New bounds to resonance eigenvalues

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New bounds to the autoionization and predissociation resonance position and width (which are associated with a complex-coordinate eigenvalue) are derived. An illustrative numerical example is presented.

The complex-coordinate method[1] enables us to isolate the resonance state from the other states in the continuum and to calculate the autoionization and predissociation resonances by techniques which were developed for bound states. The complex-coordinate method has been successfully employed to atomic, molecular, van der Waals, and gas-surface scattering resonances by a Rayleigh-Ritz—like variational procedure, based on square-integrable basis functions.[1] However, the complex analog of the variational theorem[2] is a stationary condition rather than a true variational one which would provide upper bounds to the exact eigenvalues of the Schrödinger equation. The purpose of this paper is to prove that if ϕ describes well enough the exact eigenfunction Ψ then,

$$|E-\bar{E}| \leq |\sigma_c| \leq \sigma_H |\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}, \quad (1)$$

where E is the exact complex resonance eigenvalue

$$\bar{E}=\langle\phi^*|\hat{H}|\phi\rangle/\langle\phi^*|\phi\rangle, \quad (2)$$

$$\hat{H}=\hat{H}(\eta r), \quad \eta=|\eta|\exp(i\theta), \quad (3)$$

and σ_c and σ_H are, respectively, the complex and Hilbert-space variances given by

$$\sigma_c^2=\langle[(\hat{H}-\bar{E})\phi]^*|(\hat{H}-\bar{E})\rangle/\langle\phi^*|\phi\rangle, \quad (4)$$

$$\sigma_H^2=\langle(\hat{H}-\bar{E})\phi|(\hat{H}-\bar{E})\phi\rangle/\langle\phi|\phi\rangle. \quad (5)$$

Note that if ϕ is a complex normalized function $\langle\phi^*|\phi\rangle=1$, then $\langle\phi|\phi\rangle>1$ and it may happen that $|E-\bar{E}|$ will be greater than σ_H. Therefore, the previously published inequality,[3] $|E-\bar{E}|\leq\sigma_H$, for specific choices of ϕ, is not always valid as pointed out before by Siedentop.[4] Our strategy will be as follows. First, we shall prove inequality (1) and explain the requirement that "ϕ describe well enough the exact eigenfunction Ψ." Then, we shall illustrate the application of the new bounds derived here by studying a simple one-dimensional model Hamiltonian.

Proof $|E-\bar{E}| \leq |\sigma_c| \leq \sigma_H |\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}$. Within the finite matrix approximation the proof is straightforward and results from the application of Gerschgorin's theorem to the tridiagonal matrix obtained by Lanczos's method. From Lanczos's method[5(a)] we know that it is possible to construct a matrix $\underline{S}$ such that the result of the similarity transformation, $\underline{S}^{-1}\underline{H}\,\underline{S}$, is a tridiagonal matrix $\underline{T}$ such that

$$T_{11}=\phi_L^T\underline{H}\phi_R\equiv\bar{E},$$

$$T_{12}^2=[(\underline{H}^T-\underline{1}\bar{E})\phi_L]^T(\underline{H}-\underline{1}\bar{E})\phi_R\equiv\sigma_c^2,$$

and $T_{1j}=0$ for $j>2$. The square (possibly non-Hermitian) matrix $\underline{H}$ and $\underline{T}$ have the same eigenvalues. If E is any eigenvalue of $\underline{H}$ (or $\underline{T}$) due to Gerschgorin's theorem, $|E-T_{11}|\leq|T_{12}|$ if the first component of the eigenvector of $\underline{T}$ has the largest modulus.[5(b)] Therefore, we get that, under this requirement, the desired result $|E-\bar{E}|\leq|\sigma_c|$ is obtained with $\phi_L=\phi_R^T$. For the sake of clarity we shall present here a more detailed proof for the case where $\hat{H}$ is an operator.

Let $\hat{H}$ be any Hamiltonian (possibly non-Hermitian) such that

$$\hat{H}|\Psi_R\rangle=E|\Psi_R\rangle, \quad (6)$$

$$\langle\Psi_L|\hat{H}=\langle\Psi_L|E, \quad \langle\Psi_L|\Psi_R\rangle=1. \quad (7)$$

(For example, in the complex-coordinate method $\langle\Psi_L|=\langle\Psi_R^*|$.) If $|\phi_R\rangle$ and $\langle\phi_L|$ are approximations to $|\Psi_R\rangle$ and $\langle\Psi_L|$ such that

$$\langle\phi_L|\phi_R\rangle=1, \quad (8)$$

then

$$\bar{E}=\langle\phi_L|\hat{H}|\phi_R\rangle \quad (9)$$

is an approximation to the exact energy E. (Note that in the complex-coordinate method $\bar{E}=\langle\phi^*|\hat{H}|\phi\rangle$ and $\langle\phi^*|\phi\rangle=1$ since if $|\phi_R\rangle\equiv|\phi\rangle$ then we choose $\langle\phi_L|=\langle\phi^*|$.) Now let us construct a bi-orthogonal basis set,

$$\langle\chi_i|\varphi_j\rangle=\delta_{ij}. \quad (10)$$

If

$$|R\rangle=(\hat{H}-\bar{E})|\phi_R\rangle, \quad \langle S|=\langle\phi_L|(\hat{H}-\bar{E}) \quad (11)$$

then two basis functions of the bi-orthogonal set are given by

$$|\varphi_1\rangle=|\phi_R\rangle, \quad \langle\chi_1|=\langle\phi_L| \quad (12)$$

and

$$|\varphi_2\rangle=\frac{|R\rangle}{(\langle S|R\rangle)^{1/2}}, \quad \langle\chi_2|=\frac{\langle S|}{(\langle S|R\rangle)^{1/2}}. \quad (13)$$

We do not need to specify here how to derive the other basis functions $|\varphi_k\rangle$ and $\langle\chi_k|$ for $k>2$, but we assume that it is possible to obtain a complete set of basis functions which satisfy the bi-orthogonality condition given in Eq. (10). Generally it is known (in order to avoid defective functions, $\langle\chi_i|\varphi_i\rangle=0$) that bi-orthonormalization is possible only when there exists an orthonormal basis sufficiently close to the non-orthonormal basis one wishes to consider. The exact wave function can be expanded in the complete set such that

$$|\Psi_R\rangle=\sum_j C_j|\varphi_j\rangle\ , \tag{14}$$

where

$$C_j=\langle\chi_j|\Psi_R\rangle\ . \tag{15}$$

By substituting Eq. (14) in Eq. (6) we get that

$$\sum_j C_j(\hat{H}-E)|\varphi_j\rangle=0\ . \tag{16}$$

By multiplying from the left-hand side of Eq. (16) by $\langle\chi_i|$, the following secular equations are obtained:

$$\sum_j C_j(H_{ij}-E\delta_{ij})=0\ , \tag{17}$$

where

$$\begin{aligned}H_{11}&=\langle\chi_1|\hat{H}|\varphi_1\rangle=\bar{E}\ ,\\ H_{12}&=\langle\chi_1|\hat{H}|\varphi_2\rangle=\langle\chi_1|\hat{H}-\bar{E}|\varphi_2\rangle=\langle S|R\rangle^{1/2}\ ,\\ H_{1k}&=\langle\chi_1|\hat{H}|\varphi_k\rangle=\langle\chi_1|\hat{H}-\bar{E}|\varphi_k\rangle\\ &=\langle S|\varphi_k\rangle=\langle\chi_2|\varphi_k\rangle\langle S|R\rangle^{1/2}=0\ \text{ for } k>2\ .\end{aligned} \tag{18}$$

Therefore,

$$\begin{bmatrix}\bar{E} & \langle S|R\rangle^{1/2} & 0 & \cdots & 0\\ & & & & \vdots\end{bmatrix}\begin{bmatrix}C_1\\ C_2\\ \vdots\end{bmatrix}=E\begin{bmatrix}C_1\\ C_2\\ \vdots\end{bmatrix}\ . \tag{19}$$

The first row of Eq. (19) reads

$$\bar{E}C_1+\langle S|R\rangle^{1/2}C_2=EC_1\ . \tag{20}$$

If $C_1\neq 0$ then

$$|E-\bar{E}|=|\langle S|R\rangle^{1/2}|\left|\frac{C_2}{C_1}\right|\ . \tag{21}$$

In the case that $|\phi_R\rangle$ is a good enough approximation to the exact wave function $|\Psi_R\rangle$ then

$$|C_2|\leq|C_1| \tag{22}$$

and the bounds for E are obtained,

$$|E-\bar{E}|\leq|\langle S|R\rangle^{1/2}|\ . \tag{23}$$

By using the Schwarz inequality we get that,

$$|E-\bar{E}|\leq|\langle S|R\rangle^{1/2}|\leq(\langle S|S\rangle\langle R|R\rangle)^{1/4}\ . \tag{24}$$

As a matter of fact the requirement of $|C_1|>|C_2|$ is not a strong one since it is expected that the overlap of the exact wave function with $\langle\chi_1|$ will be much greater than the overlap with the "residual" function $\langle\chi_2|$.

TABLE I. The resonance complex-coordinate eigenvalues $\bar{E}$ and the corresponding deviation from the exact value E as function of N, the number of the even-parity harmonic-oscillator basis functions.

N	$\bar{E}$	$\lvert E-\bar{E}\rvert$
5	$2.130\,049\,1-0.020\,965\,6i$	6.2×10^{-2}
10	$2.126\,966\,8-0.015\,337\,0i$	2.5×10^{-4}
15	$2.127\,225\,4-0.015\,416\,8i$	4.1×10^{-5}
20	$2.127\,196\,7-0.015\,460\,8i$	1.3×10^{-5}
25	$2.127\,196\,2-0.015\,419\,5i$	5.5×10^{-6}
30	$2.127\,197\,1-0.015\,449\,7i$	2.4×10^{-6}
35	$2.127\,197\,5-0.015\,446\,3i$	1.1×10^{-6}
45	$2.127\,197\,3-0.015\,447\,3i$	~0

If $\hat{H}$ is the complex-coordinate Hamiltonian $\hat{H}(re^{i\theta})$ then[6]

$$|\langle S|R\rangle|=\left|\frac{\langle[(\hat{H}-\bar{E})\phi]^*|(\hat{H}-\bar{E})\phi\rangle}{\langle\phi^*|\phi\rangle}\right|\equiv|\sigma_c|^2\ , \tag{25}$$

$$\begin{aligned}\langle S|S\rangle&=\langle R|R\rangle\\ &=|\langle(\hat{H}-\bar{E})\phi|(\hat{H}-\bar{E})\phi\rangle/\langle\phi^*|\phi\rangle|\\ &=\sigma_H^2|\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}\end{aligned} \tag{26}$$

and therefore from Eqs. (24)–(26) we get that if $\bar{E}=\langle\phi^*|H|\phi\rangle/\langle\phi^*|\phi\rangle$ is obtained by the complex-coordinate method then

$$|E-\bar{E}|\leq|\sigma_c|\leq\sigma_H|\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}\ . \tag{27}$$

It has been shown on the basis of the Hermitian representation of the complex-coordinate method[7] that

$$|E-\bar{E}|\geq\min(\sigma_H) \tag{28}$$

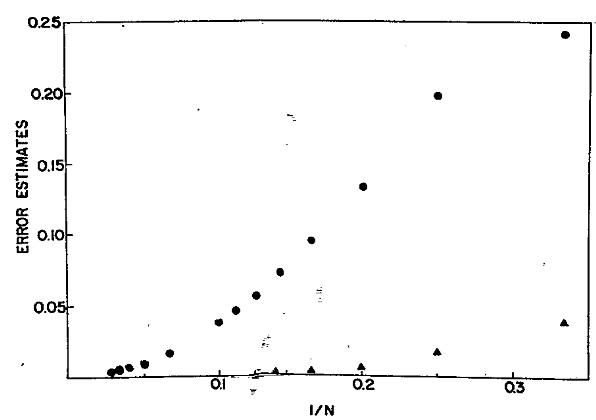

FIG. 1. The bounds $|\sigma_c|$ (denoted by ●) of the resonance complex-coordinate eigenvalue and $|E-\bar{E}|$ (denoted by ▲) for the model Hamiltonian given in Eq. (30), as function of $1/N$, the reciprocal of the number of basis functions.

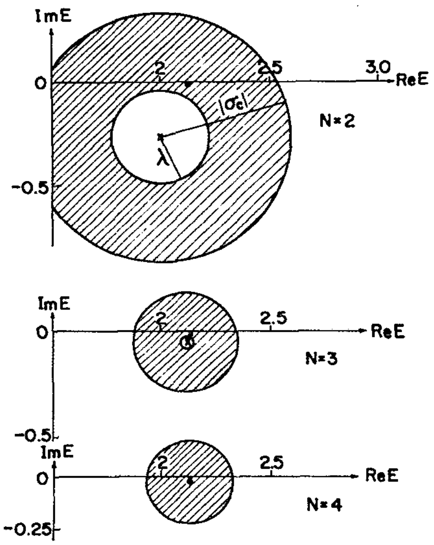

FIG. 2. Bounds of the estimate complex-coordinate resonance eigenvalue $\bar{E}$, obtained for N even-parity harmonic oscillator basis functions. $\bar{E}$ are indicated by the signs " + " and the exact value E by a dot. The dashed areas give an optimal estimate of the resonance location.

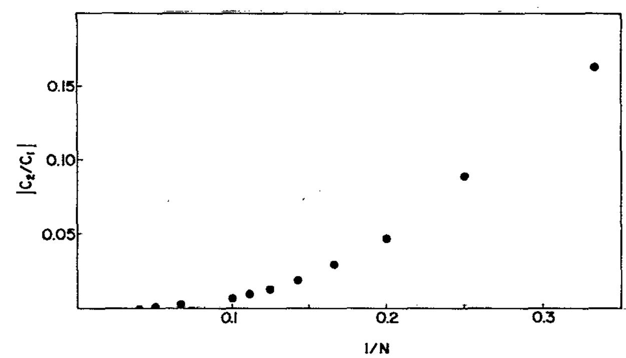

FIG. 3. $|C_2/C_1|$ vs number of basis functions. $|C_2/C_1|$ is defined in the text in Eq. (15).

where $\min(\sigma_H)$ implies $\delta\sigma_H/\delta\phi=0$ for fixed $\bar{E}$ [i.e., $\min(\sigma_H)$ is the *lowest* eigenvalue of $(\hat{H}-\bar{E})^*(\hat{H}-\bar{E})$.] We can summarize it by the following inequality:

$$\min(\sigma_H)\leq|E-\bar{E}|\leq|\sigma_c| \leq\sigma_H\,|\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}\,. \quad (29)$$

An illustrative numerical example. The following model Hamiltonian

$$\hat{H}=-\frac{1}{2}\frac{d^2}{dx^2}+(\tfrac{1}{2}x^2-0.8)\exp(-0.1x^2)+0.8\,, \quad (30)$$

which exhibits predissociation resonances has been used previously to illustrate the variational calculations by the complex-coordinate method[2] and by the Hermitian representation of the complex-coordinate method.[7(c)] As a basis set we used even-parity harmonic-oscillator wave functions. The potential matrix elements were obtained by using the Harris, Harrington, Luintz and Gwinn method[8] which was adverted by Dickinson and Certain to be equivalent to Gaussian quadratures.[9] The matrix elements of $\hat{H}^2\equiv\hat{H}\hat{1}\hat{H}$ and $\hat{H}^*\hat{H}\equiv\hat{H}^*\hat{1}\hat{H}$ were obtained by using the approximate resolution of the identity

$$\hat{1}\simeq\sum_{k=0}^{l}|k\rangle\langle k| \quad (31)$$

and l is large enough such that the $|\sigma_c|$, σ_H, and $\min(\sigma_H)$ are obtained to 6 digits of accuracy.

In the first step of the calculations, a resonance position E_r and width Γ, which are associated with the complex-coordinate eigenvalue $E=E_r-i/2\Gamma$ and the corresponding eigenfunction ϕ, were obtained at a fixed rotation angle $\theta=0.275$ rad (optimal for $N=5$) as a function of the number N of basis functions. From the results which are presented in Table I one can see that for 10 basis functions, for example, a good estimate of the resonance position and width are obtained. However, as one can see from the results presented in Fig. 1, the bound $|\sigma_c|$ obtained for the same 10 even-parity basis functions is quite poor (in Fig. 1, $\sigma_H|\langle\phi|\phi\rangle/\langle\phi^*|\phi\rangle|^{1/2}$ values coincide with $|\sigma_c|$). This result could be expected since (in the case of Hermitian Hamiltonian), the usual experience is that good lower bounds are obtained only for relatively large basis sets. As shown in Fig. 2, the bound $\lambda=\min(\sigma_H)$, together with the lower bounds which are presented in this paper for non-Hermitian Hamiltonians yield an improvement of the error estimate for the resonance position and width. Finally, the condition given in Eq. (22) which should be satisfied if the new bounds are used are easy to fulfill as it is shown in Fig. 3. (Note that $|C_2/C_1|\ll 1$ for any value of $N>1$.)

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