

AN IMPROVEMENT TO THE COMPARISON EQUATION METHOD FOR SOLVING THE SCHRÖDINGER EQUATION

J. GIRALDO

Departamento de Física, Universidad Nacional de Colombia, Bogotá, D.E., Colombia

R.G. BARRERA

Institute of Physics, University of Mexico, Mexico 20, D.F., Mexico

and

G.A. ESTÉVEZ

Department of Mathematics, Chemistry, Physics and Computer Science, Interamerican University, San Germán, Puerto Rico 00753, USA

Received 29 June 1984

A systematic improved comparison equation method to solve the Schrödinger equation is described. The method is useful in quantum mechanical calculations involving two or more transition or turning points and is applicable to real potentials with continuous derivatives. As a computational example of the method, a study of the bound-state problem using the Morse potential is given.

1. Introduction

Several problems in chemical physics are reduced to the solution of a system of N coupled linear second-order differential equations, the quantum mechanical equations of motion for the different kind of collisions being one of the most remarkable examples [1–3]. This problem, and the single one-dimensional Schrödinger equation (with some exceptions) cannot be solved exactly by analytical methods. Indeed, completely analytical solutions to the Schrödinger equation have been obtained for only a handful of problems; in atomic and molecular physics these consist of a few one- and two-electron systems. One has thus to resort to an approximate analytical method or to direct numerical solution of the Schrödinger equation. It appears that the close-coupling approach is currently the most accurate method to treat multi-channel problems [1,2]. Its solutions are obtained mainly computationally, although, in principle, there are always two ways of solving the problem: the ana-

lytical and the numerical

Major strides have been made during the past fifteen years in the development of highly efficient and accurate numerical integrators to solve the N coupled channel problem [1,2,4–8]. Nevertheless, as the experimental techniques are further developed to discern among the various fine effects present in the scattering phenomena, e.g., rotational, vibrational and electronic excitations, it has proved necessary to include an increasingly large number of channels (see, for instance, the expository article by Secrest in ref. [1]), thus causing the computational time to escalate. Indeed, the computational time grows as N^3 , N being the number of coupled equations to be solved.

Among the various computational methods referred to above, the approximate-potential approach [1,2], pioneered and implemented on different grounds by Gordon [4] and by Light [5], have come into prominence in recent years [6–9]. To have a tractable (approximate) form of the reference equation (a particular comparison form, as will be seen soon), only the

first terms in a Taylor series expansion of the potential need be considered.

The uniform approximation treatment [10], based on the Miller—Good transformation [11], is an analytical tool to solve the Schrödinger equation asymptotically [12]. It is a semiclassical approximation, belonging to the comparison equation procedures [13], in which two similar-structure homogeneous-like equations are compared.

It is the main purpose of this report to present a new method to solve the Schrödinger-like equation, partly analytically, partly numerically, ridden from semiclassical approximations and without severe restrictions regarding the way by which the comparison (reference) potential adapts to the original one. The new approach seems to be highly efficient when a great accuracy is required and a great number of channels have to be included, it is also amenable to several approximations, which reduce significantly computational efforts in various situations. To some extent it is an analytical generalization on the potential treatment given in ref. [4], implemented computationally using any of the various techniques actively being developed

2. Derivation

The basic methodology of the approach here proposed will be illustrated by considering the usual one-dimensional stationary Schrödinger equation. An extension of the derivation to include many-channel problems is straightforward.

To overcome some of the limitations of the JWKB method [14] * to solve the Schrödinger-like equation, Miller and Good [11] have proposed to utilize a convenient simultaneous non-singular transformation of the wavefunction and the spatial coordinate to transform the homogeneous-like equation

$$[d^2/dx^2 + p^2(x)] \psi(x) = 0, \quad (1)$$

into a similar relation:

$$[d^2/dt^2 + q_{MG}^2(t)] \phi(t) = 0, \quad (2)$$

where q_{MG}^2 is a comparison potential to be adequately

selected. Usually, an analytic expression for $q_{MG}^2(t)$ is chosen such that it resembles the real function $p^2(x)$ [11]. Miller and Good used a modulating amplitude factor $T = (t')^{-1/2}$, where $t' = dt/dx$ so that

$$\psi(x) = (t')^{-1/2} \phi(t). \quad (3)$$

Comparing eqs. (1) and (2) and using eq. (3), Miller and Good obtained the following relationship to determine the new spatial coordinate t .

$$(t')^2 = [p^2(x) - \frac{1}{2} \{t, x\}] / q_{MG}^2(t) \quad (4)$$

The second term within the square brackets on the right-hand side of eq. (4) involves the Schwartzian derivatives [11,12,15].

$$\{t, x\} = t'''/t' - \frac{3}{2}(t''/t')^2. \quad (5)$$

It can be seen that eq. (4) is a non-linear third-order differential equation. Given the involved structure of eq. (5), the odds that eq. (4) can be solved analytically are rather slim, while it must be a Herculean task to solve eq. (4) numerically. To obtain approximate analytical solutions, perturbational approaches have been advanced by Hecht and Mayer [15], and more recently by Pechukas [16]. The present approach implements the Miller—Good transformation so that the Schwartzian derivatives term does not appear explicitly in the differential equation which defines t .

Instead of the homogeneous-like equation (2), the inhomogeneous form

$$[d^2/dt^2 + q^2(t)] \phi(t) = h(t)\phi(t), \quad (6)$$

is considered here, where $h(t)$ is a perturbation-like potential term [7]. After performing the Miller—Good transformation given by eq. (3), it is seen that eq. (1) is cast in the form of eq. (6) when the following identification is made.

$$h(t) = \frac{1}{2}(t')^{-2} \{t, x\}, \quad (7)$$

in which case

$$(t')^2 = p^2(x)/q^2(t). \quad (8)$$

It can be noted in passing that eq. (4) reduces to the simpler form given by eq. (8) if $\{t, x\}$ is taken to be zero. This particular case is equivalent, within the present scheme, to approximating eq. (6) to the homogeneous form eq. (2). Superficially, the difficult problem of solving eq. (4) has been transformed to solving another difficult one, eq. (6). This is *not* so as alterna-

* The literature on the JWKB approximation is now large and we cite here only one recent reference.

tive techniques, such as the standard Green function method [17], exist to deal with inhomogeneous-like equations, whereas the involved mathematical structure of eq. (4) is hardly manageable, even in supposedly simple situations. Furthermore, within the present scheme, once an appropriate comparison momentum $q^2(t)$ has been selected, the transformation $t = t(x)$ can be determined *exactly* by using the following equations [10]:

$$\int_{t_0}^t |q^2(\tau)|^{1/2} d\tau = \int_{x_0}^x |p^2(\xi)|^{1/2} d\xi \quad (9)$$

and

$$\int_{t_i}^{t_{i+1}} |q^2(\tau)|^{1/2} d\tau = \int_{x_i}^{x_{i+1}} |p^2(\xi)|^{1/2} d\xi, \quad (10)$$

where t_0 is an arbitrary integration constant, arising from the solution of the first-order differential equation (8); t_i is a classical transition or turning point of the transformed potential, set in correspondence with the classical turning point x_i of the true potential. The quantity $q^2(\tau)$ involves the determination of $n - 1$ parameters from eq. (10), n being the number of classical turning points.

Where in the conventional treatments of comparison-equation and uniform approximations [10–12,15,16], several semiclassical approximations are made to obtain eqs. (9) and (10), within the present scheme they are *exact* relationships. The one-to-one correspondence between the classical turning points of true and transformed potentials guarantees the continuity of the transformation for real potentials.

Once $t = t(x)$ has been determined exactly, one turns to the solution of eq. (6) for $\phi(t)$. From knowledge of t and $\phi(t)$ there follows from eq. (3) the value of ψ , the solution to eq. (1). There are currently available alternative analytical techniques [17,18], and numerical methods [1–9], which make use of the homogeneous form

$$[d^2/dt^2 + q^2(t)]\phi_0(t) = 0, \quad (11)$$

to solve the inhomogeneous-like equation (6). The comparison method adopted in this Letter is similar in some respects to, but somewhat more general than, Gordon's reference potential method. To keep the parallelism with Gordon's approximate potential ap-

proach (a propagator procedure), the advantages of the preceding scheme will be illustrated using the variation of parameters treatment (special method of perturbations) [18]. In this case, if $A(t)$ and $B(t)$ are two analytically exact linearly independent solutions of eq. (11), the most general solution of eq. (6) is then expressible in the form

$$\phi(t) = \alpha(t)A(t) + \beta(t)B(t), \quad (12)$$

where $\alpha(t)$ and $\beta(t)$ are functions of t to be determined [17,18]. The constraint

$$\dot{\alpha}A + \dot{\beta}B = 0, \quad (13)$$

where $\dot{\alpha} = d\alpha/dt$ and $\dot{\beta} = d\beta/dt$, will be adopted in this paper [4,5]. Substituting eq. (12) into eq. (6), and using eqs. (11) and (13), yields:

$$\dot{\alpha}(t) = -W_t^{-1}[A, B]Bh(t)[\alpha A + \beta B], \quad (14a)$$

$$\dot{\beta}(t) = W_t^{-1}[A, B]Ah(t)[\alpha A + \beta B], \quad (14b)$$

where $W_t[A, B]$ denotes the Wronskian of the two real independent solutions to eq. (11) and is a constant.

3. Test calculation

The Morse potential is written as [19]

$$U(x) = D \exp[a(\xi_0 - x)] \{ \exp[a(\xi_0 - x)] - 2 \}, \quad (15)$$

where D and a are empirical parameters and ξ_0 is the equilibrium distance parameter. The Morse potential has been an excellent test case for the effectiveness of several numerical methods for bound states. As is well known the radial Schrödinger equation corresponding to the Morse potential ($0 \leq r < \infty$) is not exactly solvable analytically [20]; its one-dimensional analogue ($-\infty < x < \infty$) is, however, of a particularly tractable form analytically, yet it must receive a careful numerical treatment. Slightly different versions of the Morse potential have been used to model double well potential [21,22] and other rather broad problems [23,24].

Over a certain range of conditions, the Morse potential in the one-dimensional case is seen to describe well the perpendicular motion of atoms or molecules incident on a solid surface [25] **. This particular multichannel problem will be the subject of a forth-

** For a recent review, see ref. [26], also, see, e.g. ref. [27].

coming article [28]. The potential described by eq. (15) ($-\infty < x < \infty$) is regarded as a good candidate to test the proposed method.

In the notation of ref. [19] the exact bound-state eigenenergies for the Morse potential are given by [19]:

$$k^2 = 2mE/\hbar^2, \quad k^2 = -\frac{1}{4}a^2b^2, \quad (16)$$

where $b = \beta - 1$, $\beta = 2(\alpha + d)$, $d = (2mD)^{1/2}/\hbar a$. In eq (16) k^2 represents the square wavevector.

The exact wavefunctions are given in terms of confluent hypergeometric series [29]. The series become polynomials when $\alpha = 0, -1, -2$, etc. Also, for bound states, b must be positive definite. Using atomic units throughout the next and taking $a = 3$, $d = 7/3$ and $m = 1000$, there are just two eigenstates with corresponding energy levels: $E_0 = -0.4114$ eV and $E_1 = -0.0850$ eV. These are derived from the expression for the eigenenergies for the Morse potential:

$$E_n = -(1/2m) (\frac{1}{2}a\hbar)^2 [2(d - n) - 1]^2. \quad (17)$$

In solving the Schrödinger equation for the Morse function within the present approach, the reduced quadratic reference potential $v(t) = \frac{1}{4}t^2$ was employed [4,11,30]. This approximation to the true potential gives rise to Weber's canonical equation [29,31]

$$d^2\phi_0/dt^2 + (\epsilon - \frac{1}{4}t^2)\phi_0 = 0, \quad (18)$$

where ϵ is an as yet undetermined parameter, independent of t . Two exact linearly independent solutions to the homogeneous form eq (11) in terms of confluent hypergeometric functions are given by [29]

$$A(t) = [\pi^{1/2}/\Gamma(\alpha' + \frac{1}{2})] \exp(-\frac{1}{4}t^2) M(\alpha', \frac{1}{2}; \frac{1}{2}t^2), \quad (19a)$$

$$B(t) = [(2\pi)^{1/2}/\Gamma(\alpha')] \exp(-\frac{1}{4}t^2) tM(\alpha' + \frac{1}{2}, \frac{3}{2}; \frac{1}{2}t^2), \quad (19b)$$

with $\alpha' = (1 - 2\epsilon)/4$. Two stationary solutions of eq. (18) are obtained with $\alpha' = 0, -1$ and the ϵ values so obtained are zeroth-order solutions to the "eigenvalue" problem of the homogeneous form corresponding to eq. (6).

Using the zeroth-order solutions as a first approximation, eqs. (14) may be solved iteratively between two points suitably removed from the turning points, where the wavefunction approaches zero. One may then seek a solution where the number of zeroes is in

agreement with the oscillation theorem. Instead, eqs. (14) were numerically integrated, utilizing a solver from the open literature and using eqs. (19) as independent solutions to eq. (18); the initial conditions were chosen such that the approximate wavefunctions matched the exact ones at the point where the integration began.

The exact normalized bound-state wavefunctions 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 agreement was more than 99.8%. Dotted and dash-dotted curves illustrate the solutions obtained when the energy values were chosen to be about 4% less than (dotted) or greater than (dash-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. It can be noted, again as expected, that: (a) the "wavefunctions" exhibit more nodes than required, and (b) the "wavefunctions" to go $-\infty$.

The best matching of boundary conditions of the computed wavefunctions yields $E_{0(\text{comp})} = -0.4115$ eV and $E_{1(\text{comp})} = -0.0851$ eV; these values are in good agreement with the exact energy levels.

The perturbation-like inhomogeneous term $h(r)$ defined in eq. (7) was evaluated numerically (results not shown) using the defining eqs. (5) and (8). It was seen to contribute order 1% through the main range of integration. In the very near transition points regions where the zeroes of $p^2(x)$ are located, it was found to be dominant, as expected from physical considerations. Further, it took its largest value well away to the right of the second classical turning point, where the Morse function differs substantially from the quadratic comparison potential given by eq (17).

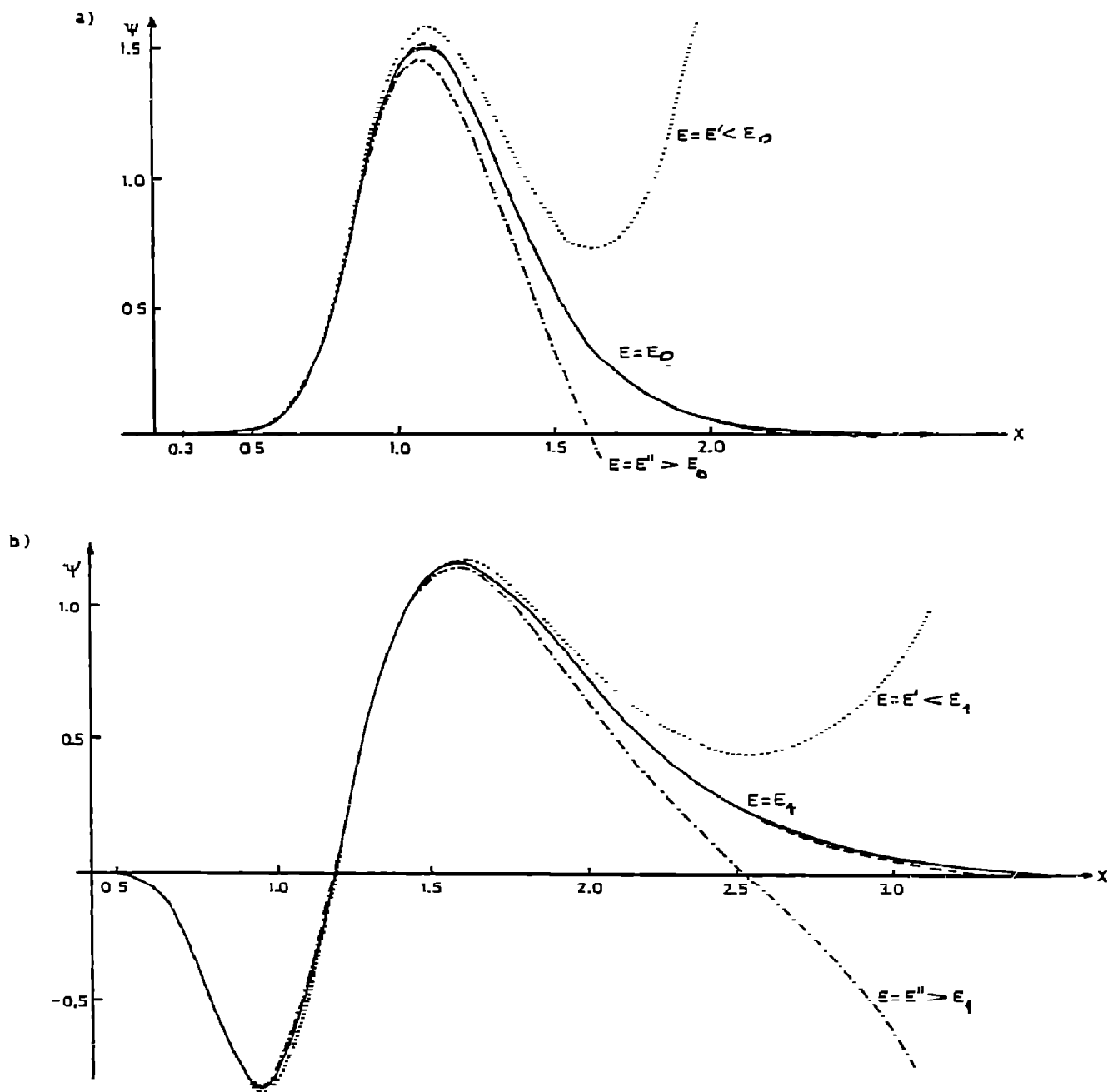


Fig. 1. Comparison of the results of the analytical and numerical methods of calculation of normalized eigenfunctions, corresponding to the two stationary states of the Morse potential for the parameters given in section 3. (a) $E_0 = -0.4114$ eV, (b), $E_1 = -0.0850$ eV. Solid lines: analytical solutions; 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 (dash-dotted) lines: numerical solutions obtained using an energy value lower (higher) than the exact one by about 4%

4. Discussion

In this Letter, a judicious amalgamated scheme to solve the Schrödinger equation, has been presented and applied to a model calculation using the Morse potential. Where other methods involve the semiclassical approximation, in which the Schwartzian derivatives term is neglected, and have limitations on the size of the integration steps (for proper adjustments to the true potential), in this method such drawbacks are removed.

In principle, one could further elaborate on pursuit of the analytical solution of the inhomogeneous-like equation (6) if the Schwartzian derivatives were easy to evaluate analytically. This is not, however, the case, the reason being that the new spatial coordinate t is not expressible in terms of elementary functions of the old spatial coordinate x . Nevertheless, whenever the true potential has an analytical well behaved form, the Schwartzian derivatives are quite readily evaluated numerically.

Since the comparison potential may be properly selected for large integration regions, the integration step lengths that can be used in the calculations have no great limitations. Moreover, boundary conditions are to be matched only at the beginning and at the end of the integration region, with great speed advantage in the computational work. An extension to multichannel problems, where this approach is seen to be most useful, is the subject of a forthcoming paper [32]. An application of the present scheme to inelastic atom—solid surface scattering where order one hundred channels are involved, and using more general potentials, is currently in progress. Finally, it is hoped that the ideas and results outlined in this Letter will stimulate further discussion.

We want to express our sincere thanks to L.B. Bhuiyan, D. Campos, E.A. Castro, M.S. Child, Alberto José Moreno-Bernal and R. Schunke for their kind encouragement in so many ways. Financial support for this work was provided in part by a grant to GE from Universidad Francisco de Paula Santander, Cúcuta, Colombia.

- [1] R.B. Bernstein, ed., *Atom molecule collision theory: a guide for the experimentalist* (Plenum Press, New York, 1979).
- [2] W.H. Miller, ed., *Dynamics of molecular collisions, Part A* (Plenum Press, New York, 1976).
- [3] F.A. Goodman and H.Y. Wachman, *Dynamics of gas—*

surface scattering (Academic Press, New York, 1976).

- [4] R.G. Gordon, *Methods Comput. Phys.* 19 (1971) 81.
- [5] J.C. Light, *Methods Comput. Phys.* 10 (1971) 111.
- [6] R.W. Anderson, *J. Chem. Phys.* 71 (1982) 4431, 5426; T.G. Mattson, M.R. Mitchell and R.W. Anderson, *Mol. Phys.* 50 (1983) 251.
- [7] J.C. Light and R.B. Walker, *J. Chem. Phys.* 65 (1976) 4272; E.B. Stechel, R.B. Walker and J.C. Light, *J. Chem. Phys.* 69 (1978) 3518.
- [8] A. Rosenthal and R.G. Gordon, *J. Chem. Phys.* 64 (1976) 1621.
- [9] P.L. de Vries, *Chem. Phys. Letters* 66 (1979) 258; P.L. de Vries and P.L. George, *Mol. Phys.* 39 (1980) 701.
- [10] M.S. Child, in: *Dynamics of molecular collisions, Part B*, ed. W.H. Miller (Plenum Press, New York, 1976) p. 171; M.S. Child, ed., *Semiclassical methods in molecular scattering and spectroscopy* (Reidel, Dordrecht, 1980).
- [11] S.C. Miller Jr. and R.H. Good Jr., *Phys. Rev.* 91 (1953) 174.
- [12] B.C. Eu, *J. Chem. Phys.* 70 (1971) 1774.
- [13] A. Erdélyi, *J. Math. Phys.* 1 (1960) 16.
- [14] N. Fröman, in: *Semiclassical methods in molecular scattering and spectroscopy*, ed. M.S. Child (Reidel, Dordrecht, 1980).
- [15] C.F. Hecht and J.E. Mayer, *Phys. Rev.* 106 (1957) 1156.
- [16] P. Pechukas, *J. Chem. Phys.* 54 (1971) 3864.
- [17] T. Lukes, in: *Solid state theory: methods and applications*, ed. P.T. Landsberg (Wiley-Interscience, New York, 1969) pp. 405–466.
- [18] A.N. Nayfeh, *Introduction to perturbation techniques* (Wiley, New York, 1981); *Perturbation methods* (Wiley, New York, 1973).
- [19] P.M. Morse, *Phys. Rev.* 34 (1929) 57.
- [20] D. ter Haar, *Phys. Rev.* 70 (1946) 222; M.M. Nieto and L. Simmons Jr., *Phys. Rev. A* 19 (1979) 438.
- [21] B.G. Wicke and D.O. Harris, *J. Chem. Phys.* 64 (1976) 5236.
- [22] J.P. Killingbeck, *Microcomputer quantum mechanics* (Hulger, London, 1983) p. 98.
- [23] I.R. Elsum and R.G. Gordon, *J. Chem. Phys.* 76 (1982) 5452.
- [24] F.M. Fernández and E.A. Castro, *J. Mol. Spectry.* 94 (1982) 28.
- [25] J.E. Lennard-Jones and C. Strachan, *Proc. Roy. Soc. A* 150 (1935) 442.
- [26] T. Engel and K.H. Rieder, *Structural studies of surfaces*, Springer tracts in Modern Physics, Vol. 91 (Springer, Berlin, 1982) p. 55.
- [27] R. Schinke, *Surface Sci.* 127 (1983) 283.
- [28] J. Giraldo, G.A. Estévez and R.G. Barrera, unpublished.
- [29] M. Abramowitz and I.A. Stegun, eds., *Handbook of mathematical functions* (Dover, New York, 1964).
- [30] R.G. Gordon, *J. Chem. Phys.* 51 (1969) 14; Z. Schulten, R.G. Gordon and D.G.M. Anderson, *J. Comput. Phys.* 42 (1981) 213.
- [31] H.F. Weber, *Math. Ann.* 1 (1869) 1.
- [32] R.G. Barrera, J. Giraldo and G.A. Estévez, unpublished