Optimized Kohn method for scattering. I. Single-channel scattering*

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An algebraic variational procedure has been developed for the calculation of the phase shift ρ of the radial wave function for a particle undergoing single-channel scattering. The method is essentially an optimization of Kohn's theory with respect to the phase parameter θ as involved in Kato's wave function. Specifically, the basis set has been transformed linearly so as to permit distinction between avoidable (spurious) and unavoidable (innate) singularities. On this basis, two new optimization procedures, which are termed the minimum-basis-dependence (MBD) and minimum-error (ME) methods, have been proposed. Various standard variational theories have also been reformulated in a unified manner. Sample basis-set calculations of ρ have been carried out for the Hazi-Taylor model potential in order to demonstrate the relative merits of the MBD and ME methods.

I. INTRODUCTION

In the algebraic variational theories of scattering,[1] the trial radial wave function $\psi_l(r)$ of a scattering particle is expanded in basis functions. After Hulthén,[2,3] Kohn,[4] and Lippmann and Schwinger[5] had developed such variational methods, Kato[6] extended them into a slightly more general form involving a phase parameter θ. His trial wave function is written as

$$\psi_{l\theta}(r) = S_{l\theta}(r) + \lambda_\theta C_{l\theta}(r) + \sum_{i=1}^{N} D_{\theta i}\chi_i(r), \tag{1}$$

where $S_{l\theta}(r)$ and $C_{l\theta}(r)$ are asymptotically

$$S_{l\theta}(r)_{r\to\infty} \sim k^{-1/2}\sin(kr - l\pi/2 + \theta), \tag{2a}$$

$$C_{l\theta}(r)_{r\to\infty} \sim k^{-1/2}\cos(kr - l\pi/2 + \theta), \tag{2b}$$

and where $\chi_i(r)$'s are square-integrable basis functions. The coefficients λ_θ and $D_{\theta i}$'s are to be determined by variation of the functional

$$[\lambda_\theta] = \lambda_\theta + 2\langle\psi_{l\theta}|\hat{H}|\psi_{l\theta}\rangle, \tag{3}$$

namely, by imposing the conditions

$$\langle\chi_i|\hat{H}|\psi_{l\theta}\rangle = 0, \quad i = 1, 2, \ldots, N \tag{4}$$

and

$$\langle C_{l\theta}|\hat{H}|\psi_{l\theta}\rangle = 0, \tag{5}$$

where $\hat{H} = E - H$, H and $E(=\frac{1}{2}k^2)$ being the scattering Hamiltonian and the energy, respectively. The λ_θ value thus obtained is a trial (zeroth-order) λ_θ. The value $[\lambda_\theta]$ correct to the first order is calculated by Eq. (3). The procedures for obtaining such $[\lambda_\theta]$ values have been a problem of central importance since it is related directly to the phase shift ρ and eventually to the cross sections for scattering.

Schwartz[7] pointed out, through his accurate and extensive calculations, that Kohn's method ($\theta = 0$) gives rise to anomalous singular solutions at certain k's, none of which has anything to do with a resonance phenomenon. Nesbest[8] showed that Rubinow's method[9] ($\theta = \pi/2$), which is also called the second Hulthén or inverse Kohn method, never gives this type of singularity at the k's of the Kohn singularity, and thus proposed alternate use of the two theories. The procedure was named the anomaly-free (AF) method. The optimized anomaly-free (OAF) method proposed recently by Nesbet and Oberoi[10] has been aimed at a removal of the discontinuity of λ against k. The minimum-norm (MN) method of Harris and Michels[11] can be regarded, like the OAF theory, as one of the methods which search an optimum θ automatically.

In this paper, we will investigate the dependence of λ upon θ in single-channel scattering. It seems likely that the anomaly arises from the choice of θ rather than from k. Such a singularity should be avoidable depending on the θ value chosen. We will clarify the situation through a specific transformation of the basis functions (S, C, and χ_i's). In this light, we will propose two promising methods to evaluate an optimum $[\lambda]$. Merits of our methods relative to the various other theories will be demonstrated by some sample calculations.

II. THEORETICAL FORMULATIONS

A. Basis transformation

For our purpose, it is more advantageous to base the theory on Kohn's original trial function ($\theta = 0$) of the form:

$$\psi = S + \lambda C + \sum_{i=1}^{N} D_i\chi_i, \tag{6}$$

where S and C are the asymptotic functions, Eq.

(2), with $\theta=0$, and where λ is the corresponding tangent of the phase shift ρ. For the sake of simplicity, both the subscript l and the radial coordinate r will be dropped off hereafter.

Using the relation

$$\begin{bmatrix} S_\theta \\ C_\theta \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} S \\ C \end{bmatrix}, \tag{7}$$

one can rewrite Eqs. (4) and (5) into

$$\langle \chi_i | \hat{H} | \psi \rangle = 0, \quad i = 1, 2, \ldots, N \tag{8}$$

and

$$\langle C - \omega S | \hat{H} | \psi \rangle = 0, \tag{9}$$

where $\omega = \tan\theta$. λ is related to λ_θ accordingly:

$$\lambda = (\omega + \lambda_\theta)/(1 - \omega\lambda_\theta). \tag{10}$$

Hereafter, we will refer to Eqs. (8) and (9) as the first and second Kohn conditions, respectively.

Equations (8) and (9) are simple simultaneous equations in the unknown variables λ and D_i's. Thus,

$$\underline{K} \begin{bmatrix} \lambda \\ D_1 \\ \vdots \\ D_N \end{bmatrix} = - \begin{bmatrix} \langle C - \omega S | \hat{H} | S \rangle \\ \langle \chi_1 | \hat{H} | S \rangle \\ \vdots \\ \langle \chi_N | \hat{H} | S \rangle \end{bmatrix}, \tag{11}$$

where

$$\underline{K} = \begin{bmatrix} \langle C - \omega S | \hat{H} | C \rangle & \langle C - \omega S | \hat{H} | \chi_1 \rangle & \cdots & \langle C - \omega S | \hat{H} | \chi_N \rangle \\ \langle \chi_1 | \hat{H} | C \rangle & \langle \chi_1 | \hat{H} | \chi_1 \rangle & \cdots & \langle \chi_1 | \hat{H} | \chi_N \rangle \\ \vdots & \vdots & & \vdots \\ \langle \chi_N | \hat{H} | C \rangle & \langle \chi_N | \hat{H} | \chi_1 \rangle & & \langle \chi_N | \hat{H} | \chi_N \rangle \end{bmatrix}. \tag{12}$$

The solutions of Eq. (11) should depend on θ if the basis set $\{\chi_i\}$ is not complete.

It may be extremely difficult to find an explicit dependence of λ on ω (and hence, on θ) through the direct solutions of Eq. (11). Since we are now discussing on the singularity of the inverse of $\underline{K}$ [Eq. (12)], it may be most beneficial to investigate the property of $\det\underline{K}$. To accomplish this, we introduce a new basis set $\{\zeta_i\}$ by transforming $\{S, C, \chi_i\text{'s}\}$ in such a manner that

$$\zeta_i = \chi_i + P_i^s S + P_i^c C, \quad i = 1, 2, \ldots, N \tag{13}$$

on the conditions

$$\langle S | \hat{H} | \zeta_i \rangle = 0 \tag{14a}$$

and

$$\langle C | \hat{H} | \zeta_i \rangle = 0. \tag{14b}$$

The coefficients P_i^s and P_i^c may be given by

$$\begin{bmatrix} P_i^s \\ P_i^c \end{bmatrix} = -\underline{M}_0^{-1} \begin{bmatrix} M_i^s \\ M_i^c \end{bmatrix} \tag{15}$$

with

$$\underline{M}_0 = \begin{bmatrix} M^{ss} & M^{sc} \\ M^{cs} & M^{cc} \end{bmatrix}, \tag{16}$$

where

$$\begin{aligned} M_i^s &= \langle S | \hat{H} | \chi_i \rangle = \langle \chi_i | \hat{H} | S \rangle, \\ M_i^c &= \langle C | \hat{H} | \chi_i \rangle = \langle \chi_i | \hat{H} | C \rangle, \end{aligned} \tag{17}$$

and

$$\begin{aligned} M^{ss} &= \langle S | \hat{H} | S \rangle, \quad M^{sc} = \langle S | \hat{H} | C \rangle, \\ M^{cs} &= \langle C | \hat{H} | S \rangle, \quad M^{cc} = \langle C | \hat{H} | C \rangle. \end{aligned} \tag{18}$$

We can always make $\det\underline{M}_0$ be nonzero by adding some square-integrable functions to S and/or C.

By use of $\{\zeta_i\}$, the wave function is now rewritten as

$$\psi = T^s S + T^c C + \sum_{i=1}^{N} D_i \zeta_i. \tag{19}$$

Comparison of Eq. (19) with Eq. (6) brings about the equalities:

$$T^s + \sum_i D_i P_i^s = 1, \tag{20a}$$

$$T^c + \sum_i D_i P_i^c = \lambda . \tag{20b}$$

The algebraic equation [Eq. (11)] is reduced to

$$\underline{K}_0 \begin{bmatrix} T_c \\ D_1 \\ \vdots \\ D_N \end{bmatrix} = -T^s \begin{bmatrix} \langle C - \omega S|\hat{H}|S\rangle \\ \langle \chi_1|\hat{H}|S\rangle \\ \vdots \\ \langle \chi_N|\hat{H}|S\rangle \end{bmatrix} , \tag{21}$$

where

$$\underline{K}_0 = \left[\begin{array}{c|c} \langle C - \omega S|\hat{H}|C\rangle & 0 \\ \hline \langle \chi_1|\hat{H}|C\rangle & \\ \vdots & \underline{X} \\ \langle \chi_N|\hat{H}|C\rangle & \end{array}\right] \tag{22}$$

with

$$\underline{X} = \begin{bmatrix} \langle \chi_1|\hat{H}|\zeta_1\rangle & \cdots & \langle \chi_1|\hat{H}|\zeta_N\rangle \\ \vdots & & \vdots \\ \langle \chi_N|\hat{H}|\zeta_1\rangle & \cdots & \langle \chi_N|\hat{H}|\zeta_N\rangle \end{bmatrix} . \tag{23}$$

From Eq. (26) we have

$$\det \underline{K}_0 = \langle C - \omega S|\hat{H}|C\rangle \det \underline{X} . \tag{24}$$

Note that $\underline{X}$ is independent of ω. The determinant of $\underline{X}$ might vanish at certain energies, and the singularities thus arising are unavoidable. On the other hand, the singularity which originates from a specified ω should be perfectly avoidable. We will consider this latter type of singularity in greater detail below.

B. Avoidable singularity

In order to eliminate D_i from Eq. (20), we will introduce the first Kohn condition. Thus

$$\sum_j \langle \chi_i|\hat{H}|\zeta_j\rangle D_j = -T^s\langle \chi_i|\hat{H}|S\rangle - T^c\langle \chi_i|\hat{H}|C\rangle . \tag{25}$$

Therefore, when $\det \underline{X}$ is not zero,

$$\underline{D} = -\underline{X}^{-1}\underline{M}^s T^s - \underline{X}^{-1}\underline{M}^c T^c , \tag{26}$$

where $\underline{D}$, $\underline{M}^s$, and $\underline{M}^c$ are the column vectors constructed of $\{D_i\}$, $\{M_i^s\}$, and $\{M_i^c\}$, respectively. Insertion of Eq. (26) into Eq. (20) results in

$$A^{ss}T^s + A^{sc}T^c = 1 , \tag{27a}$$

$$A^{cs}T^s + A^{cc}T^c = \lambda , \tag{27b}$$

where

$$\begin{aligned} A^{ss} &= 1 - \underline{P}^s\underline{X}^{-1}\underline{M}^s , \quad A^{sc} = -\underline{P}^s\underline{X}^{-1}\underline{M}^c , \\ A^{cs} &= -\underline{P}^c\underline{X}^{-1}\underline{M}^s , \quad A^{cc} = 1 - \underline{P}^c\underline{X}^{-1}\underline{M}^c , \end{aligned} \tag{28}$$

and where $\underline{P}^s$ and $\underline{P}^c$ are the row vectors of $\{P_i^s\}$ and $\{P_i^c\}$, respectively. Notice that none of A^{ss} to A^{cc} depends on ω.

On the other hand, from the second Kohn condition [Eq. (9)] and the property of ζ_i [Eq. (14)], one obtains

$$\langle C - \omega S|\hat{H}|T^s S + T^c C\rangle = 0 . \tag{29}$$

Use of Eqs. (27) and (29) gives

$$\lambda = (\beta - \alpha\omega)/(\gamma\omega - \delta) , \tag{30}$$

$$T^s = (M^{sc}\omega - M^{cc})/(\gamma\omega - \delta) , \tag{31a}$$

$$T^c = (M^{cs} - M^{ss}\omega)/(\gamma\omega - \delta) , \tag{31b}$$

where

$$\begin{aligned} &\alpha = A^{cc}M^{ss} - A^{cs}M^{sc} , \quad \beta = A^{cc}M^{cs} - A^{cs}M^{cc} , \\ &\gamma = A^{ss}M^{sc} - A^{sc}M^{ss} , \quad \delta = A^{ss}M^{cc} - A^{sc}M^{cc} . \end{aligned} \tag{32}$$

Clearly, λ depends on ω in a hyperbolic manner. That is, for any given k, there exists one, and only one, spurious singularity on the ω axis at

$$\omega_d = \delta/\gamma . \tag{33}$$

Conversely, if one chooses ω different from ω_d, such a kind of singularity can be avoided. Therefore, it never concerns a true resonance but is merely a spurious resonance. The singularity pointed out by Schwartz[7] is to take place when k passes through the point at which $\delta = 0$.

Generally, the λ obtained by Eq. (30) is not accurate enough; it contains the first-order error. According to Kato,[6] λ_θ involved in $\psi_{l\theta}$ should be corrected by Eq. (3) to give $[\lambda_\theta]$. The $[\lambda_\theta]$ may be converted to the corresponding first-order correction of λ by the relationship analogous to Eq. (10). The result is

$$[\lambda] = (\omega - [\lambda_\theta])/(1 - [\lambda_\theta]\omega) , \tag{34}$$

which is equivalent to a more general first-order correction formula

$$[\lambda] = (\lambda + 2\langle S|\hat{H}|\psi\rangle)/(1 - 2\langle C|\hat{H}|\psi\rangle) , \tag{35}$$

as long as ψ satisfies the Kohn conditions. Both Eqs. (34) and (35) can be expressed in terms of ω as follows:

$$[\lambda] = [(\beta - 2M_0) - \alpha\omega]/[(\gamma + 2M_0)\omega - \delta] , \tag{36}$$

where M_0 stands for $\det \underline{M}_0$.

III. PROPOSAL OF NEW OPTIMIZATION PROCEDURES

A. Minimum-basis-dependence method

When the basis set $\{\chi_i\}$ by itself approaches a complete one, both the coefficients T^s and T^c should come to zero. This is evident from the following two points. Firstly, if the wave function is exact, neither λ nor D_i's involved in it will depend on ω, so that both T^s and T^c should be constants, regardless of ω. Secondly, T^s and T^c should identically fulfill Eq. (29), which forces them to depend on ω unless $T^s = T^c = 0$. On the contrary, if the basis set chosen is insufficient or if the ω in Eq. (9) is fixed at a wrong point such as $\omega = \delta/\gamma$, then either T^s or T^c, or occasionally both of them, will inevitably tend to depend on ω, taking some values of large magnitude.

The situations delineated above provide a good reason for demanding the norm

$$I_{\mathrm{MBD}} = (T^s)^2 + (T^c)^2 \tag{37}$$

to take on a minimal value possible. There exists a single point which minimizes I_{MBD} on the ω axis. It is

$$\omega_{\mathrm{MBD}} = (A^{ss}M^{cs} + A^{sc}M^{cc})/(A^{ss}M^{ss} + A^{sc}M^{sc}) . \tag{38}$$

Once we obtain ω_{MBD}, the calculations of ψ and $[\lambda]$ are made in a straightforward way. It is clear that λ obtained by this method does not experience the avoidable singularity; if T^s and T^c are bound, so will λ be [Eqs. (30)–(32)]. The present minimum-basis-dependence (MBD) method can readily be extended to multichannel scatterings.[12]

B. Minimum-error method

Suppose that the exact wave function $\bar{\psi}$ is expanded in a complete set of square-integrable basis functions:

$$\bar{\psi} = S + \bar{\lambda}C + \sum_{i=1}^{\infty} \bar{d}_i \chi_i . \tag{39}$$

Because

$$\bar{\lambda} = \lambda + 2\langle \bar{\psi} | \hat{H} | \psi \rangle , \tag{40}$$

the origin of the error of $[\lambda]$ will then be

$$2 \sum_{i=N+1}^{\infty} \bar{d}_i \langle \chi_i | \hat{H} | \psi \rangle = (\bar{\lambda} - \lambda) - 2\langle S | \hat{H} | \psi \rangle - 2\bar{\lambda}\langle C | \hat{H} | \psi \rangle . \tag{41}$$

The right-hand side of Eq. (41) will depend on ω in a hyperbolic manner. Therefore, one might seek for the ω which minimizes

$$I_{\mathrm{ME}} = (\bar{\lambda} - \lambda)^2 + 4\langle S | \hat{H} | \psi \rangle^2 + 4\bar{\lambda}^2 \langle C | \hat{H} | \psi \rangle^2 . \tag{42}$$

Imposing the condition $dI_{\mathrm{ME}}/d\omega = 0$, we have

$$[(\alpha\delta - \gamma\beta)(\alpha + \bar{\lambda}\gamma) + 4\bar{\lambda}^2 M_0^2 \delta]\omega_{\mathrm{ME}} = (\alpha\delta - \gamma\beta)(\bar{\lambda}\delta + \beta) - 4M_0^2 \gamma . \tag{43}$$

Equation (43) as it stands is useless because $\bar{\lambda}$ is unknown. We are thus obliged to replace $\bar{\lambda}$ by Eq. (36). The resulting equation is cubic in ω. Of the three ω values obtained by solving it, only the ω which gives the smallest I_{ME} is physically acceptable.

IV. COMPARISONS WITH OTHER THEORIES

A. Choices of ω

The radial wave functions as used in the Kohn,[4] Rubinow,[9] Hulthén,[2,3] minimum-norm (MN),[11] and optimized anomaly-free (OAF)[10] methods all fulfill the Kohn condition. Therefore, their functional forms as well as the resulting $[\lambda]$ are completely determinate, once their characteristic ω values have been specified. In Table I, such ω's pertinent to these various variational theories are summarized, together with those for our minimum-basis-dependence (MBD) and minimum-error (ME) methods.

A few words seem to be in order regarding the Hulthén method. Nesbet[8] and Shimamura[13] have already shown that Hulthén's condition, $\langle \psi | \hat{H} | \psi \rangle = 0$,[2,3] does not necessarily hold in the vicinity of the eigenvalues of the matrix $\langle \chi_i | \hat{H} | \chi_j \rangle$ as long

TABLE I. ω for various variational theories.

Method	ω
Kohn	0
Rubinow	$\pm\infty$
Hulthén [a]	$\dfrac{\beta+\gamma \pm [(\beta+\gamma)^2 - 4\alpha\delta]^{1/2}}{2\alpha}$
Extended Hulthén	$\dfrac{\delta(\gamma-\beta)}{\gamma(\gamma+\beta) - 2\alpha\delta}$
MN	$-\gamma/\delta$
OAF [a,b]	$\dfrac{-(\alpha-\delta) \pm [(\alpha-\delta)^2 + 4\gamma\beta]^{1/2}}{2\gamma}$
ME	Eq. (43)
MBD	Eq. (38)

[a] The correct sign should be taken so that the calculated I_{MBD}, Eq. (37), may be minimized.

[b] This does not always give real ω values. In such cases, the original formulation of Nesbet (Ref. 10) should be referred to.

TABLE II. Phase shifts $[\rho]$ calculated by various methods for the case where $N=15$ and $a=0.15$. The entries are 10^5 times the deviations from the exact ρ values. [a]

Method	E = 0.198 601 2 ρ_{exact} = 0.254 41	0.306 747 1 −0.336 81	0.466 122 7 0.717 52	0.466 302 9 1.500 66	0.561 486 6 1.902 52	0.757 047 1 1.482 82
Kohn	−599	781	−904	−1610	−502	−52
Rubinow	−2917	−835	47	−156	−95	−71
Hulthén	−1990	−1110	1737	−1820	−447	−53
MN	−923	−626	−297	−4887	−413	−56
OAF	−230	244	−349	5616	···[b]	−74
ME	−2095	−940	−150	−1720	−465	−53
MBD	−807	−379	−367	−3519	−427	−56

[a] Hazi and Taylor, Ref. 14.
[b] Real solution was not found.

as the first Kohn condition is imposed on ψ. For such cases, Hulthén's method had better be extended to a form such that ω minimizes $|\langle\psi|\hat{H}|\psi\rangle|$. The ω value is then given by

$$\omega = \delta(\gamma-\beta)/[\gamma(\gamma+\beta)-2\alpha\delta]. \tag{44}$$

We will refer to this method as the extended Hulthén method. It is easy to prove that, as k is varied, Eq. (44) is connected continuously with the ω for the original Hulthén method (Table I). The extension enables to define Hulthén's ω for any given k.

B. Numerical examples

We have performed sample calculations of the phase shift $\rho=\tan^{-1}\lambda$ by the various methods mentioned in the foregoing sections. Their variational corrections $[\rho]=\tan^{-1}[\lambda]$ are all given through Eq. (35). In place of the effective potential $V_{\text{eff}}(r)=V(r)+l(l+1)/2r^2$, the model potential function of Hazi and Taylor[14] was used:

$$V(x)=\begin{cases}\frac{1}{2}x^2 & (x<0)\\ \frac{1}{2}x^2 e^{-ax^2} & (x>0)\end{cases}. \tag{45}$$

TABLE III. The basis-size dependences of the phase shifts at $E=0.198\,601\,2$ a.u. and $a=0.15$. The entries for ρ and $[\rho]$ are 10^5 times the deviations from the exact ρ value (0.254 41).

Method	N=	5	10	15	20	30	40
Kohn	ρ	34 650	22 161	8 021	2804	−134	−1
	$[\rho]$	−146 240	−9 982	−599	−25	0	0
Rubinow	ρ	8 835	91 492	−7 465	−663	−8	−1
	$[\rho]$	8 330	16 617	−2 917	−93	0	0
Hulthén	$\rho=[\rho]$	−165 881 [a]	−45 555 [a]	−1 990	−81	0	0
MN	ρ	54 455	23 182	5 464	636	−15	−1
	$[\rho]$	−99 578	−8 957	−923	−67	0	0
	I_M [b,c]	0.9646(0)	0.1276(−1)	0.7277(−3)	0.3422(−4)	0.1041(−7)	0.6015(−11)
OAF	ρ	82 123	28 957	11 103	5178	−68	−1
	$[\rho]$	−28 123	−4 021	−230	21	0	0
ME	ρ	86 077	−4 731	−2 656	279	−5	0
	$[\rho]$	−20 084	−87 684	−2 095	473	0	0
MBD	ρ	27 793	20 167	6 364	1585	−15	−1
	$[\rho]$	−158 456	−12 150	−807	−48	0	0
	I_{MBD} [d,c]	0.9607(−1)	0.1049(−2)	0.5725(−4)	0.3826(−6)	0.3729(−8)	0.7905(−12)

[a] The extended Hulthén method, Eq. (44).
[b] $I_M=\langle S|\hat{H}|\psi\rangle^2+\langle C|\hat{H}|\psi\rangle^2$.
[c] The figures given in parentheses indicate the multiplicative power of 10.
[d] Equation (37).

The square-integrable basis functions $\{x_i\}$ used were the Hermite functions. The size N of the basis was varied between 5 and 40. As the asymptotic functions S and C, the following functions were adopted:

$$S = \begin{cases} k^{-1/2} \sin kx & (x > 0) \\ k^{-1/2} e^{-bx^2} \sin kx & (x < 0) \end{cases} \tag{46a}$$

and

$$C = \begin{cases} k^{-1/2} \cos kx & (x > 0) \\ k^{-1/2} e^{-bx^2} \cos kx & (x < 0) \end{cases} \tag{46b}$$

with the damping factor b being fixed at 0.15 in atomic units (a.u.).

First, we have examined the energy dependences of $[\rho]$ for a potential for which $a = 0.15$ in a.u. The energy ranges examined were limited to those for which exact solutions are available.[14] The results obtained for the size $N = 15$ are summarized in Table II. Since there was no avoidable singularity in the energy region of our present test, no significant differences in the resulting $[\rho]$ values were encountered. The Rubinow and OAF methods occasionally gave the best results at given energies. The MN and MBD methods provided nearly equally good results steadily over the entire energy ranges examined.

In Table III, the basis-size dependences of both ρ and $[\rho]$ are shown for a case of $E = 0.1986012$ and $a = 0.15$, both in a.u. The $[\rho]$ values are sufficiently close to the exact phase shift (0.25441) when N is larger than 15. With N greater than 30, exact ρ values are obtainable by any of the methods here examined. For the sake of comparison, the values of I_{MBD} and $I_M = \langle S|\hat{H}|\psi\rangle^2 + \langle C|\hat{H}|\psi\rangle^2$ calculated at varying N are also listed. Both these I's converge to zero in a monotonous manner. However, in case where E is in the vicinity of the critical E at which $\det \underline{X} = 0$, these monotonous behaviors will break down. Nonetheless, we may regard these I's as useful measures of the accuracy of the basis-set calculations.

The way that λ is corrected to $[\lambda]$ is illustrated in Fig. 1 for the case where $E = 0.3067471$ a.u., $N = 15$, and $a = 0.15$. Both λ and $[\lambda]$ vary hyperbolically with ω:

$$\lambda = -0.33122 - 0.07503/(\omega - 0.37129), \tag{47}$$

$$[\lambda] = -0.35956 - 0.00732/(\omega - 0.40305). \tag{48}$$

The constant term (−0.35956) for $[\lambda]$ is much nearer to the exact value (−0.35015) than is that (−0.33122) for λ. The numerator (0.00732) for $[\lambda]$ is about one-tenth that (0.07503) for λ. The latter result indicates that the dependence of $[\lambda]$ on ω, and hence on the methods, should be relatively small. The range of ω for divergence should accordingly be narrower.

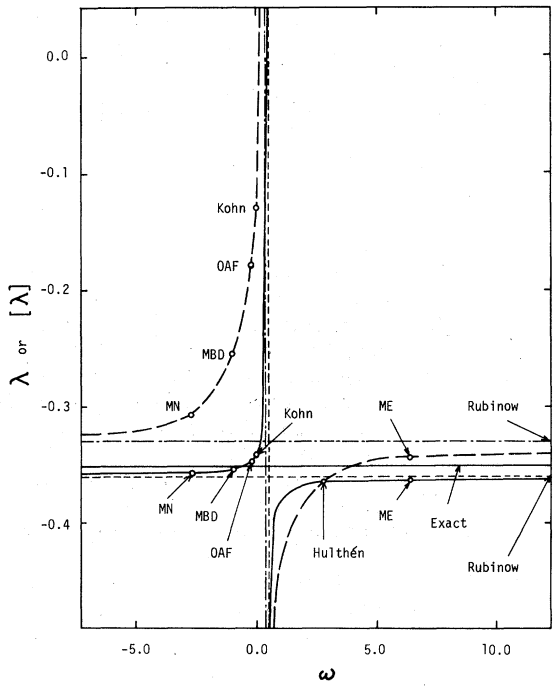

FIG. 1. Schematic representation of the hyperbolic curves of λ and $[\lambda]$ vs ω for the case where $E = 0.3067471$ a.u., $N = 15$, and $a = 0.15$. – – –, $\lambda = -0.33122 - 0.07503/(\omega - 0.37129)$; ——, $[\lambda] = -0.25956 - 0.00732/(\omega - 0.40305)$; $\lambda_{\mathrm{exact}} = \tan\rho_{\mathrm{exact}} = -0.35015$.

V. CONCLUDING REMARKS

We have examined the dependences of both λ and $[\lambda]$ upon $\omega = \tan\theta$ in a systematic manner, to clarify mutual relationships among various variational methods. This was accomplished by the help of a basis-transformation scheme which was introduced in order to distinguish avoidable (spurious) singularities from unavoidable (innate) ones.

In connection with the above, we have proposed two new optimization procedures for the calculation of λ. They have been termed the minimum-basis-dependence (MBD) and minimum-error (ME) methods. Both the methods are free from avoidable singularities. The MBD method seems to be more promising than any other existing variational theory for the following reasons: (i) it is capable of providing an optimum λ through simple linear equations without any cumbersome diagonalization procedure; (ii) it permits a def-

inition of I_{MBD} as a useful measure of the sufficiency of the basis functions used; and (iii) no special device is required even in the vicinity of the eigenvalues of the matrix $\langle\chi_i|\hat{H}|\chi_j\rangle$.

In the succeeding paper, we will extend the MBD method to cover multichannel scatterings. Further, the characteristics of the unavoidable singularity, particularly in regard to its relationship with the true resonance, will be discussed elsewhere.

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