

Comment on the stabilization method: Variational calculation of the resonance width

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We clarify the computational procedure used in a stabilization calculation of the resonance energy. We propose a new, variational method for the calculation of the resonance width for elastic scattering. The method is based on a minimum principle for the width which holds for L^2 trial functions satisfying certain assumptions. The method gives all the resonance parameters, including the background phase shift, without requiring traditional scattering calculations.

The purpose of this paper is twofold. First, we discuss the computational procedure used in a stabilization calculation of the resonance energy in order to clarify some misconceptions which exist in the literature concerning the method. The discussion is motivated, in part, by a recent paper¹ in which Oppenheimer and Doyle proposed an interesting new method for calculating resonance wave functions. Their method, unlike stabilization, requires a prior knowledge of the background phase shift. Our second purpose is to propose a new variational method for the computation of the resonance width for elastic scattering. The method is based on a minimum principle which holds for L^2 trial functions satisfying certain assumptions. Previous calculations have shown that resonance wave functions obtained in the stabilization procedure satisfy the required assumptions. The proposed method allows for a variational refinement of the nonlinear parameters in the resonance wave function as given by the stabilization procedure. For elastic scattering, the method gives the background phase shift, the width, and the "shifted" resonance energy without requiring a traditional scattering calculation.

Stabilization is a method for computing the energy, width Γ , and background phase shift δ_B of a short-lived complex. It attempts to fit to a discrete basis the most localized continuum wave function in the energy region where a resonance is believed to exist.² Many publications have erroneously described this as a procedure which simply consists of diagonalizing Hamiltonian matrices over successively larger sets of configurations (of which even the smallest is presumed to be sufficient to describe the inner part of the continuum wave function representing the resonance state) and then scanning the resultant eigenvalues for the continual appearance of a stabilized value which,

unlike the others, is insensitive to the size of the basis.³ This prescription is, however, an oversimplification of the definitive procedure we have used for computing resonance states and can easily lead to inaccuracies in reporting resonance energies which would not have resulted through a rigorous application of the stabilization method.

To understand the inadequacy of the above procedure we need only recall that in the time-dependent picture a resonance is a localized wave packet that resembles for a time $1/\Gamma$ a bound state. Therefore upon Fourier transforming to energy space the packet is made up of not just one energy eigenfunction but of many of them, all with energies falling within the width of the so-called packet center.⁴ Each eigenfunction can be expected to resemble the "quasibound state"⁵ in the inner region, so that they contribute constructively in this region. In the outer region, however, these functions should interfere destructively and should be out of phase there. In the procedure mentioned in the first paragraph, all that can be obtained is just one of these functions whose energy can fall anywhere within the width of the resonance. For a very narrow resonance this is of little consequence and good results can be expected provided the initial guess for the state was reasonable. However, the same cannot be said for the more general case of a broader resonance. In a rigorous application of the stabilization method, however, we seek not just any one of the eigenfunctions, but rather that particular one which is the most localized function of the wave packet. It is this fundamental concept of maximal localization which allows us to obtain results devoid of the uncertainties intrinsic to a more simplistic approach.

Having established the basic ideas involved, we will now describe our procedure for stabilization. It starts by guessing, on a physical basis, the most

likely electronic structure in a Hartree-Fock sense⁶ for the state in question. A self-consistent-field⁷ (SCF) calculation is then performed in which, as usual, the orbitals are expressed in terms of some primitive one-electron basis. The result (Ψ^{SCF}) represents a first guess at the inner part of the resonance function being sought. However, at this point, we have no idea of which eigenfunction in the packet we have found. Since the degree of localization is controlled by the nonlinear parameters (referred to collectively as $\bar{\alpha}$) in the one-electron basis being employed, we generate a set of these functions by performing a series of SCF calculations using different values of α . If it is found that the SCF procedure will not converge properly regardless of our choice of α , this indicates that no resonance exists (at least as we have envisioned it). However, we usually do find that proper solutions can be obtained for several values of α (α_i , $i=1, 2, \dots, m$). For each α , we perform a series of configuration-interaction (CI) calculations⁸ in which the basis consists of the SCF wave function obtained for the given α_i and those other configurations (involving the same α_i) which could possibly mix significantly with it. In keeping with the criteria of maximal localization, in the analysis of these calculations it is the eigenvectors which are of immediate importance and not the eigenvalues. In each of these CI's we look for a vector having a high overlap with the SCF wave function. If no such high overlap is found, it indicates that a resonance does not exist. We usually find, however, that for each CI such a vector does exist and that the corresponding eigenvalue is stable with respect to the addition of more configurations. All of the stable eigenvalues obtained in this manner lie within and become a rough measure of the total width of the resonance. Finally, from these m stabilized solutions (each with a different α_i and each representing one of the energy eigenfunctions in the packet mentioned above) we choose that one having the highest overlap with the corresponding SCF wave function. This choice represents the most localized continuum function of the wave packet, and we take its eigenvalue to be the resonance energy. One should note that our procedure fits the whole continuum wave function and not just its innermost part [which in Feshbach's⁹ language is referred to as $Q\psi$ (Ref. 5)], and, as such, it gives the "shifted" resonance energy.¹⁰ Formally, it is quite useful to define Q as the projector onto our stabilized function. This means $P\psi$ is negligible until one reaches the large distance at which the basis becomes inadequate.

This procedure for stabilization was first described in 1967 and has been justified both formally¹⁰ and in actual computations for such broad

resonances as H^{2-} (Ref. 11) and $\text{H}_2^{-}({}^2\Sigma_u)$ (Ref. 2). This method differs from those of Feshbach,⁹ Holoien,¹² Lipsky, and Russek,¹³ and Miller.¹⁴ If variation of nonlinear parameters is not feasible, an alternate procedure for extracting the resonance energies and widths may be used which has been formulated by one of us and Fels¹⁵ and has been elegantly applied by Bhatia.¹⁶ Another method for extracting the width and background phase shift at the resonance energy is given in Ref. 5 and in a note by Lippmann.¹⁷ This latter method has the particular disadvantage of having to extract numerical values for the resonant wave function as a function of position, a procedure not easy to do accurately with standard CI programs.

Lastly, we would like to point out that the perturbation method developed by Drake and Dalgarno¹⁸ is equivalent to all the steps of stabilization described here. Basically, what they have is a variation-perturbation principle for determining the correction to an unperturbed function (which is equivalent to our initial guess) which minimizes the norm of the correction function with respect to scale. If in our CI wave functions we had chosen a normalization which set the coefficient Ψ^{SCF} to unity then their criteria and our overlap criteria would be the same (and are not the criteria of Holoien).

In the following, we consider a new method for obtaining the background phase shift δ_B and the width Γ which is useful in single-channel problems and which involves only integrals of the stabilized function. Hopefully these integrals can be obtained more accurately than values of the resonance function at a point. The method is based on the observation⁵ that for distances spanned by the basis set a stabilized eigenfunction θ_n with energy E_n corresponds, within a normalization constant, to the total scattering function at $E = E_n$. That is,

$$\psi_T^+(E_n) = \text{const} \times \theta_n(E_n) \quad (1)$$

for all stabilized eigenvalues $E_n = \frac{1}{2}k_n^2$. Consequently, for a single open channel, the total phase shift δ_T can be extracted from the normalization-independent K -matrix formula¹⁹:

$$K = \tan \delta_T(E_n) = \frac{\langle \theta_n | H - E_n | S(k_n r) \rangle}{\langle \theta_n | H - E_n | C(k_n r) \rangle} \equiv \frac{S_n}{C_n}, \quad (2)$$

where $S(kr)$ and $C(kr)$ are the Ricatti-Bessel and Ricatti-Neuman functions, respectively.

In the discussion above, we have argued that the most localized resonance function (call it θ_r) obtained in the stabilization procedure corresponds to the center of the resonance, i.e., $E_n = E_r$. Now using the fact that at $E = E_r$

$$\delta_T(E_r) = \delta_B + \frac{1}{2}\pi, \quad (3)$$

and using the relation

$$\lim_{x \rightarrow \pi/2} \tan(\delta_B + x) = -1/\tan\delta_B, \quad (4)$$

we obtain the formula used in Ref. 1,

$$\tan\delta_B = -\frac{\langle \theta_r | H - E_r | C(k_r, r) \rangle}{\langle \theta_r | H - E_r | S(k_r, r) \rangle} \equiv -\frac{C_n}{S_n}. \quad (5)$$

Hence knowing θ_r and E_r gives δ_B . Now Γ can be obtained using the formula for the width given by Hazi and Fels,¹⁵

$$\Gamma = (4/k_r) |\langle \theta | H - E_r | [(\cos\delta_B)S(k_r, r) - (\sin\delta_B)C(k_r, r)] \rangle|^2. \quad (6)$$

Interestingly, in Ref. 1, a prior knowledge of δ_B (from a scattering computation) was used in Eq. (5) to determine the optimal α and therefore θ_r and E_r . We have inverted this line of thought, since we claim to know θ_r and E_r from the stabilization procedure.

Oppenheimer and Doyle have found¹ that the formula in Eq. (5) was sensitive to the detailed form of θ_r , and, as such, they used it to determine the nonlinear parameters α . This result has led us to examine in detail the magnitude of the error in the calculated width which can be expected when the resonance function is slightly off the center of the resonance. The analysis given in the Appendix shows that for an eigenfunction θ_n with $E_n = E_r + \frac{1}{2}\gamma$

$$\Gamma_t = \Gamma(1 + \gamma^2/\Gamma^2). \quad (7)$$

Here Γ is the exact width and Γ_t is the approximate width which is obtained from Eqs. (5) and (6) under the assumption that $E_n = E_r$. The result in Eq. (7) holds rigorously for any θ_n which lies within the width of the resonance, i.e., if $2|E_n - E_r| = \gamma < \Gamma$, and which satisfies the relationship

$$\psi_T^+(E_n) = [e^{i\delta_B}\Gamma^{1/2}/2\pi(E_n - E_r + \frac{1}{2}i\Gamma)]\theta_n(E_n). \quad (8)$$

This result is essentially Eq. (1), with the explicit form of the normalization constant derived from Feshbach's theory. Several previous calculations^{1, 15, 16} have shown that resonance wave functions obtained by the stabilization procedure satisfy these two conditions, provided the basis sets are sufficiently large to span the range of the potentials.

The importance of the result in Eq. (7) stems from the observation that Γ_t computed from Eqs. (5) and (6) is an upper bound to the exact width, provided Eq. (8) is valid. Thus we now have a minimum principle at our disposal: The nonlinear parameters α of the basis set can be varied to minimize Γ_t . The minimum value so obtained gives the width of the resonance. Since the minimum occurs for $\gamma = 0$, i.e., $E_n = E_r$, the energy

eigenvalue corresponding to an optimized θ_n (giving the smallest Γ_t) gives the resonance energy including the "shift." The background phase shift δ_B is obtained by using the optimized θ_n in Eq. (5). Again, we emphasize that these conclusions hold provided Eq. (8) is valid for the resonance functions θ_n . Insofar as Eq. (8) is satisfied only approximately, the computed values of E_r , Γ , and δ_B will be approximate.

In an actual computation, the idea of maximum localization should be used first to determine E_r and θ_r . This requires only bound-bound integrals, which are available from standard atomic and molecular computer codes. The minimum principle for Γ is used when δ_B is calculated. It is an added refinement that gives E_r , θ_r , and δ_B to an accuracy, to which the idea of maximum localization, with its emphasis on the inner part of the wave function, is insensitive. The minimum procedure for Γ and the calculation of δ_B require bound-continuum integrals.

The proposed variational procedure for refining the values of the resonance parameters can be utilized not only with the stabilization method, but also with the method of Oppenheimer and Doyle. If a reasonable, but not necessarily accurate, guess for δ_B is available from independent sources, Eq. (5) can be used to find the initial values of the nonlinear parameters α which occur in θ_n .¹ Then Γ_t can be minimized to obtain an improved resonance function θ_n , and from that better values of Γ , E_r , and δ_B can be found.

For multichannel resonances, the stabilization method gives E_r . From a single stabilized wave function the partial widths cannot be obtained, since one does not have the N independent solutions needed to get full multichannel information for N open channels. Although we have not proven it, we believe that it should be possible to get the total width from the stabilized function. This belief is based on the fact that the initial step of stabilization gives a range of stabilized energies and this range is of the order of the total width.

APPENDIX

Consider a normalized resonance function θ_n with energy E_n . If θ_n is stable with respect to increasing the basis set, then E_n satisfies⁵

$$2|E_n - E_r| < \Gamma, \quad (A1)$$

where E_r and Γ denote the exact resonance energy and width, respectively. For sufficiently large basis sets which span the range of the potential, θ_n is proportional to the exact scattering function at $E = E_n$ (except in the asymptotic region), i.e., θ_n satisfies Eq. (1). The normalization constant

can be expressed in terms of the resonance parameters using the Feshbach formalism,⁹ with the result given in Eq. (8).

One of us and Fels have shown¹⁵ that a trial value of the width, Γ_t , can be calculated from θ_n using the formula

$$\Gamma_t = (4/k_n) |\langle \theta_n | H - E_n | \sin(k_n \gamma + \delta_{Bt}) \rangle|^2, \quad (\text{A2})$$

where δ_{Bt} denotes the trial value of the background phase shift. Using Eq. (8) in (A2), one obtains the result¹⁵

$$\Gamma_t = [\Gamma^{1/2} \cos(\delta_{Bt} - \delta_B) + 2\Gamma^{-1/2}(E_n - E_r) \sin(\delta_{Bt} - \delta_B)]^2, \quad (\text{A3})$$

where δ_B denotes the exact background phase shift. The validity of Eq. (A3) for stabilized resonance functions has been verified by several groups.^{1, 15, 16} If we assume that for E near E_r the energy dependence of the total phase shift $\delta_T(E)$ is given by the Breit-Wigner form, then δ_B is given by

$$\delta_B = \delta_T(E_n) - \tan^{-1}[\Gamma/2(E_r - E_n)]. \quad (\text{A4})$$

Defining $E_n = E_r + \frac{1}{2}\gamma$ and using Eq. (2) for $\delta_T(E_n)$, we obtain

$$\tan \delta_B = (S_n \gamma + C_n \Gamma) / (C_n \gamma - S_n \Gamma). \quad (\text{A5})$$

Equation (A5) is equivalent to

$$\sin \delta_B = -(S_n \gamma + C_n \Gamma) [(S_n^2 + C_n^2)(\Gamma^2 + \gamma^2)]^{-1/2}, \quad (\text{A6})$$

$$\cos \delta_B = (S_n \Gamma - C_n \gamma) [(S_n^2 + C_n^2)(\Gamma^2 + \gamma^2)]^{-1/2}, \quad (\text{A7})$$

The above choice of signs is consistent with Eq. (3).

On the other hand, the trial value of the background phase shift, δ_{Bt} , is obtained from Eq. (5), or by assuming that $E_n = E_r$ or $\gamma = 0$:

$$\sin \delta_{Bt} = -C_n (S_n^2 + C_n^2)^{-1/2}, \quad (\text{A8})$$

$$\cos \delta_{Bt} = S_n (S_n^2 + C_n^2)^{-1/2}. \quad (\text{A9})$$

Substituting Eqs. (A6)–(A9) into Eq. (A3), one obtains after some algebra

$$\Gamma_t = \Gamma(1 + \gamma^2/\Gamma^2).$$

It is interesting to note that the error in Γ is independent of the “bound-continuum” matrix elements S_n and C_n , and it depends only on how far θ_n and E_n are removed from the true center of the resonance.

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⁶This wave function is usually a restricted Hartree-Fock wave function which, in most instances, consists of a single Slater determinant. However, if we are dealing with a state which can correlate significantly, it may be a linear combination of such configurations. For example, the wave function for He⁻ S[1s2s²] would be C[1s2s²] + C[1s2p²].

⁷Care must be taken not to require tight Hartree-Fock convergence limits, since, in the process of refining the wave function, the non-bound-state nature of the state will cause the SCF procedure to find sinusoidal functions that represent larger-radius parts of the function.

⁸The key idea upon which this whole method rests is, of course, the fact that a diagonalization procedure, given a basis set, “chooses” the coefficients and eigenvalues that best fit continuum eigenfunctions (Ref. 4). For a discrete basis, this fit can best be made where the continuum resembles a bound state, i.e., near the resonance energy E_r . Hence one obtains a good fit (large coefficient) when one has a continuum function that is part of the resonant packet.

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