$$\times\left\{e_x^1(\boldsymbol{k})\sum_{i=1}^{4}C_{pix}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)+e_y^1(\boldsymbol{k})\sum_{i=1}^{4}C_{piy}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)\right\}$$

$$-\frac{2}{mMN}\sum_{k>0}\frac{1}{\omega_1^2(\boldsymbol{k})}\left\{e_x^2(\boldsymbol{k})\sum_{k=1}^{4}C_{pix}\cos(\boldsymbol{k}\cdot\boldsymbol{l}_i)+e_y^2(\boldsymbol{k})\sum_{i=1}^{4}C_{piy}\cos(\boldsymbol{k}\cdot\boldsymbol{l}_i)\right\}$$

$$\times\left\{e_x^2(\boldsymbol{k})\sum_{i=1}^{4}C_{pix}\cos(\boldsymbol{k}\cdot\boldsymbol{l}_i)+e_y^2(\boldsymbol{k})\sum_{i=1}^{4}C_{piy}\cos(\boldsymbol{k}\cdot\boldsymbol{l}_i)\right\}$$

$$-\frac{2}{mMN}\sum_{k>0}\frac{1}{\omega_1^2(\boldsymbol{k})}\left\{e_x^2(\boldsymbol{k})\sum_{k=1}^{4}C_{pix}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)+e_y^2(\boldsymbol{k})\sum_{i=1}^{4}C_{piy}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)\right\}$$

$$\times\left\{e_x^2(\boldsymbol{k})\sum_{i=1}^{4}C_{pix}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)+e_y^2(\boldsymbol{k})\sum_{i=1}^{4}C_{piy}\sin(\boldsymbol{k}\cdot\boldsymbol{l}_i)\right\}$$

where $p=x, y, z$ and $q=x, y, z$.

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Width Operator for Resonance Width Determination

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The resonance width may be directly determined by solving an eigenvalue equation for width operator which is derived in this work based on the method of complex scaling transformation. The width operator approach is advantageous to the conventional rotating coordinate method in twofold; 1) calculation can be done in real arithmetics and, 2) so-called θ-trajectory is not required for determining the resonance widths. Application to one- and two-dimensional model problems can be easily implemented.

Introduction

Resonance phenomena occur in various physico-chemical processes including electron-molecule scattering,[1] simple gas-phase reactions such as $H+H_2$.[2] Thus they play important roles in understanding chemical reactions from the dynamical viewpoint. In addition, attempts have been made to relate resonance states with the transition state of chemical reactions.[3,4] The resonance phenomena are generally described as the sharp variations of cross sections at certain energies E_R (resonant energies) and are related to the existence of nearly bound states.[5]

Theoretically resonance can be accurately determined as the pole of scattering matrix.[5] Evaluation of the scattering

matrix, however, requires very large amount of computation even for simple dynamical processes. Another approaches which probably require less computation are the complex L^2 techniques including the rotating coordinate method[6~8] and the method by complex basis set.[9~11] These methods are based on the change of boundary conditions imposed on the Schrödinger equation by introducing complex coordinates or complex basis set.

In the rotating coordinate method, real coordinates are transformed to complex coordinates by complex scaling and the Hamiltonian becomes complex accordingly. Since this transformation is unbounded from real to complex, the spectrum of the Hamiltonian is changed. New complex energies are thus revealed while the discrete eigenvalues for bound states are retained as real by the transformation.[12] As the rotation angle θ is increased, complex energies associated with physical resonances (E_R-$i\Gamma/2$) may be determined.

In the complex basis set method, the Hamiltonian is evaluated in complex bases and the complex energies are obtained from the diagonalization of the Hamiltonian. By varying the number of basis, stationary eigenvalues with respect to basis set size are found to be related with resonance states. Although these methods are relatively simple and efficient compared with the scattering calculations, they may be still computationally very demanding for accurate determination of resonance widths. Evaluation of resonance width, Γ, may be greatly facilitated if the width operator is directly obtained and then an eigenvalue equation for the operator is solved. In this paper the width operator is explicitly derived based on the complex scaling formalism.

Complex Scaling Transformation

Complex scaling transformation rotates ordinary coordinates into complex plane by complex scaling operator (which is not unitary) $\mathbf{U}(\theta)$ given by

$$\mathbf{U}(\theta)=\exp(i\mathbf{S}\theta) \tag{1}$$

where θ is rotation angle and an antihermitian operator $\mathbf{S}$ is given as follows;

$$\mathbf{S}=\frac{1}{2}\left[\frac{d}{dx}x+x\frac{d}{dx}-1\right] \tag{2}$$

With the scaling generator $\mathbf{S}$ given above, $\mathbf{U}$ becomes $(\mathbf{U}^{\dagger})^{-1}=\mathbf{U}^{*}$. A similarity transformation, where the operator $\mathbf{U}$ satisfies above relation, is referred to as a restricted similarity transformation by which the Hamiltonian is changed to be complex symmetric.[12]

Application of $\mathbf{U}(\theta)$ to a coordinate x yields a complex coordinate $xe^{i\theta}$ and a wavefunction $\psi(x)$ is transformed as

$$\mathbf{U}(\theta)\Psi(x)=\Psi(xe^{i\theta}) \tag{3}$$

The Hamiltonian $\mathbf{H}$ is scaled to $\mathbf{H}(\theta)$ as given below

$$\mathbf{H}(\theta)=\mathbf{U}(\theta)\mathbf{H}\mathbf{U}(\theta)^{-1} \tag{4}$$

where $\mathbf{H}(\theta)$ becomes complex symmetric as $\mathbf{H}(\theta)^{\dagger}=\mathbf{H}(\theta)^{*}$.

Width Operator

Scaling the time-independent Schrödinger equation by $\mathbf{U}(\theta)$ yields the following

$$\mathbf{H}(\theta)\psi(xe^{i\theta})=E\psi(xe^{i\theta}) \tag{5}$$

which shows that the discrete eigenvalues are not affected by the transformation. However, new complex eigenvalues are produced from the diagonalization of $\mathbf{H}(\theta)$ since the transformation is unbounded. The complex energies depend on θ as $E(\theta)=E_R(\theta)-i[\Gamma(\theta)/2]$. The complex Hamiltonian can be decomposed as $\mathbf{H}(\theta)=\mathbf{H}_R(\theta)+i\mathbf{H}_I(\theta)$, where both the real and imaginary parts $\mathbf{H}_R(\theta)$ and $\mathbf{H}_I(\theta)$ are hermitian satisfying the complex symmetric property of $\mathbf{H}(\theta)$. Since the diagonalization of $\mathbf{H}(\theta)$ yields complex energies $E_R(\theta)-i[\Gamma(\theta)/2]$ and both $\mathbf{H}_R(\theta)$ and $\mathbf{H}_I(\theta)$ are hermitian, we are led to the following eigenvalue equation for $\mathbf{H}_I(\theta)$

$$\mathbf{H}_I(\theta)\psi(\theta)=-\frac{\Gamma(\theta)}{2}\psi(\theta) \tag{6}$$

where the coordinate dependence of the wavefunction is supressed. From Eq. (6), the width operator $\Gamma(\theta)$ for given angle θ may be defined as

$$\Gamma(\theta)\equiv-2\mathbf{H}_I(\theta) \tag{7}$$

Applying Baker-Housedorf theorem[13] to Eq. (4), $\mathbf{H}(\theta)$ is obtained as an infinite sum of multiple commutator bracket between $\mathbf{S}$ and $\mathbf{H}$ both of which are real as follows

$$\begin{aligned}\mathbf{H}(\theta)&=\exp(i\mathbf{S}\theta)\mathbf{H}\exp(-i\mathbf{S}\theta)\\&=\mathbf{H}+\frac{i\theta}{1!}[\mathbf{S},\mathbf{H}]+\frac{(i\theta)^2}{2!}[\mathbf{S},[\mathbf{S},\mathbf{H}]]+\frac{(i\theta)^3}{3!}\\&\quad[\mathbf{S},[\mathbf{S},[\mathbf{S},\mathbf{H}]]]+\cdots\\&=\mathbf{H}_R(\theta)+i\mathbf{H}_I(\theta)\end{aligned} \tag{8}$$

Since the commutator bracket between the antihermitian $\mathbf{S}$ and the hermitian operator $\mathbf{H}$ is hermitian, all the commutators in Eq. (8) are hermitian operators which satisfy the hermiticity of both $\mathbf{H}_R(\theta)$ and $\mathbf{H}_I(\theta)$. The imaginary part of Eq. (8) gives the detailed expression for $\mathbf{H}_I(\theta)$ as,

$$\begin{aligned}\mathbf{H}_I(\theta)&=\frac{\theta}{1!}[\mathbf{S},\mathbf{H}]-\frac{\theta^3}{3!}[\mathbf{S},[\mathbf{S},[\mathbf{S},\mathbf{H}]]]+\frac{\theta^5}{5!}\\&\quad[\mathbf{S},[\mathbf{S},[\mathbf{S},[\mathbf{S},[\mathbf{S},\mathbf{H}]]]]]+\cdots\\&=\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}\theta^{2n+1}\overbrace{[\mathbf{S},[\mathbf{S},\cdots,[\mathbf{S},\mathbf{H}]\cdots]]}^{2n+1\text{ brackets}}\\&=\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}\theta^{2n+1}C_{\mathbf{S}}{}^{2n+1}\mathbf{H}\end{aligned} \tag{9}$$

where the operator $C_{\mathbf{S}}{}^{2n+1}\mathbf{H}$ is a $(2n+1)$-multiple commutator between $\mathbf{S}$ and $\mathbf{H}$ which is defined as follows

$$\begin{aligned}C_{\mathbf{S}}{}^{2n+1}\mathbf{H}&\equiv\overbrace{[\mathbf{S},[\mathbf{S},\cdots,[\mathbf{S},\mathbf{H}]\cdots]]}^{2n+1\text{ brackets}}\\&=\sum_{l=0}^{2n}(-1)^l\frac{(2n)!}{l!(2n-l)!}\mathbf{S}^{2n-l}[\mathbf{S},\mathbf{H}]\mathbf{S}^{l}\end{aligned} \tag{10}$$

The width operator $\Gamma(\theta)$, which is hermitian, is obtained by combining Eqs. (7), (9), and (10) as below

$$\Gamma(\theta)=-2\sin(\theta C_{\mathbf{S}})\mathbf{H} \tag{11}$$

where $C_{\mathbf{S}}\mathbf{H}$ is $C_{\mathbf{S}}\mathbf{H}=[\mathbf{S},\mathbf{H}]$.[14] Eigensolutions for the opera-

tor $\Gamma(\theta)$ are the widths as functions of θ as shown below

$$\Gamma(\theta)\phi_n(\theta)=\Gamma_n(\theta)\phi_n(\theta) \tag{12}$$

where $\Gamma(\theta)$ is given in Eq. (11) and its eigenvalues $\Gamma_n(\theta)$ are real. To solve Eq. (12), consider a following eigenvalue equation for $[\mathbf{S}, \mathbf{H}]$,

$$[\mathbf{S}, \mathbf{H}]|m>=\alpha_m|m> \tag{13}$$

The operator $[\mathbf{S}, \mathbf{H}]$ can be evaluated explicitly using Eqs. (2) and (13) as shown below

$$[\mathbf{S}, \mathbf{H}]=-2\left[\frac{\mathbf{p}^2}{2m}+V_{eff}\right] \tag{14}$$

where $V_{eff}(x)$ is $V_{eff}(x)=-(1/2)x(dV/dx)$ and $V(x)$ is the potential energy of the system. Since $[\mathbf{S}, \mathbf{H}]$ is bounded in certain regions of space, a number of its lower eigenstates may be bounded which are of our interest for the determination of resonance widths. If the multiple commutator for $n>0$ of Eq. (10) is applied to $|m>$ which is the bound eigenstate of $[\mathbf{S}, \mathbf{H}]$, the result will include the terms containing $\mathbf{S}^l|m>$ for l upto $2n$. Since $|m>$ is bounded, $\mathbf{S}^l|m>$ would become bounded and its norm, however, would be progressively smaller as l is increased ($\|\mathbf{S}|m>\|<\||m>\|$). We may therefore truncate the infinite sum of Eq. (9) according to the desired accuracy. Taking the series upto $n=1$, the width operator $\Gamma(\theta)$ can be approximated as follows

$$\Gamma(\theta)_{appr}=-2\left\{\frac{\theta}{1!}[\mathbf{S}, \mathbf{H}]-\frac{\theta^3}{3!}\left(\mathbf{S}^2[\mathbf{S}, \mathbf{H}]+[\mathbf{S}, \mathbf{H}]\mathbf{S}^2-2\mathbf{S}[\mathbf{S}, \mathbf{H}]\mathbf{S}\right)\right\} \tag{15}$$

The θ-dependent widths $\Gamma_n(\theta)$ may be obtained approximately by evaluating the expectation values of $\Gamma(\theta)_{appr}$ in terms of bound eigenstates of $[\mathbf{S}, \mathbf{H}]$ given below

$$\Gamma_n(\theta)\approx<n|\Gamma(\theta)_{appr}|n>$$
$$=-2\left\{\theta\alpha_n-\frac{\theta^3}{3}\left(\alpha_n<n|\mathbf{S}^2|n>-<n|\mathbf{S}[\mathbf{S}, \mathbf{H}]\mathbf{S}|n>\right)\right\} \tag{16}$$

In order to determine the physical resonances from the θ-dependent widths, $\Gamma_n(\theta)$, we have to find out the optimal value of θ at which $<n|d\Gamma(\theta)/d\theta|n>|_{\theta_0}$ is stationary with respect to variation of θ around θ_0 implying[15]

$$<n|\frac{d\Gamma(\theta)}{d\theta}|n>|_{\theta_0}=0 \tag{17}$$

From Eq. (16), θ_0 may be obtained as

$$\theta_0=\left(\frac{\alpha_n}{\alpha_n<n|\mathbf{S}^2|n>-<n|\mathbf{S}[\mathbf{S}, \mathbf{H}]\mathbf{S}|n>}\right)^{1/2} \tag{18}$$

As the derivation shows, we only need to solve the eigenvalue equation of $[\mathbf{S}, \mathbf{H}]$ (Eq. (13)) in order to determine the resonance widths approximately with desired accuracy. Once the bound eigenstates $|m>$ are obtained, $\mathbf{S}^l|m>$ may be easily evaluated. All these calculations can be done in real arithmetics because of the hermitian nature of the operators involved. In addition, θ-dependent calculations may not be repeated which are required in the usual rotating coordinate method. Application to one- and two-dimensional problems can be easily implemented.

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