$$

where each Φ_σ is a normalized N-electron Slater determinant constructed from the orbital functions $\{\phi_i;\phi_a\}$. The coefficients c_σ^p are obtained as a normalized eigenvector of the N-electron configuration interaction matrix $H_{\sigma\sigma'}$, corresponding to energy eigenvalue E_p. If E is the total energy of the system, an open-channel k value is defined by

$$\tfrac{1}{2}k_p{}^2 = E - E_p\,, \tag{11}$$

for energies in Hartree atomic units, if $E - E_p$ is non-negative. The operator H is the nonrelativistic Schrödinger Hamiltonian, either for N or for $N+1$ electrons, according to context here.

The linearity of the Schrödinger equation makes it possible to express Eq. (3) in the form

$$\Psi = \sum_I \sum_p \alpha_{Ip}\Big(\sum_\sigma \Phi_\sigma^{Ip} c_\sigma^p + \sum_\mu \Phi_\mu c_\mu^{Ip}\Big), \tag{12}$$

where the coefficients α_{Ip}, with $I = 0, 1$, are defined in Eq. (8), and the coefficients c_σ^p are the target state eigenvector coefficients of Eq. (10). The coefficients c_μ of Eq. (3), which are to be determined by the variational scattering calculation, are expanded as

$$c_\mu = \sum_p (\alpha_{0p} c_\mu^{0p} + \alpha_{1p} c_\mu^{1p}). \tag{13}$$

The unnormalized $N+1$-electron Slater determinants Φ_σ^{Ip} are defined by

$$\Phi_\sigma^{0p} = \mathcal{A}\,\Phi_\sigma S_p\,, \quad \Phi_\sigma^{1p} = \mathcal{A}\,\Phi_\sigma C_p\,. \tag{14}$$

It is convenient to define the $N+1$-electron unnormalized functions as

$$\Theta^{Ip} = \sum_\sigma \Phi_\sigma^{Ip} c_\sigma^p\,. \tag{15}$$

These definitions make it possible to apply the multichannel anomaly-free variational method, described previously,[9] to the general wave function given by Eqs. (3) or (12). The auxiliary matrix M_{ij}^{pq}, from which R-matrix elements are determined by the Kohn and inverse Kohn variational formulas,[9] is of the form

$$M_{ij}^{pq} = M_{IJ}^{pq} - \sum_\mu \sum_\nu M_{I\mu}^p (M^{-1})_{\mu\nu} M_{\nu J}{}^q, \tag{16}$$

where $i = I$, $j = J$ with values 0, 1 as in Eq. (12), and p, q are open channel indices. Here M denotes $H - E$, where H is the $N+1$-electron Hamiltonian. The matrices combined in Eq. (16) are the *bound-bound matrix* (Hermitian)

$$M_{\mu\nu} = H_{\mu\nu} - E\delta_{\mu\nu}\,, \tag{17}$$

where

$$H_{\mu\nu} = (\Phi_\mu, H\Phi_\nu); \tag{18}$$

the *bound-free matrix* (Hermitian)

$$M_{\mu I}{}^p = (\Phi_\mu, (H-E)\Theta^{Ip}); \tag{19}$$

and the *free-free matrix* (non-Hermitian)

$$M_{IJ}^{pq} = (\Theta^{Ip}, (H-E)\Theta^{Jq})\,. \tag{20}$$

Details of the computational procedures will be given in a separate publication.[11] One point that is important in searching for resonances is that Eq. (16) is evaluated by triangular factorization of the bound-bound matrix.[12] Since all matrix elements considered here are real numbers, this can be expressed in the form

$$M_{\mu\nu} = \sum_\rho \sigma_\rho T_{\mu\rho} T_{\nu\rho}\,, \tag{21}$$

defining the lower triangular matrix $T_{\mu\rho}$ and a diagonal sign matrix σ_ρ, whose diagonal elements are ±1 only. An auxiliary rectangular matrix B is defined in terms of the bound-free matrix by

$$\sum_\rho T_{\mu\rho} B_{\rho I}^p = M_{\mu I}^p\,. \tag{22}$$

Equation (16) is evaluated in the form

$$M_{ij}^{pq} = M_{IJ}^{pq} - \sum_\mu \sigma_\mu B_{\mu I}^p B_{\mu J}^q\,. \tag{23}$$

Multichannel scattering can be considered in terms of *eigenchannels*, defined formally by an orthogonal transformation that diagonalizes the R matrix. Because channels with different k_p values are combined, it is desirable to avoid the explicit appearance of k_p in the variational formulas. This can be done by multiplying the functions S_p and C_p, Eqs. (9), by $k_p{}^{-1/2}$, as done by Mott and Massey.[4] This has the effect of multiplying each element of M_{ij}^{pq}, Eq. (16), by $(k_p k_q)^{-1/2}$. This will be referred to here as the dimensionless form of this matrix, since the surface integral given by $M_{01}^{pp} - M_{10}^{pp}$ becomes a pure number for the modified matrices. It can easily be verified from analysis given previously[9] that this removes any explicit dependence on k_p from the Kohn and inverse Kohn variational formulas.

III. LOCATION OF A BOUND-BOUND EIGENVALUE

If the eigenvalues E_α of $H_{\mu\nu}$ are nondegenerate, it can easily be shown that the number n_σ of negative-sign elements of σ_ρ, in Eq. (21), is equal to the number of eigenvalues E_α less than E. This number changes by unity as E passes through an eigenvalue.[12] The first step of the resonance search procedure is to monitor n_σ over a relatively coarse grid of reference-channel k values (where $\tfrac{1}{2}k^2 = E - E_0$, with E_0 the lowest eigenvalue of the target atom configuration interaction matrix). The change of n_σ is used to bracket the eigenvalue on a narrower scale by a specified number of cycles of interval halving. Only the bound-bound matrix is needed for this step; the T matrix of Eq. (21) is constructed for each k value, but bound-free and free-free matrix elements are not computed.

When an eigenvalue E_α has been bracketed in a sufficiently small interval, between reference-channel k values that can be denoted by k_1 and k_3, analytic properties of the matrix M_{ij}^{pq} are used to obtain an accurate estimate of the eigenvalue. Bound-free and free-free matrix elements are required, so calculations in this and subsequent steps are equivalent to full phase shift calculations. It has been shown[9] that each element of M_{ij}^{pq} has a simple pole at E_α. Moreover, the determinant of any principal submatrix of M_{ij}^{pq} also has a simple pole at E_α.

If the normalized eigenchannel vectors $x_{\alpha p}$ were known for the corresponding eigenchannels, then M_{ij}^{pq} could be contracted to define dimensionless matrix elements

$$M_{ij}^{\alpha\beta}=\sum_p\sum_q x_{\alpha p}x_{\beta q}M_{ij}^{pq}(k_pk_q)^{-1/2}. \qquad (24)$$

The inverse transformation is

$$M_{ij}^{pq}=\sum_\beta\sum_\gamma x_{\beta p}x_{\gamma q}M_{ij}^{\beta\gamma}(k_pk_q)^{1/2}. \qquad (25)$$

Near an eigenvalue E_α, a unique eigenchannel $\{x_{\alpha p}\}$ is expected to be coupled to the bound-bound eigenfunction denoted by index α. Under this condition, Eq. (16) shows that the pole in M_{ij}^{pq} arises only from elements $M_{ij}^{\alpha\alpha}$, and near E_α Eq. (25) can be approximated by

$$M_{ij}^{pq}\cong x_{\alpha p}x_{\alpha q}M_{ij}^{\alpha\alpha}(k_pk_q)^{1/2}. \qquad (26)$$

Because the vector $x_{\alpha p}$ is normalized to unity, this approximation implies, for E near E_α,

$$M_{ij}^{\alpha\alpha}\cong[\sum_p\sum_q(M_{ij}^{pq})^2/k_pk_q]^{1/2}\operatorname{sgn}(M_{ij}^{11}), \qquad (27)$$

if $x_{\alpha 1}$ is taken to be positive.

Each element of $M_{ij}^{\alpha\alpha}$, computed by Eq. (27), and of the 2× 2 determinant

$$\det M_{ij}^{\alpha\alpha}=M_{00}^{\alpha\alpha}M_{11}^{\alpha\alpha}-M_{01}^{\alpha\alpha}M_{10}^{\alpha\alpha}, \qquad (28)$$

has a simple pole at E_α. This fact is used in the resonance search procedure to determine a value k_2 intermediate between k_1 and k_3 (which bracket E_α) by two-term interpolation to the expected pole of $\det M_{ij}^{\alpha\alpha}$. If $f(k^2)$ is a function with a simple pole between ${k_1}^2$ and ${k_3}^2$, then the interpolated location of the pole is

$${k_2}^2=[f({k_3}^2){k_3}^2-f({k_1}^2){k_1}^2]/[f({k_3}^2)-f({k_1}^2)]. \qquad (29)$$

This formula is used with $f(k^2)$ taken to be $\det M_{ij}^{\alpha\alpha}$ defined by Eqs. (27) and (28).

The full calculation of M_{ij}^{pq} is repeated at k_2. This makes it possible to use a three-point interpolation formula for k_α (corresponding to the eigenvalue $E_\alpha=E_0+\frac{1}{2}{k_\alpha}^2$) and for the residues of the matrix elements $M_{ij}^{\alpha\alpha}$ and of $\det M_{ij}^{\alpha\alpha}$ at E_α. Near a simple pole the function $f(k^2)$ can be represented by

$$f(k^2)=f_0+2a/(k^2-{k_\alpha}^2), \qquad (30)$$

where a is the residue with respect to energy (in Hartree atomic units). The three parameters f_0, a, and k_α can be determined from three values of k near the pole. The required formulas can be derived most easily by differencing values of Eq. (30) in pairs. Thus we have

$$f({k_3}^2)-f({k_1}^2)=\frac{2a({k_3}^2-{k_1}^2)}{({k_3}^2-{k_\alpha}^2)({k_\alpha}^2-{k_1}^2)}, \qquad (31)$$

$$f({k_2}^2)-f({k_1}^2)=\frac{2a({k_2}^2-{k_1}^2)}{({k_2}^2-{k_\alpha}^2)({k_\alpha}^2-{k_1}^2)}, \qquad (32)$$

$$f({k_3}^2)-f({k_2}^2)=\frac{2a({k_3}^2-{k_2}^2)}{({k_3}^2-{k_\alpha}^2)({k_\alpha}^2-{k_2}^2)}. \qquad (33)$$

The parameter a can be eliminated from the last two of these equations to give a formula for ${k_\alpha}^2$:

$${k_\alpha}^2={k_2}^2+[f({k_3}^2)-f({k_1}^2)]\times\left(\frac{f({k_3}^2)-f({k_2}^2)}{{k_3}^2-{k_2}^2}-\frac{f({k_2}^2)-f({k_1}^2)}{{k_2}^2-{k_1}^2}\right)^{-1}. \qquad (34)$$

Since k_1 and k_3 bracket the pole at k_α, if the original interval is sufficiently small $f({k_3}^2)$ and $f({k_1}^2)$ have opposite algebraic signs. Because k_2 is originally determined by linear interpolation to be a reasonable estimate of k_α, the denominator in Eq. (34) is dominated by the terms in $f({k_2}^2)$, both of the same algebraic sign. Thus there is no loss of accuracy due to cancellation and this formula should provide a very accurate value of the small correction ${k_\alpha}^2-{k_2}^2$. This formula is used with $f(k^2)$ taken to be $\det M_{ij}^{\alpha\alpha}$.

The computed value of ${k_\alpha}^2$ can be substituted into Eq. (31) to evaluate the residue parameter a. This determines

$$a^\alpha=\operatorname{Res}_\alpha\det M_{ij}^{\alpha\alpha}=\lim_{E\to E_\alpha}(E-E_\alpha)\det M_{ij}^{\alpha\alpha} \qquad (35)$$

and the matrix elements

$$a_{ij}^\alpha=\operatorname{Res}_\alpha M_{ij}^{\alpha\alpha}=\lim_{E\to E_\alpha}(E-E_\alpha)M_{ij}^{\alpha\alpha}. \qquad (36)$$

IV. INITIAL EIGENCHANNEL PARAMETERS

Since k_2 is close to k_α, Eq. (26) should be valid for $M_{ij}^{pq}(k_2)$. By fixing the index $q=1$, this equation can be used to estimate the normalized eigenchannel vector $x_{\alpha p}$ for the eigenchannel associated with the bound-bound eigenvalue $E_\alpha(k_\alpha)$:

$$X_{\alpha p}\cong M_{ij}^{p1}[\sum_r(M_{ij}^{r1})^2(k_p/k_r)]^{-1/2}. \qquad (37)$$

Since this estimate should be independent of the indices ij, the particular matrix elements 00 are used.

When there is only a single open channel (elastic scattering), variational formulas for the phase shift reduce to simple expressions in terms of the 2×2 matrix M_{ij}.[9] The phase shift at an eigenvalue E_α depends only on the residues

$$\lim_{E\to E_\alpha}(E-E_\alpha)M_{ij}(E). \qquad (38)$$

From Eq. (16) it is clear that these residues involve only the bound-free matrix elements. A formula of this kind, taking advantage of limiting behavior at an eigenvalue E_α, was proposed by Harris[13] as a general computational method for elastic scattering. These formulas should be valid for the eigenphase in eigenchannel $\{x_{\alpha p}\}$ in the vicinity of an eigenvalue E_α, if $M_{ij}^{\alpha\alpha}$ as defined by Eq. (24) is used in the single-channel formulas. The further approximation, Eq. (27), also valid near E_α, is used to define eigenchannel matrix elements and the residues are evaluated by Eqs. (35) and (36).

For a single channel, the Rubinow (inverse Kohn) value t_R of $\tan\delta$ is given by

$$t_R = -\tfrac{1}{2}\Gamma_\alpha^R(E)/[E - E_\alpha - \Delta_\alpha^R(E)], \tag{39}$$

where

$$\Gamma_\alpha^R(E) = 4k^{-1}(E - E_\alpha)M_{00} \tag{40}$$

and

$$\Delta_\alpha^R(E) = -2k^{-1}(E - E_\alpha)(M_{10} - 2k^{-1}\det M). \tag{41}$$

The Kohn value t_k of $\tan\delta$ is given by[9]

$$t_K = [E - E_\alpha - \Delta_\alpha^K(E)]/\tfrac{1}{2}\Gamma_\alpha^K(E), \tag{42}$$

where

$$\Gamma_\alpha^K(E) = 4k^{-1}(E - E_\alpha)\, M_{11} \tag{43}$$

and

$$\Delta_\alpha^K(E) = 2k^{-1}(E - E_\alpha)(M_{01} + 2k^{-1}\det M). \tag{44}$$

In the limit $E \to E_\alpha$ these parameters all have well-defined values expressed in terms of residues of M_{ij} and of $\det M$. In particular, for dimensionless matrix elements, we have

$$\Delta_\alpha^R(E_\alpha) = -2(a_{10} - 2a), \quad \Delta_\alpha^K(E_\alpha) = 2(a_{01} + 2a), \tag{45}$$

where the residues are defined by Eqs. (35) and (36). The single-channel formulas given here show clearly that dimensionless matrix elements are obtained by absorbing a factor k^{-1} into each matrix element M_{ij}.

The residues at a single eigenvalue near a resonance do not give enough information to determine the resonance parameters (δ^0, Γ_r, E_r or k_r), since at least the first derivatives of the functions $\Gamma(E)$ and $\Delta(E)$ are needed. However, Eq. (39) implies that a zero of $\cot\delta$ occurs at a displacement from E_α approximated by $\Delta_\alpha^R(E_\alpha)$, and Eq. (42) implies that a zero of $\tan\delta$ occurs at the approximate displacement $\Delta_\alpha^K(E_\alpha)$. Since these two points must be separated by a phase interval of $\tfrac{1}{2}\pi$, if a resonance occurs in the vicinity of E_α the relative separation of these points can be used to fix the magnitude of the interval of E or k to be scanned for the resonance.

Since an interval ΔE in Hartree atomic units corresponds to an interval $k\Delta k$, Eqs. (45), applied to the residues of $M_{ij}^{\alpha\alpha}$, define two values of k expected to span the width of the resonance:

$$\begin{aligned} k^R &= k_\alpha - 2k_\alpha{}^{-1}(a_{10}^{\alpha\alpha} - 2a^{\alpha\alpha}), \\ k^K &= k_\alpha + 2k_\alpha{}^{-1}(a_{01}^{\alpha\alpha} + 2a^{\alpha\alpha}). \end{aligned} \tag{46}$$

For a single channel, the residues a_{ij} for dimensionless matrix elements reduce to products of bound-free matrix elements,[9]

$$a_{00} = k^{-1} M_{\alpha S}^2, \quad a_{10} = a_{01} = k^{-1} M_{\alpha S} M_{\alpha C},$$

$$a_{11} = k^{-1} M_{\alpha C}^2 \;, \tag{47}$$

where index α refers to an eigenvector of the bound-bound matrix. The residue a of $\det M$ cannot be expressed in terms of $M_{\alpha S}$ and $M_{\alpha C}$.[9] If a factor $k^{-1/2}$ is absorbed into functions S, C to give S', C' appropriate to dimensionless free-free matrix elements, Eqs. (47) imply

$$M_{\alpha S'} = (a_{00})^{1/2}, \quad M_{\alpha C'} = (a_{11})^{1/2}\operatorname{sgn} a_{10}, \tag{48}$$

if the arbitrary phase of eigenvector α is chosen to make $M_{\alpha S'}$ positive. Together with the residue a, these bound-free matrix elements can be used, as in the Harris method,[13] to compute the scattering phase shift at E_α.[9] In the present method, Eqs. (48) are used to give effective bound-free matrix elements for the eigenchannel α. The eigenphase is given by the usual single-channel formulas. These bound-free elements for the eigenchannel can also be used to compute resonance parameters by the method of Hazi and Fels[7] if two or more stabilized eigenvalues are located near a given resonance.

Because the two energy displacements given by Eqs. (45) approximately locate zeroes, respectively, of $\cot\delta$ and $\tan\delta$, their difference gives an estimate of the energy interval in which δ changes by $\tfrac{1}{2}\pi$. From Eq. (1), if this interval were centered at the resonant energy E_r, it would be equal to the width Γ_r. Hence Eqs. (45) give an estimated width in the form

$$\Gamma_r \cong |\Delta_\alpha^K - \Delta_\alpha^R| = 2|(a_{01} + a_{10})|. \tag{49}$$

From Eqs. (40), (43), and (47)–(49), this can be expressed as

$$\begin{aligned} \Gamma_r &\simeq 4k^{-1}|M_{\alpha S} M_{\alpha C}| = 4|M_{\alpha S'} M_{\alpha C'}| \\ &= 4(a_{00}a_{11})^{1/2} = [\Gamma_\alpha^R(E_\alpha)\Gamma_\alpha^K(E_\alpha)]^{1/2}. \end{aligned} \tag{50}$$

This geometrical mean formula, which has not been derived previously, makes it possible to estimate the resonance width from bound-free matrix elements at a *single* eigenvalue E_α.

Because this estimate of Γ_r makes use of both the Kohn and inverse-Kohn variational formulas, it is not valid near a zero of either M_{00} or M_{11}.[9] This requires $M_{\alpha S'}$ and $M_{\alpha C'}$ to be of comparable magnitude. From its derivation, it is clear that Eq. (50) will be inaccurate unless the derivatives of $\Delta_\alpha^R(E)$ and $\Delta_\alpha^K(E)$ are small compared with their respective values at E_α. These derivatives cannot be estimated from information available at a single eigenvalue E_α.

V. DETERMINATION OF RESONANCE PARAMETERS

Only those eigenvalues E_α that are insensitive to augmentation of the basis Hilbert space for the bound-bound matrix, in the sense of the stabilization method, correspond to actual resonances. Generally some prior knowledge is available to suggest the quantum numbers and location of a resonance.[1,2] The present search procedure is intended for use in this context.

If E_α corresponds to a true resonance, the phase shift in the resonant eigenchannel will be described by Eq. (1) near E_α. If E is sufficiently close to E_r, a three-parameter formula can be used to fit the eigenphase. Expressed in terms of the reference-channel k value, this is

$$\delta(k^2) = \delta_0 + \tan^{-1}[\Gamma_r/(k_r^2 - k^2)]. \qquad (51)$$

For each value of k, a full multichannel calculation is carried out, determining eigenphases and eigenchannel vectors. The sum of the eigenphases is computed for all open channels that are not orthogonal to the comparison channel vector, and this sum is used in Eq. (51) as if it were the phase shift $\delta(k^2)$ for a single resonant channel.

Three eigenphases δ_1, δ_2, and δ_3, for three values of k (k_1, k_2, k_3), can be used to determine the three parameters k_r, Γ_r, and δ_0 in Eq. (51). Instead of δ_0, it is somewhat more convenient to use the phase shift at resonance

$$\delta_r = \delta_0 + \tfrac{1}{2}\pi \qquad (52)$$

as the third parameter. From Eq. (51), we have

$$\tan(\delta_r - \delta_k) = (k_r^2 - k^2)/\Gamma_r, \qquad (53)$$

where δ_k denotes $\delta(k^2)$.

The multiple-angle formula for $\tan(\alpha - \beta)$ can be used to eliminate δ_r, giving the expressions:

$$(k_2^2 - k_1^2)\cot(\delta_2 - \delta_1) = \Gamma_r + \Gamma_r^{-1}(k_r^2 - k_2^2)(k_r^2 - k_1^2), \qquad (54)$$

$$(k_3^2 - k_2^2)\cot(\delta_3 - \delta_2) = \Gamma_r + \Gamma_r^{-1}(k_r^2 - k_3^2)(k_r^2 - k_2^2).$$

Subtracting these two equations and using Eq. (53) to replace $(k_r^2 - k_2^2)/\Gamma_r$ by $\tan(\delta_r - \delta_2)$ results in

$$\delta_r = \delta_2 + \tan^{-1}\left(\frac{(k_2^2 - k_1^2)\cot(\delta_2 - \delta_1) - (k_3^2 - k_2^2)\cot(\delta_3 - \delta_2)}{k_3^2 - k_1^2}\right). \qquad (55)$$

If this value of δ_r is used to compute $\tan(\delta_r - \delta_1)$ and $\tan(\delta_r - \delta_3)$, Eq. (53) can be used to derive exact three-point formulas for Γ_r and k_r^2:

$$\Gamma_r = (k_3^2 - k_1^2)/[\tan(\delta_r - \delta_1) - \tan(\delta_r - \delta_3)], \qquad (56)$$

$$k_r^2 = [k_3^2\tan(\delta_r - \delta_1) - k_1^2\tan(\delta_r - \delta_3)]/[\tan(\delta_r - \delta_1) - \tan(\delta_r - \delta_3)]. \qquad (57)$$

TABLE I. Orbital exponents for basis set A.

$1s$	0.0625, 0.125, 0.25, 0.5, 1.0, 1.5
$2s$	0.5
$2p$	0.1, 0.25, 0.5, 1.0, 1.5, 2.0
$3d$	2.0, 3.0

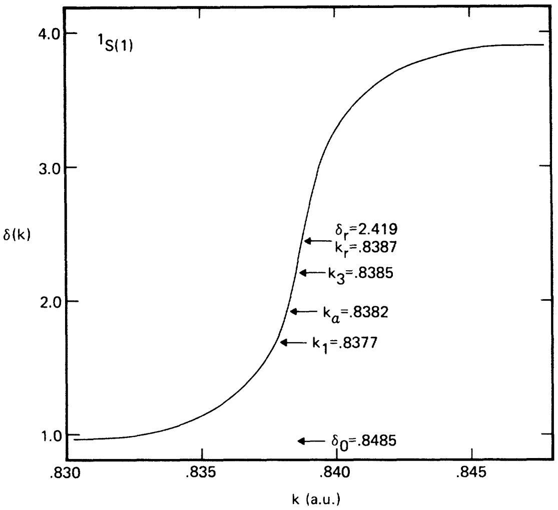

FIG. 1. Phase shift for $^1S^e(1)$ resonance.

These three-point formulas are used iteratively, starting with k_1 equal to the lesser of k^R, k^K of Eq. (46), k_2 equal to their arithmetic mean, and k_3 equal to the greater of them. At each iteration, the computed k_r is compared with the current k_i: k_1, k_2, and k_3. If Δk is the interval $|k_r - k_i|$ of smallest magnitude, the k values for the next iteration are taken to be $k_r - \Delta k$, k_r, and $k_r + \Delta k$, requiring only two new phase-shift calculations. The search terminates when Δk is smaller than some criterion, taken to be 10^{-6} a.u. in the examples given here.

If there is no resonance in the eigenchannels determined by the eigenvalue E_α, limited experience with this iterative search indicates that it diverges rapidly, and can be terminated by testing Δk against an upper limit.

VI. EXAMPLES: e^--H RESONANCES

As a first example of the resonance search procedure we have considered the two lowest $^1S^e$ and the lowest $^3S^e$ resonances in e^- −H scattering, below the $n = 2$ threshold. The computed phase shifts near these resonances are shown in Figs. 1–3. The computations used the orbital basis set defined in Table I. The basis functions are exponentials multiplied by powers of r and spherical harmonics. Further details of these calculations, including the choice of basis orbitals, will be published separately. Despite the fact that these are single-channel resonances, by using a variational wave function of the form of Eq. (1), constrained only by $M_L = 0$, $M_S = 0$, parity even, maximum $l_p = 0$, the calculations treated an effective two-channel problem. The

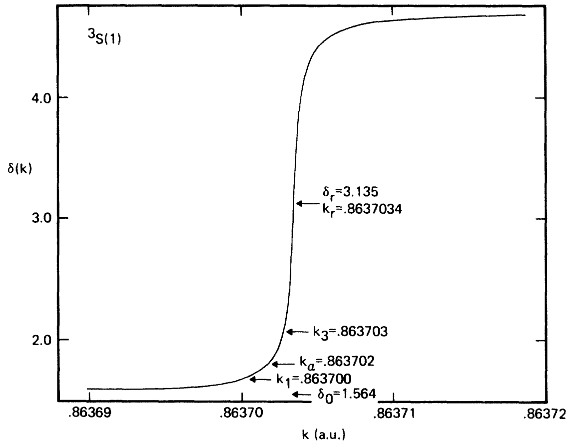

FIG. 2. Phase shift for $^3S^e(1)$ resonance.

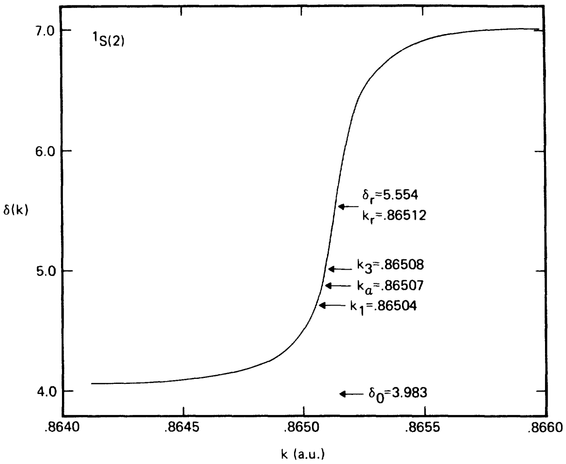

FIG. 3. Phase shift for $^1S^e(2)$ resonance.

Hilbert space $\{\Phi_\mu\}$ included all two-electron functions defined by the basis orbitals. In this example, a unique resonant eigenchannel is defined by symmetry, and the search procedure identified the appropriate singlet or triplet eigenchannel in each case.

Points that are significant in the resonance search procedure are indicated in Figs. 1–3. These include the location of the eigenvalue at k_α [Eq. (34)], the estimated zeros of tan δ and cot δ at k_1 and k_3 [Eqs. (46)], and the actual resonance position k_r [Eq. (57)]. The computed background phase shift δ_0 is also indicated, as is the resonant phase shift δ_r [Eq. (55)]. The figures have been plotted by computing many more points than are required for the resonance search procedure. They verify the qualitative validity of this procedure. In particular, k_α is close to the final k_r, and k_3-k_1 is the same order of magnitude as the resonance width.

Our computed resonance parameters are compared with prior calculations on these hydrogen CE1 resonances in Table II. There is substantial agreement with earlier results, which include the best previous work known to us. The greatest disagreement is in the case of the $^1S^e(2)$ resonance, where further expansion and optimization of our orbital basis set is required. These results are very satisfactory in view of the modest expenditure of computer time; the entire resonance search for $^1S^e(2)$ reported here required 194 sec of CPU time on an IBM 360/91 computer, starting from an eigenvalue search in the k range 0.865 (0.0001) 0.866.

As a second example, we have considered a true $^3S^e$ multichannel CE1 resonance below the $n=3$ threshold. The wave function is constrained by $M_L=1$, $M_S=0$, parity even, maximum $l_p=0$. Because this excludes functions $(2pkp)^3S$, only two ^3S channels are open: $(1sks)$ and $(2sks)$. The two eigenphase shifts $\delta_1(k)$ and $\delta_2(k)$ are plotted in Fig. 4. The figure also shows $\sum\delta=\delta_1+\delta_2$, fitted to the single-channel resonance formula by our search procedure. Values of k_α, k_r, k_1, and k_3 given by the search procedure are indicated, together with $\sum\delta_r$ and $\sum\delta_0$. As in the case of single channels, the validity of the multichannel search procedure is qualitatively evident from the figure.

The orbital basis set used for this calculation is defined in Table III. Because the basis set contains little more than the hydrogenic 1s, 2sp, and 3spd orbitals, it is not expected to provide an accurate

TABLE II. Single-channel resonance energies and widths (eV). (Superscript indicates multiplying power of ten.)

	$^1S(1)$		$^1S(2)$		$^3S(1)$	
	E	Γ	E	Γ	E	Γ
Present work	9.571	4.918^{-2}	10.183	3.615^{-3}	10.150	1.949^{-5}
SOC[a]	9.574	5.44^{-2}	10.178	2.31^{-3}	10.151	1.90^{-5}
Chen[b]	9.559	4.1^{-2}	10.170	2.18^{-3}	10.149	2.01^{-5}
BOW[c]	9.575	5.43^{-2}	10.178	2.41^{-3}	10.151	1.89^{-5}
TB[d]	9.560	4.75^{-2}	10.178	2.19^{-3}	10.150	2.06^{-5}

[a] G. J. Seiler, R. S. Oberoi, and J. Callaway, Phys. Rev. A 3, 2006 (1971).

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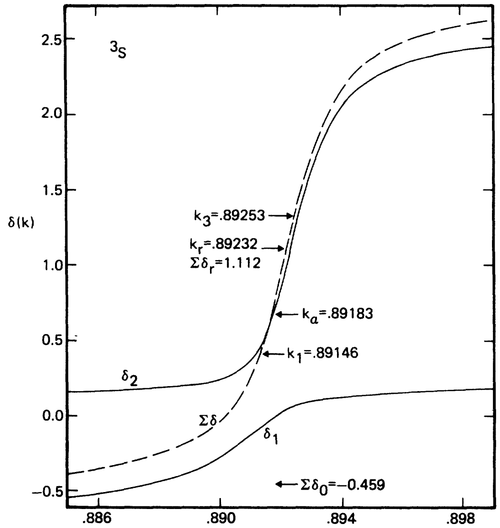

FIG. 4. Eigenphase shifts for $^3S^e$ resonance.

representation either of the channel orbitals or of virtual excitations that describe nonresonant polarization of the target atom. Moreover, the $(2pkp)\,^3S$ channel is omitted. For these reasons this example can be considered only as a model problem, and results should not be compared with other calculations or with experiment.

TABLE III. Orbital exponents for basis set B.

1*s*	0.3333, 0.5, 1.0
2*s*	0.3333, 0.5
3*s*	0.3333
2*p*	0.3333, 0.5, 1.0
3*p*	0.3333
3*d*	0.3333, 0.5, 1.0

The computed width Γ_r, for the example of Fig. 4, is $0.181\,79\times10^{-2}$ hartree, or 4.947×10^{-2} eV. With this width, together with $k_r = 0.892\,32$ a.u., obtained from the search procedure, a satisfactory fit to the computed functions $\delta_1(k)$ and $\delta_2(k)$ is obtained from Eq. (2) with $y^2_{1,2} = 0.8819$, $y^2_{2,1} = 0.1181$. Here the double subscript (1, 2) refers to the background eigenchannel approached by δ_1 for $k < k_r$, and by δ_2 for $k > k_r$, and similarly for subscript (2, 1). The background phases are assumed to be constants: $\delta^0_{1,2} = -0.625\,33$ and $\delta^0_{2,1} = 0.165\,48$.

In this example, the estimated "resonant eigenchannel" vector of Eq. (37) did not give a useful estimate of the weight coefficients y^2_i in Eq. (2). In fact, the projection of the vector computed by Eq. (37) onto the background eigenchannels indicated values $y^2_{1,2} = 0.2560$, $y^2_{2,1} = 0.7440$. This discrepency may be due to inadequate representation of the metastable H$^-$ wave function associated with the resonance, because of the very limited orbital basis used here. Nonetheless, the search procedure using $\sum\delta$ as an effective single-channel resonant phase shift has worked successfully to obtain Γ_r and k_r. In practical applications, accurate values of the parameters δ^0_i and y^2_i in Eq. (2) could be obtained by curve-fitting, with only a few additional phase shift calculations.

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