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AN EXACT UNIFORM SOLUTION OF THE SCHRÖDINGER EQUATION VIA COMPARISON EQUATIONS

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ABSTRACT

Limitations in the use of the conventional comparison equation and reference (approximate) potential methods for obtaining solutions to the Schrödinger equation in calculations involving the classical transition region are reviewed. The origins of these limitations are discussed and a systematic improved method applicable to real potentials with continuous derivatives is formulated. As a computational example of the method, a

details study of the bound-state problem using the Morse potential is presented. Extension of the method to the many-channel problem is discussed.

RESUMEN

Se reseñan las limitaciones en el uso de la ecuación de comparación convencional y métodos de potenciales (aproximados) de referencia para obtener soluciones de la ecuación de Schrödinger en cálculos que consideran la región de transición clásica. Se discuten los orígenes de estas limitaciones y se formula un método sistemático mejorado aplicable a potenciales reales con derivadas continuas. Como un ejemplo computacional del método, se presenta un estudio detallado del problema de estados ligados usando el potencial de Morse. Se discute la extensión del método al problema de muchos canales.

1. INTRODUCTION

The classic WKBJ approximation to the analytical solution of the Schrödinger equation has found extensive applications in boundstate and scattering problems in diverse fields of physics[1]. A variety of modifications, refinements and extensions intended to overcome its several drawbacks (*i.e.*, singularities at the classical turning or transition points, Stokes's phenomena, etc.) have been proposed[2-7]. These modifications generally have been limited to the finite-dimensional case. An extension of the WKBJ method to the infinite-dimensional case has been recently reported[8]. Foremost among the relatively successful improvements of the WKBJ theory is the Miller-Good (MG) transformations[3]. It has given rise to the often cited "comparison method"[5] and to a type of uniform approximation[9-10]. The general procedure in these approaches is to neglect the resulting Schwartzian derivatives (SD) term.

In the usual WKBJ method, the original Schrödinger equation is compared to an ordinary-differential equation with constant coefficients. In the classically forbidden domain the solutions are growing or decaying exponential functions, while outside this domain they are sinusoidally varying functions. This procedure excludes from the outset the construction of a smooth, approximating wavefunction near the turning points since it makes an abrupt change in this transition region. Further, the solutions are to be considered in regions far removed from the classical turning points. We will see that the uniform approximations do not represent the correct solutions across the transition region accurately enough (see

Sects. 2 and 3). They have been designed mainly to remove the wavefunction discontinuity across the classical turning points, the solutions so obtained being basically asymptotic in character[10]. These are given in terms of one, or more than one, convenient parameters. In quantal calculations the relevant parameter is related to Planck's constant[9-11]. For the kind of uniform approximations we shall refer to in this work, the validity of the semiclassical approximation (where the SD term is neglected) gives rise to some doubts, mainly in the very-near turning-point regions (see Sec. 2).

To improve the accuracy of the conventional comparison equation treatment, two iterative schemes, similar to the familiar perturbation technique, but differing in character, have been proposed[4,11]. As much as we are aware, these improvements have not received extensive applications. One of these seems appropriately designed for scattering problems[4], and the other for bound-state problems[11]. The main objetive of this report is to present a systematic and simple improvement on the usual comparison method, encompassing both situations, free from the semiclassical approximation: the improved comparison equation method (ICEM).

The solution of a system of coupled one-dimensional linear second-order differential equations is the starting point in several calculations, both in classical mechanics and nonrelativistic quantum mechanics. It can be shown by straightforward manipulation that the problem just posed may be reduced to an equivalent coupled first-order differential equations system[12]. However, when several channels are present and a great accuracy is required, the method is usually onerous due to the complexity of the large scale numerical calculations involved. Therefore a limit to accuracy is imposed for practical reasons. Such is the case in calculations in the gas-surface interface scattering[13] and the gas phase scattering of reactive systems[14]. This restriction becomes more critical when "closed channels" or "states diffracted into the surface" have to be included, due to the effect on the scattering matrix elements[13], or if the interaction potential does not vary slowly. A close-coupling approach would therefore seem relatively expensive and one must resort to approximations not readily justifiable and perhaps not valid in some situations[15].

Among the various numerical methods of solution of the

Schrödinger equation, the finite-element method[16], originally developed for engineering problems, and implemented by Gordon[17] has been used extensively. It involves dividing the integration region into conveniently small domains and approximating the correct potential within each domain by a "reference potential". This reference potential must be so chosen that the solutions to the reference or "etalon" equation, corresponding to our homogeneous one, are relatively easy to determine analytically. In practice the method consists of stepping the interaction at each integration interval of the resulting set of coupled first-order differential equations[17-19]. In problems requiring great accuracy each interval must be small enough to guarantee an appropriate approximation of the constant, linear or quadratic reference potential to the true potential. For further developments of those approaches during the last ten years, the reader is referred to Ref. 19a and references therein. A new method to solve the Schrödinger-like equation is presented, partly analytically, partly numerically, free from semiclassical approximations, and without severe restrictions regarding the way by which the comparison potential adapts to the original one.

In section 2 the general formalism upon which the present work is based is summarized. It is seen in this section that the iterative approximations within the context of the MG method are better replaced by a perturbative approach similar in some respects to, but more general than, the reference potential method[17]. As a result, the homogeneous-like equation becomes an inhomogeneous-like one. In section 3 a standard technique is used to split this last equation into first-order equations. Then it is shown that the Gordon method may be formally incorporated within a more general scheme of comparison equations. Contrasted with the Gordon method, the distinctive feature of the ICEM is that the reference potential covers large regions which sometimes may be extended over the entire integration region. Moreover, it is not limited to approximate potentials of polynomial form. In section 4 the ICEM is tested and compared to the exact analytical results of the bound-state problem for the case of the Morse potential. In this section some features and applications of this potential are also discussed. The appplications to many-channel problems, for which the present scheme is likely to be more beneficial, are

discussed in section 5. Finally, in the sixth section, we present a brief summary of the method, a discussion of the results and a prognosis for future investigations. The main conclusion is that the ICEM may be employed with better accuracy for problems usually considered within the framework of the conventional uniform treatments. The method advocated here may be particularly useful for clos-coupling calculations with a higher efficiency than the reference or approximate-potential method, mainly in many-channel problems.

2. GENERAL FORMALISM

The basic elements of the ICEM can be seen by studying a simple example. In order to avoid terminological confusion, throughout this paper the word *method* will be utilized to connote techniques that formulate the bound-state or scattering problem, while the word *procedure* will be applied to computational algorithms for solving the equations generated by the methods. To start, the one-dimensional stationary-state Schrödinger equation is considered. An extension to many-channel problems is discussed in Sec 5. Here attention is focused upon the homogeneous-like equation

$$\left[\frac{d^2}{dx^2} + p^2(x)\right]\psi(x) = 0 \quad , \tag{1}$$

where

$$p^2(x) = \frac{2m}{\hbar^2}\left[E - V(x)\right] \quad , \tag{2}$$

E being the energy of a nonrelativistic particle with mass m moving in the potential field V(x). It is assumed that $p^2(x)$ is real on the real axis, *i.e.*, V(x) real.

The Gordon approximate-potential method[17] involves writing Eq. (1) as an inhomogeneous-like equation

$$\left[\frac{d^2}{dx^2} + p_0^2(x)\right]\psi(x) = -g(x)\psi(x) \quad , \tag{1a}$$

where

$$p_0^2(x) = p^2(x) - g(x) \quad , \tag{2a}$$

contains a potential similar to, but simpler than $p^2(x)$. One then seeks solutions to Eq. (1) via the nontrivial solutions to the homogeneous differential equation

$$\left[\frac{d^2}{dx^2} + p_0^2(x)\right]\psi_0(x) = 0 \quad . \tag{1b}$$

The MG method[3], on the other hand, employs a simultaneous transformation of the wavefunction and the spatial coordinate. The following homogeneous-like equation is obtained instead of Eq. (1)[3]:

$$\left[\frac{d^2}{dt^2} + q_0^2(t)\right]\phi\ (t) = 0 \quad , \tag{3}$$

where $q_0^2(t)$ denotes a comparison momentum to be conveniently chosen and t is a function of x to be determined. Once Eq. (3) has been solved, the solutions to Eq. (1) are obtained from the inverse transformation (see Eqs. (5)).

Instead of following either of the two approaches mentioned above, they are combined and Eq. (1) is compared to an inhomogeneous-like equation:

$$\left[\frac{d^2}{dt^2} + q^2(t)\right]\phi(t) = f(t)\phi(t) \quad , \tag{4}$$

where $q^2(t)$ denotes a general "reference" or "comparison" momentum whose properties will be specified later in this section and f(t) is a perturbation-like potential term (see below).

To obtain Eq. (4) a transformation is performed, looking for a monotonously increasing function t(x) that possesses continuous derivatives $t' = dt/dx$, $t'' = d^2t/dx^2$, etc. Following Miller and Good[3], a continuous and differentiable function $\chi(x)$ is introduced, to be determined such that

$$\psi(x) = \chi(x)\,\phi\,(t(x)) \quad . \tag{5a}$$

The function $\chi(x)$ modulates to some extent the amplitude of the new wavefunction. It is thus highly desirable to choose $\chi(x)$ such that $q^2(t)$ resembles the main features of $p^2(x)$ or, similarly, that $\phi(T)$ has qualitatively the same behavior as the solution $\psi(x)$ of the original equation. Substitution of Eq. (5a) into Eq. (1) yields

$$t'^2\chi\left[\frac{d^2}{dt^2} + t'^{-2}p^2(x)\right]\phi + (t''\chi + 2t'\chi')\,\frac{d\phi}{dt} = -\chi''\phi \quad . \tag{4a}$$

This expression converts to the inhomogeneous-like equation (4) if the coefficient of $d\phi/dt$ is set to zero; we thus take

$$\chi(x) = t'^{-\frac{1}{2}} \quad , \tag{6}$$

and identify $f(t)$ with

$$f(t) = -\chi''\chi^{-1}t'^{-2} \quad , \tag{7a}$$

which can also be written

$$f(t) = \frac{1}{2}\,t'^{-2}\langle t;\, x\rangle \quad , \tag{7b}$$

where

$$\langle t;\, x\rangle \quad \frac{t'''}{t'} - \frac{3}{2}\left(\frac{t''}{t'}\right)^2 = -\,2t'^{\frac{1}{2}}\,\frac{d^2}{dx^2}\,(t'^{-\frac{1}{2}}) \quad , \tag{8}$$

is the SD expression[3,4].

Instead of trying to solve Eq. (1) directly, an attempt is made to find solutions to the exactly equivalent equation (4), where

$$\psi(x) = t'^{-\frac{1}{2}}\,\phi(t(x)) \quad , \tag{5b}$$

and t is given by the nonlinear first-order differential equation

$$\left(\frac{dt}{dx}\right)^2 = \frac{p^2(x)}{q^2(t)} \qquad (9)$$

An analytical transformation similar to Eq. (5b) has been found useful in investigations of propagation and scattering of electromagnetic and acoustic waves in continuously layered media[20].

The MG transformation yields after comparing Eqs. (1) and (3)

$$\left(\frac{dt}{dx}\right)^2 = \frac{p^2(x) - \frac{1}{2}\langle t; x\rangle}{q_0^2(t)} \qquad (10)$$

In applications, the SD term appearing in Eq. (10) has been customarily neglected. In this case Eq. (10) reduces itself to the simpler relationship Eq. (9). This procedure has been referred to in the literature by the terms "comparison equation"[5] and "uniform approximation"[9,10]. The name "comparison equation" originates from the fact that one compares Eq. (1), whose solutions are unknown, to Eq. (3), where $q_0^2(t)$ is to be chosen so that the comparison equation possesses simple and analytical solutions. The name "uniform approximation" means that, after neglecting the SD term and selecting an appropriate comparison potential, t' can be made continuous over the entire domain, including the transition regions. As a result, a smooth wavefunction is obtained across the classical turning points where the usual WKBJ solutions are singular.

Several questions about the range of validity of the conventional comparison and uniform treatments arise. The number of available comparison momenta is greatly restricted by the assumption of negligible SD values. At any rate, they must be similar to the original momentum $p^2(x)$. Apparently, no known attempts have been made to assess the assumption of neglecting the SD term resulting from the most utilized comparison equations, namely, the Airy and Weber equations. The validity of this approach depends mainly upon the nature of the externally imposed potential or interparticle potential at hand. Moreover, as will be seen

in Sec. 3, the values of the neglected term, similar to g(x) in Eq. (1a), determines the behavior of the wavefunction at the very-near turning points regions. Neglecting the SD term in Eq. (10) it would give rise to serious miscalculations in some problems; such is the case of the scattering problem at intermediate energies in situations where differences in the phase-shift values might be significant.

The only manageable situation for which g(x), *i.e.*, the SD term (see Eq. (18)), can be made exactly zero over a certain finite region for every potential is for the transformation

$$p^2(x) = cq^2(t), \qquad (c = \text{constant}) \quad .$$

As simple as it is, there is a case in which this transformation may be useful. Suppose that the comparison potential is the linear one. The solutions are given in terms of the well-known Airy functions. It is always possible to linearize the potential in a conveniently small region on the x-axis. If one compares the true potential with the linear potential via the MG transformation outside a singular point of $p^2(x)$, and performs a linearization of the potential in a small region containing the transition point, it is possible to obtain both smooth solutions over the entire domain, and exactly zero SD values through the transition regions. This feature has been recently used to guarantee the validity of the (numerical) uniform solutions across the turning points in a many-channel scattering problem[21]. It is worth noting that linearizing the potential step by step within conveniently small regions, as is done in Ref. 17, yields directly the Airy functions as solutions to Eq. (3).

Another question stems from the symmetry of the conventional comparison method. This symmetry means that one could construct $\phi(t)$ out of $\psi(x)$ via the inverse transformation of the spatial coordinate $x = x(t)$[11]. As will be seen later in this section (see the discussion following Eq. (11)) this symmetrical situation requires a one-to-one correspondence between the spectra of the Hamilton operators for both equations: (1) and (3). This requirement introduces a complication mainly in bound-state problems. An isospectral correspondence between discrete eigenvalues does not exist on comparing, for example, the Weber equation,

which is associated with a harmonic oscillator potential, with any other potential having a finite number of bound states (see Sec. 4 for an example). It means that, in general, one cannot pretend to solve arbitrarily any of the two comparison equations by solving the other one for the entire spectrum. Nevertheless, one must recognize that, from a pragmatic point of view, this fact has not any importance. The interest in practice reduces to solving a non-directly integrable equation by comparing it with a simpler one, and usually for a very specific state.

Equation (9) which determines t as a function of x is remarkably simpler than the corresponding MG equation (10). In turn, this analytical simplicity imposes one requirement: once a comparison potential has been selected, one must solve the inhomogeneous like Eq. (4), instead of the homogeneous one, Eq. (3). However, it should be noted that there exist several methods to deal with inhomogeneous-like equations, whereas the involved mathematical structure of Eq. (10) is hardly manageable even in simple situations. Furthermore, it is worthwhile to note that this apparently disadvantageous situation of the presence of the inhomogeneous term avoids the problem posed by the symmetry of the conventional method, since there is not such a symmetry within the ICEM method. If the right hand side of Eq. (4) is neglected, the present approach reduces to the conventional one. It is a consequence of the fact that Eq. (10) reduces to the exact and simple equation (9) after neglecting the SD term. Whenever a better accuracy is sought two possibilities exist: The first of these is trying to solve the rather cumbersome Eq. (10) exactly, following the MG prescription without modifications[4,11], in which case the comparison equation takes the simpler form given by Eq. (3). The second possibility consists of using the transformation introduced by MG and solving the more difficult equation (4), determining t from the simpler relationship Eq. (9). It will be shown in Sec. 5 that the later choice, namely, the ICEM, is largely more beneficial in many-channel problems. Section 4 illustrates the efficiency of the method advocated in this report in bound-state problems. The former alternative has been worked out within the context of iterative schemes[4,11], which are not substantially different from the familiar perturbation technique.

It should be stressed that deciding which comparison potential

should be used does not imply that the new spacial coordinate t has been completely specified as a function of x. From Eq. (5b) t' may be rewritten as

$$t' = \frac{\phi^2(t)}{\psi^2(t)}$$

This last expression shows that t is a strictly increasing function of x, as required, if ψ and ϕ are real functions. If they are not, one could still choose a comparison potential such that t' given by Eq. (11) were always positive. Equations (9) and (11) suggest setting t_i congruent with x_i, where x_i desginates the nodes of $p^2(x)$ and $\psi^2(x)$, and t_i those of $q^2(t)$ and $\phi^2(t)$. This fruitful choice will make t' regular and will avoid singularities or zeroes for t' upon the additional assumption of continuous differentiability of the four functions ψ^2, ϕ^2, p^2 and q^2. It imposes some restrictions over the comparison equations at our disposal. But these do not bring major complications as long as the application is restricted to comparison potentials which have qualitatively the same behavior as the original one.

Once a comparison potential resembling the original one has been chosen, the following prescription allows the determination of t as a function of x.

For the solution of the first-order differential equation (9) one needs to fix a constant of integration. Therefore, without limitation of generality one may set $t = t_0$ at an appropriate fixed point corresponding to $x = x_0$, say the location of the first turning point to the left, thus

$$\int_{t_0}^{t} |q^2(\tau)|^{\frac{1}{2}} d\tau = \int_{x_0}^{x} |p^2(\xi)|^{\frac{1}{2}} d\xi$$

For a simple-turning-point problem the function t will be completely specified for a certain comparison potential. In problems with more than one classical turning point, additional constraints must be imposed to fit the requirement of turning points congruency. It may be achieved by including n-1 adjustable parameters into the comparison mementa equations,

where n is the number of classical turning points[10]. These parameters may be determined from

$$\int_{t_0}^{t_i} |\varepsilon - v(t)|^{\frac{1}{2}} dt = \int_{x_0}^{x_i} |E - V(x)|^{\frac{1}{2}} dx \quad , \tag{12b}$$

where t_i (x_i) corresponds to the ith turning point of the potential. This last condition is an obvious generalization of Eq. (22) in Ref. 3. It sets the turning points in one-to-one correspondence. A problem mathematically similar to this one, the case of two turning points in acoustics and electromagnetic theory, has been considered in a number of studies[22]. In the bound-state problem, Eq. (12b) provides an eigenvalue E for each "eigenvalue" ε of the comparison potential $v(t) = (\hbar^2/2m)[\varepsilon - q^2(t)]$.

Superficially, Eq. (12b) seems to be a basic approximate relationship. It resembles the Poincaré-Cartan invariant integral of classical mechanics[23], which does not have an exact analogue in quantum mechanics. In contrast to the MG treatment, in which Eq. (12b) is obtained from Eq. (10) as a semiclassical approximation[11] (expansion in $\hbar^2$), within the present scheme it is an exact relationship; it is obtained from Eq. (9) and appropriately adjusted to the simple criteria stipulated above. It must be noticed that the "comparison potential" in Eq. (4) is modified by a perturbation-like potential term: $\frac{1}{2}(\hbar^2/2m)t'^{-2}\langle t; x\rangle$, which is missing in Eq. (12b). Within the present scheme, Eq. (4) is not a legitimate or well-defined physical eigenvalue equation, as is Eq. (1). The semiclassical approximation used in other approaches replaces Eq. (4) by the "eigenvalue" equation (3). In the ICEM, solutions to Eq. (1) are being sought which satisfy prescribed boundary conditions. Whenever one considers Eq. (1) as an eigenvalue equation, the present scheme requires that it be solved by adjusting appropriate solutions, via $t'^{-\frac{1}{2}}$, to the inhomogeneous like equation (4). Moreover, as will be seen in the next section, the solutions to Eq. (4) are sought by using acceptable[24] solutions to the homogeneous-like equation (3)[21]. These admissible solutions are not eigenfunctions but linearly exact independent solutions of the homogeneous form.

3. SOLUTION OF THE INHOMOGENEOUS-LIKE SCHRÖDINGER EQUATION

In this section the advantages of the ICEM over the approximate or reference potential, and the comparison equation methods is illustrated. It is stressed that the ICEM works well within any other technique to solve the inhomogeneous second-order differential equation.

It is convenient to rewrite Eq. (1) as

$$\left[\frac{d^2}{dx^2} + p^2(x) + \frac{1}{Z}\langle t;\, x\rangle\right] \psi(x) = \frac{1}{Z}\langle t;\, x\rangle\psi(x) \quad . \tag{13a}$$

Written in this way, Eq. (1) resembles an inhomogeneous equation. The inhomogeneous driving terms consist of the wavefunction itself multiplied by the SD expression, which must be computed numerically. Since the SD values are usually small, the right hand side of Eq. (13a) may be viewed as a perturbation term. The disadvantages of introducing this complication is far out-weighed by the advantages, namely, a greater accuracy and a simpler equation to determine $t = t(x)$.

Applying the MG transformation given by Eq. (5b) to Eq. (13a), selecting a comparison potential which satisfies Eq. (9) and employing Eqs. (12) to determine $t(x)$, $\psi(x)$ is obtained after solving Eq. (4), which is rewritten as follows:

$$\left[\frac{d^2}{dt^2} + q^2(t)\right]\phi(t) = \frac{1}{Z}\, t'^{-2}\langle t;\, x\rangle\phi(t) \quad . \tag{13b}$$

If two linearly independent exact solutions, A(t) and B(t), of the homogeneous form corresponding to Eq. (13b)

$$\left[\frac{d^2}{dt^2} + q^2(t)\right]\phi_0(t) = 0 \quad , \tag{14a}$$

are easily determined analytically, then the solution to Eq. (13a), (or Eq. (13b)), can be facilitated. Among the several methods of constructing the solution to Eq. (13a), the familiar method of variation of parameters

(special method of perturbations)[25] is considered here:

$$\psi(x) = \tilde{\alpha}(x)\tilde{A}(x) + \tilde{\beta}(x)\tilde{B}(x) \quad , \tag{15a}$$

$$\phi(t) = \alpha(t)A(t) + \beta(t)B(t) \quad ,$$

where $\tilde{A}(x) = t'^{-\frac{1}{2}} A(t(x))$, etc., and $\tilde{\alpha}(x) = \alpha(t(x))$, etc. This last property may be readily verified directly employing Eqs. (9), (13), (14), and (15). The quantities $\tilde{A}(x)$ and $\tilde{B}(x)$ can be viewed formally as independent solutions of the homogeneous form of Eq. (13a):

$$\left[\frac{d^2}{dx^2} + p^2(x) + \frac{1}{2}\langle t; x\rangle\right]\psi(x) = 0 \quad . \tag{14b}$$

The constraint

$$\dot{\alpha}A + \dot{\beta}B = 0 \quad , \tag{16}$$

will be utilized in this report[17]. The reader is referred to a more general constraint in Sec. 5. From Eqs. (13) to (16) the following fundamental system of linear, first-order differential equations for the coefficients $\tilde{\alpha}(x)$ and $\tilde{\beta}(x)$ is obtained:

$$\tilde{\alpha}'(x) = -W_x^{-1}[\tilde{A}, \tilde{B}]\tilde{B}(x)g(x)[\tilde{\alpha}\tilde{A} + \tilde{\beta}\tilde{B}] \quad , \tag{17a}$$

$$\tilde{\beta}'(x) = W_x^{-1}[\tilde{A}, \tilde{B}]\tilde{A}(x)g(x)[\tilde{\alpha}\tilde{A} + \tilde{\beta}\tilde{B}] \quad , \tag{17b}$$

where $W_x[\tilde{A}, \tilde{B}] = W_t[A, B]$ is the Wronskian determinant of the reference solutions, and

$$g(x) = -\frac{1}{2}\langle t; x\rangle \quad . \tag{18}$$

Equations similar to (17) may be written for the t-dependent coefficients $\alpha(t)$ and $\beta(t)$. The functional x (or t) independence of the Wronskian

follows from the linear independency of the solutions to the Schrödinger-type equations.

Notice that hitherto no ad hoc approximations have been made in the ICEM, a rigurous treatment that will be maintained in Sec. 5. Indeed one could obtain analytical solutions to Eq. (17) only if there was a way to express $\tilde{A}$, $\tilde{B}$ and g analytically. In order to achieve this goal, after finding analytical solutions to the homogeneous-like equation (14a), it would remain to express t as a function of x. This could be made in principle from Eqs. (12). However, for most of the interaction potentials, there is not an elementary way to express t in terms of x, and one must resort to numerical methods.

Several methods to solve close-coupled equations have been developed during the last fifteen years[14,17,19,26]. Within a close-coupling approach, an arbitrary accuracy is supposedly achieved, the primary limitation arising from practical reasons of saving computer time. Before ending this section, some general advantages of the ICEM over the approximate potential methods currently in use in close-coupling calculations must be emphasized. The discussion will be limited to comparing it with Gordon's method[17], mainly because the close parallelism between the methods and because, as it will be seen soon, Gordon's method may be considered a particular case of our approach.

From a formal point of view, Gordon's approach has severe restrictions. The reference potential used in this method may be viewed as a comparison approach to the true potential via a Taylor expansion. Therefore, it is limited to polynomial expressions. In practice, if one wants to maintain a simple structure of the comparison equation, the linear and/or the constant terms are the only ones to be kept in a series expansion[17]. Moreover, boundary conditions must be adjusted at each step of the integration. The inconveniencies of this method result on enormous computer time consumption, mainly for potentials which vary strongly with the spatial coordinate.

The above limitations are not found within the present scheme. The ICEM is an analytical method without severe restrictions, the main restriction being to set in congruency special points. Nevertheless, it is amenable to practical approximations which can be adjusted satisfactorily

whenever a great accuracy is required. The most obvious approximation is to take into account the SD term only at those regions within which it contributes substantially. As a rule of thumb, the SD term is mostly meaningful within the transition regions. In these regions $p^2(x)$ and $q^2(t)$ both tend to zero. Therefore, the inhomogeneous-like SD term in the r.h.s. of Eqs. (13), which plays the role of $g(x)$ in Eq. (1a), determines the actual behavior of the second-order differential equation and should not be neglected therein. This point will be illustrated in Section 4. It should be noticed that the uniform approximations cannot represent the exact solutions across the transition regions since they neglect the SD term everywhere.

Another useful approximation parallels Gordon's method. Instead of limiting the discussion to expanding the true (real) potential in a Taylor series, a further step is taken to express the true, the comparison momenta and the new spatial coordinate as infinite series around an arbitrary point x_0:

$$\left.\begin{aligned} p^2(x) &= \sum_{n=0}^{\infty} a_n u^n \\ q^2(t(x)) &= \sum_{n=0}^{\infty} b_n u^n \\ t(x) &= \sum_{n=0}^{\infty} c_n u^n \end{aligned}\right\} , \tag{19}$$

where $u = x - x_0$. The quantity t' is readily determined from Eq. (9) once the b_n coefficients have been determined. It only requires to evaluate the t derivatives at x_0. Implicit derivation permits evaluation of higher derivatives at any point. As an example,

$$t'' = \left\{ [p^2(x)]' - t'^2 [q^2(t(x))]' \right\} / 2q^2(t(x))t' \tag{20}$$

This procedure was adopted to evaluate numerically the SD function in the very -near turning-point regions for the case considered in Sec. 4, where a direct evaluation would cause numerical instabilities. Moreover, this procedure illustrates how to incorporate Gordon's method and other

approximate-potential methods whithin the more general ICEM, since the comparison equation is still Eq. (13b).

4. THE BOUND STATE PROBLEM EXEMPLIFIED

The discussion, up to this stage, has been general in character. From the practical point of view, it is highly desirable to have vanishingly small values for the perturbation-like term, f(t), in a large integration region[25]. This would result in slowly varying functions for the variable coefficients. This can be an advantage numerically because a reasonably large step-length (commonly called h) can be used in the integration. If the coupling matrix elements of the potential in a close-coupling approach to the many-channel problem are large, further approximations may be made. If this is not the case, the SD term plays the role of the coupling potential and must be carefully evaluated.

To describe accurately the vibrational levels of diatomic molecules Morse introduced in 1929 the exponential potential[27]

$$V(x) = D\exp[-a(x - x_0)]\left\{\exp[-a(x - x_0)] - 2\right\} \quad , \tag{21}$$

which sometimes is conveniently written as

$$V(x) = \left\{1 - D\exp\left[-a(x - x_0)\right]\right\}^2 \quad . \tag{21a}$$

The depth and width parameters D and a are empirically determined, while x_0 is the equilibrium distance parameter.

The Morse potential was soon afterwards extended to cover a wide variety of problems, *e.g.*, neutron-proton scattering[28], molecule-solid surface interactions[29], etc. Slightly different versions of it have been used to model double well potentials[30a,b] and other rather broad problems like the one considered in Ref. 30c and in the admirable work of Fernández and Castro[30d]. Several processes in molecular[30-33] and surface physics[34-37], are suitably described by the Morse potential given by Eq. (21). The radial Schrödinger equation for the Morse potential is not exactly solvable analytically, as has been pointed out by ter Haar[38].

The one-dimensional analogue and the radial equation have been treated analytically on several occasions[39,40], almost always to obtain only the eigenenergies of the anharmonic oscillator. Numerical studies employing the Morse potential have been done several times to compare the merits of different approximate procedures of eigenvalue calculation. An analytical treatment of the one-dimensional bound-state problem for the Morse potential in terms of exact, normalized, closed form wavefunctions has been given by Nieto and Simmons[41].

The perpendicular motion of atoms or molecules incident on a solid surface is often described by a strong repulsive term near or inside the surface and a long-range attractive part which are well fitted by the potential given in Eq. (21). Slight modifications of the Morse potential allows the inclusion of dissociation or similar processes[36]. It can be mentioned in passing that the atom (molecule)-solid surface scattering is a case in which a large number of open and closed channels must be included[34,36]. Since the one-dimensional uncoupled problem is exactly solvable, while a strong interaction demands a careful numerical treatment, the Morse potential is regarded as a good candidate to test the procedure.

For completeness sake, the analytical solution of the Schrödinger equation for the Morse potential is briefly presented, and the exact eigenfunctions and eigenvalues for a particular case where there are only two discrete eigenenergies are determined. With the change of variable $y = \exp[-a(x - x_0)]$, the Schrödinger equation

$$\left[\frac{d^2}{dx^2} + k^2 - U(x)\right]\psi(x) = 0 \quad , \tag{22}$$

where $k^2 = 2mE/\hbar^2$ and $U(x) = 2mV(x)/\hbar^2$, becomes

$$\left[\frac{d^2}{dy^2} + \frac{1}{y}\frac{d}{dy} + \frac{1}{a^2}\left[\frac{k^2}{y^2} + \frac{2D'}{y} - D'\right]\right]\psi = 0 \quad .$$

Here $D' = 2mD/\hbar^2$. The substitution $\psi = \exp(-yd)y^{b/2}F$, where b and d are constants to be determined, gives

$$y\frac{d^2F}{dy^2} + (b+1-2yd)\frac{dF}{dy} + \left[\frac{\frac{k^2}{a^2}+\frac{b^2}{4}}{y} + \frac{2D'}{a^2} - d(b+1) + \left(d^2 - \frac{D'}{a^2}\right)y\right]F = 0 \ . \quad (23a)$$

Eq. (23a) is not in the most convenient form to take advantage of standard mathematical information. Setting $z = 2yd$, and making the definitions

$$\beta \equiv b + 1, \qquad \alpha \equiv \beta/2 - d \quad (24)$$

equation (23a) becomes

$$\left[z\frac{d^2}{dz^2} + (\beta - z)\frac{d}{dz} - \alpha\right]F(z) = 0 \ , \quad (23b)$$

which is Kummer's standard form of the confluent hypergeometric equation[42]. The parameters b and d are determined by means of the relations

$$b^2 = -4k^2/a^2, \qquad d = \sqrt{D'}/a \quad (25)$$

A common pair of linearly independent solutions of equation (23b) are given in terms of the confluent hypergeometric series of z, $M(\alpha, \beta; z)$. This series can be accurately summed up by using either a generalized Euler transformation[43] or the classical and highly practical method of Padé-Frobenius approximants[44]. The solutions of Eq. (23b) are the nonelementary functions[42]

$$F_1(z) = M(\alpha, \beta; z) \quad (26a)$$

$$F_2(z) = z^{1-\beta}M(1+\alpha-\beta, 2-\beta; z) \ . \quad (26b)$$

For the entire range, $-\infty < z < \infty$, the first solution becomes a finite polynomial if $\alpha = -n$, $n = 0,1,2, \ldots$ From Eqs. (24), (25) and (26) the following expression for the eigenenergies is readily derived

$$E_n = -\frac{1}{2m}\left(\frac{a\hbar}{2}\right)^2\left[2(d-n)-1\right]^2 \quad . \tag{27}$$

Since the energy eigenvalues are independent of the choice of the equilibrium distance parameter, x_0, this parameter was arbitrarily chosen to be unity. Using atomic units throughout and taking for convenience $a = 3$, $d = 7/3$, and $m = 1000$, we found [from the requirement that $\psi(y \to \infty) = 0$], that two values of α, namely $\alpha = 0$ and $\alpha = -1$ gave rise to one bound state each. The exact discrete eigenvalues for the Morse function are then

$$E_0 = -0.4114 \text{ eV}, \qquad E_1 = -0.0850 \text{ eV}.$$

Before proceeding to solve the foregoing eigenvalue problem using the ICEM, it should be mentioned that an estimate of the eigenenergy value can be inferred from the homogeneous-like equation (14a). In spite of the fact that Eq. (14a) is not a proper eigenvalue equation, the perturbation-like term which modifies it [see Eq. (13b)] is often small compared to $q^2(t)$ in Eq. (13a). Therefore, an "eigenvalue" for ε in Eq. (14a) determines a zeroth-order eigenvalue for E in Eq. (12b). The value of E so obtained may be regarded as a trial value to the energy of the eigenvalue problem posed by Eq. (1).

A tractable comparison potential is the quadratic form

$$v(t) = \frac{1}{4}t^2 \quad . \tag{28}$$

This approximation to the true potential gives rise to Weber's canonical equation[45],

$$\frac{d^2\phi_0}{dt^2} + \left(\varepsilon - \frac{1}{4}t^2\right)\phi_0 = 0 \quad , \tag{29}$$

where ε is an as yet undetermined parameter, independent of t. Eq. (29)

may be solved exactly in terms of parabolic cylinder functions[45,46]. For this discussion it is preferable to consider the two linearly independent solutions A(t) and B(t), in terms of confluent hypergeometric functions, given by[47]

$$A(t) = \frac{\pi^{\frac{1}{2}}}{\Gamma(\alpha' + \frac{1}{2})} \exp\left(-\tfrac{1}{4} t^2\right) M(\alpha', \tfrac{1}{2}; \tfrac{1}{2}t^2) \quad , \tag{30a}$$

$$B(t) = \frac{(2\pi)^{\frac{1}{2}}}{\Gamma(\alpha')} \exp\left(-\tfrac{1}{4}t\right) tM\left(\alpha' + \frac{1}{2}, \frac{3}{2}; \frac{1}{2} t^2\right) \quad , \tag{30b}$$

with $\alpha' = (1 - 2\varepsilon)/4$. Two stationary solutions of Eq. (29) are obtained with $\alpha' = 0, -1$ and the ε-values so obtained are zeroth-order solutions to the "eigenvalue" problem given by Eq. (14a).

It should be noticed that, apart from the bound-state energies previously determined, Weber's equation supports an infinite sequence of spurious discrete eigenvalues. They are spurious with respect to the Morse potential as was seen after solving the problem analytically since it gives rise to two eigenstates for the range and depth considered in the example. This peculiarity should not be a matter of astonishment. One recalls that the transformation utilized within the context of the ICEM does not establish an isospectral correspondence between two bound-state problems. Indeed, this would be the case in the conventional comparison equations method (see Sec. 3), including the cases where an iterative procedure is used.

Using the zeroth-order solutions as a first approximation, equations (17) may be solved iteratively between two points suitably removed from the turning points, where $\psi(x)$ given by Eq. (15) approaches zero. One may then seek a solution where the number of zeroes is in agreement with the oscillation theorem[48]. Instead, Eqs. (17) were numerically integrated, utilizing a solver from the open literature, and using Eqs. (30) as independent solutions to Eq. (29); the initial conditions were chosen such that the approximate wavefunctions matched the exact ones at the point where the integration began.

Exact normalized bound-state wavefunctions obtained from Eq. (26) are shown as solid lines in Figs. 1a and 1b. The computed approximate wavefunctions corresponding to the exact eigenenergies are represented in the drawings by dashed lines. They are graphically indistinguishable from the exact solutions up to values about $r \approx 2.0$ in Fig. 1a, and up to values about $r \approx 2.5$ in Fig. 1b. The numerical results are most encouraging. Indeed, up to those values of r the difference in the results was less than 0.2%. Dotted and dashed-dotted curves illustrate the solutions obtained when the energy values were chosen to be about 4% less than (dotted) or greater than (dashed-dotted) the exact eigenenergies. In the former case the "wavefunctions" do not turn down as much, failing to match the node to the right of the first (second) turning point in Fig. 1a (Fig. 1b); for large distances the "wavefunctions" go to $+\infty$. This behavior is to be expected from an analytical treatment of the problem. In the latter case the "wavefunctions" peak sooner and they descend more rapidly than the corresponding exact wavefunctions. We notice, again as expected, that : (a) the "wavefunctions" exhibit more nodes than required, and (b) the "wavefunctions" go to $-\infty$.

The perturbation-like term $f(t(x))$ defined by Eq. (7b) was evaluated numerically using Eqs. (8) and (9). In the very-near turning-points regions it was evaluated as described in Sec. 3. Figure 2 compares the values of $f(t(x))$ for the ground-state as a function of x with those of $q^2(t(x))$, of which potential it may be regarded as a perturbation. It is seen that its values are of the order of 1% for the main range of integration. It is certainly dominant at the classic turning-points regions. It takes its largest values far to the right of the second turning-point, where the Morse potential differs substantially from the harmonic oscillator potential.

5. THE MANY-CHANNEL PROBLEM

Ordinary one-dimensional linear second-order differential equations can be numerically solved rapidly and very accurately using any of the several highly efficient integrators available[12]. This is not, however, the case, in a many-coupled-channel problem[14,17,26]. As was

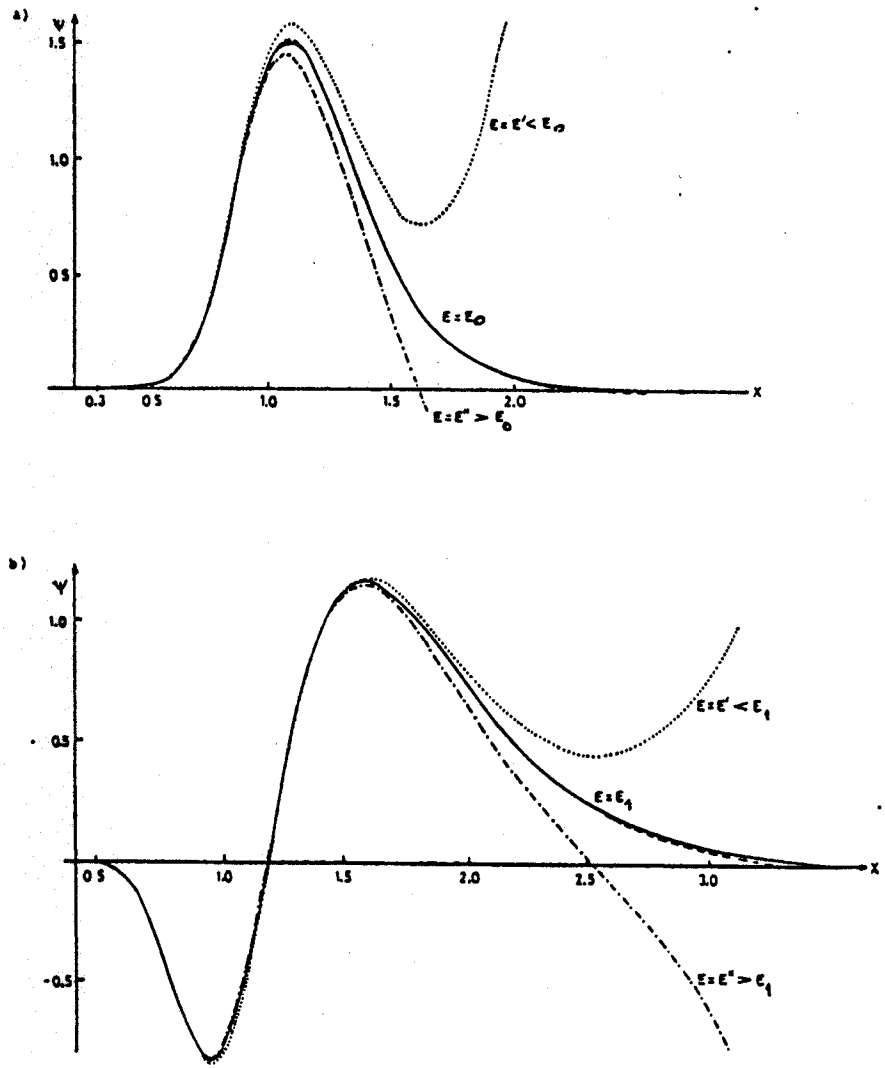

Fig. 1. Comparison of the results of the analytical and numerical methods of calculation of normalized eigenfunctions, corresponding to the two stationary states of the Morse potential for the parameters given in Sec. 3. Figure 1a: E_0 = -0.4114 eV. Figure 1b: E_1 = -0.0850 eV. Solid lines: analytical solutions; dashed lines: numerical solutions generated using the exact eigenenergy value. The agreement of the computed and the exact bound-state eigenfunctions is excellent even for the lowest eigenvalue. Dotted (dashed-dotted) lines: numerical solutions obtained using and energy value lower (higher) than the exact one by about 4%.

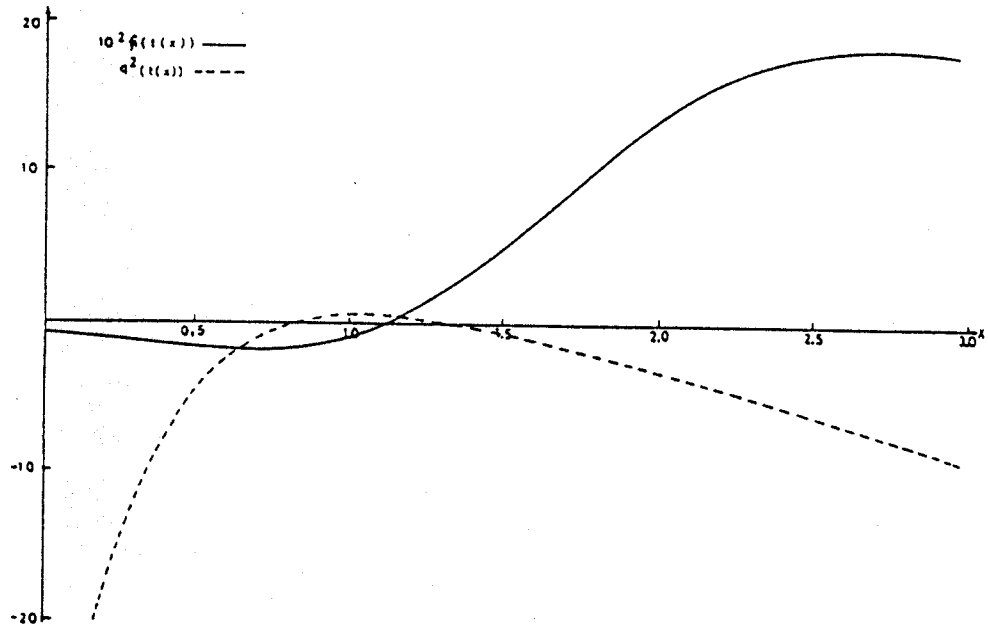

Fig. 2. The perturbation-like term f(t) (see Eq. (7b)) and the comparison momentum $q^2(t)$ for the ground state as a function of x.

pointed out in the Introduction, the main limitation in this case is the amount of computer time available. It becomes almost prohibitive when the number of channels is of order one-hundred[26]. It is our believe that it is for this case that the ICEM is most useful.

The discussion is limited to the case for which the many-channel problem is reduced to solve the following set of coupled-Schrödinger equations:

$$\left[\frac{d^2}{dx^2} + p_\xi^2(x)\right]\psi_\xi(x) = \sum_\zeta V_{\xi\zeta}(x)\psi_\zeta(x) \tag{31}$$

ξ and ζ being the channel indices.

According to the procedures employed in Sec. 3, we rewrite Eq. (31) in the revised form:

$$\left[\frac{d^2}{dx^2} + p_\xi^2(x) + \frac{1}{2}\langle t_\zeta; x\rangle\right]\psi_\xi(x) = \sum_\zeta \left[\frac{1}{2}\langle t_\zeta; x\rangle\delta_{\xi\zeta} + V_{\xi\zeta}(x)\right]\psi_\zeta(x). \tag{32a}$$

After using the MG transformation

$$\psi_\xi(x) = t_\xi'^{-\frac{1}{2}}\phi_\xi(t_\xi)$$

one readily obtains:

$$\left[\frac{d^2}{dt^2_\xi} + q_\xi^2(t_\xi)\right]\phi_\xi(t_\xi) = \sum_\zeta t_\xi'^{-2}\left[\frac{1}{2}\langle t_\xi; x\rangle\delta_{\xi\zeta} + V_{\xi\zeta}(x)\right]\phi_\zeta \quad . \tag{32b}$$

There is now a new and different spatial coordinate t_ξ for each channel related to the old and new corresponding momenta by

$$t_\xi' = \frac{p_\xi^2(x)}{g_\xi^2(t_\xi)} \quad , \tag{33}$$

and determined uniquely from relationships similar to Eqs. (12).

The choice of the ansatz

$$\psi_\xi(x) = \tilde{A}_\xi(x)\tilde{\alpha}_\xi(x) + \tilde{B}_\xi(x)\tilde{\beta}_\xi(x) \quad , \tag{34a}$$

and the constraints

$$\tilde{A}_\xi(x)\tilde{\alpha}_\xi'(x) + \tilde{B}_\xi(x)\tilde{\beta}_\xi^{\,1}(x) = 0 \tag{34b}$$

yield

$$\tilde{\alpha}'(x) = -W_x^{-1}[\tilde{A}_\xi, \tilde{B}_\xi]\tilde{B}_\xi(x)\sum_\zeta\left[\frac{1}{2}\langle t_\zeta; x\rangle\delta_{\xi\zeta} + V_{\xi\zeta}\right]\psi_\zeta \quad , \tag{35a}$$

$$\tilde{\beta}'(x) = W_x^{-1}[\tilde{A}_\xi, \tilde{B}_\xi]\tilde{A}_\xi(x)\sum_\zeta\left[\frac{1}{2}\langle t_\zeta; x\rangle\delta_{\xi\zeta} + V_{\xi\zeta}\right]\psi_\zeta \quad . \tag{35b}$$

This is the starting point common to several calculations[9,14,17,21,26,34,49].

In heavy-particle collisions including energy transfers and chemical reactions, Eq. (31) assumes a somewhat more complex mathematical structure. The main feature being the inclusion of a first derivative of the wavefunction with respect to the spatial coordinate. Before applying the preceding scheme, a unitary transformation is made to simplify the structure of the equation[49]. In those cases it is useful to change the constraint given by Eq. (34b) to the following convenient matrix equation constraint[49]:

$$\tilde{\tilde{A}}\alpha' + \tilde{\tilde{B}}\beta' + \pi(\tilde{\tilde{A}}\alpha + \tilde{\tilde{B}}\beta) = 0 \quad , \tag{36}$$

where π denotes a square matrix whose terms include first order differential operators[21,49]. Clearly, the first two terms in Eq. (36) reduce to Eq. (34b) if π were not present. The procedure used to obtain the solution to the generalized Eq. (35) is straighforward. It is seen that the only effect is to add a diagonal term, the SD term, to the coupling potential matrix elements. As it is seen from Eq. (35) the structure of the resulting first-order differential equations is not more complicated than that of Eqs. (17) after incorporating the SD term. Therefore, one can take advantage of the analytical simplicity of the ICEM (extended comparison equation or uniform approximation methods) and the numerical easiness of the reference potential procedure to perform efficient close-coupling calculations whenever great accuracy is required in a many-channel problem.

6. SUMMARY AND DISCUSSION

It has been shown that the improved comparison equation method, ICEM, is markedly superior to both the analytical comparison equation or uniform approximation method which uses the Miller-Good transformation[3-5,9-11], and the numerical approximate potential calculation method implemented by Gordon[16-19] in solving Schrödinger-like equations. Maintaining the simplicity introduced by MG, the rigor is preserved

without the need to use complicated iterative schemes. In spite of its simplicity, in the present method the computational efforts are reduced in those situations which require considerable numerical accuracy. The method is also amenable to a variety of approximations which further simplify the problem and reduce still further the computational time.

The gist of the comparison equation method is to utilize a convenient simultaneous nonsingular transformation of the wavefunction and the spatial coordinate, to transform the original linear second-order ordinary differential equation to a simpler form. It is an analytical approach. Yet the procedures in use[3,5,9] make approximations that are not always legitimate. Further, the iterative schemes proposed to improve accuracy[4,11] do not differ basically from the perturbational approaches, including all their inconveniences[21,25].

In the reference (numerical) potential scheme the true potential expression is approximated by a simpler form which permits an analytical solution. The solution obtained for the approximate problem is then utilized for solving the original problem. In principle, a convenient handling of the numerical procedure adopted guarantees the achievement of any desired accuracy. The renowned Gordon method[16,17] includes the unpleasant feature that one must match the logarithmic derivative of the wavefunction at the extremes of each small domain into which the range of integration is decomposed. It is therefore onerous for computational purposes, especially in problems requiring great accuracy and where many channels are to be dealt with.

In the present proposal the above two schemes are blended properly in a *mariage de convenance*. The reference potential is obtained after an analytical transformation is performed. Further, the same reference potential may be utilized for the entire range of integration. The comparison is then made with a different-structure equation, namely, a homogeneous one to an inhomogeneous form. This procedure brings the comparison method close to the reference potential scheme, allowing one to make use of the own advantages that each method posseses.

Two additional appealing features of the method that are worth noting are: first, it compares favorably to the conventional comparison

equation method, guaranteeing an exact determination of the new spatial coordinate, without any semiclassical approximations; second, it compares favorably to the reference potential method, because the computational efforts are reduced while a great accuracy has been maintained.

The added complication of the present method is the necessity to evaluate the Schwartzian derivatives which is usually done numerically. Nevertheless, if one initially accepts that the problem must be grasped numerically, a promising and powerful amalgamated procedure emerges; it consists of looking for Schrödinger-homogeneous-like equations that have a potential with the following characteristics: It resembles the old potential in a very crude way, and it should be simple enough to permit an analytical solution of the Schrödinger-like equation in terms of non-elementary functions. These functions are used to construct numerical solutions to the problem under consideration.

The main disadvantage of the comparison equation approach is that the Schwartzian derivatives neglected; it thus fails to yield an exact solution through the classical transition points, wherein both $p^2(x)$ and $q^2(t)$ go to zero, and the SD term determines the behavior of the wavefunction. The usual reference potential method employs a Taylor series expansion of the true potential and only the first term is kept. Whenever a great accuracy is required, both procedures have their limitations. These are overcome in the present approach.

The advantages of the method proposed here are still greater in many-channel problems. In such cases one simply adds the SD term as a diagonal term to the coupling potential matrix elements (see Eqs. (32)). If the set of coupled-second-order equations is reduced to a first-order system, the appearance of the (exact) last one does not represent substantial complications over the one obtained when neglecting the SD values. Further, whenever the approximations made within either the conventional comparison equation or reference potential methods are valid, it is an easy matter to carry over these approximations within our scheme. There is a final important theoretical feature of the method advocated here which is not shared by conventional comparison equation and reference potential treatments. We do not *neglect* terms. Thus *any* comparison

equation may be used in practice.

In light of the discussion above, the saving in computational time and the reliability of the solutions obtained should appear obvious. Recent experimental studies of elastic and inelastic atom-solid surface scattering[50-51] is spurring growing interest to describe these scattering systems theoritically[36,37,52]. An application of the present scheme to scattering of atoms by a surface, where upt to fifty channels are involved[34-37], is currently in progress. Further applications of the method to scattering problems (from purely repulsive or purely atractive regular potentials) in quantum mechanics is envisaged.

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