Morse potential, symmetric Morse potential and bracketed bound-state energies

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Abstract

For the needs of non-perturbative quantum theory an upgraded concept of solvability is proposed. In a broader methodical context the innovation involves Schrödinger equations which are piece-wise analytic and piece-wise solvable in terms of special (in our illustrative example, Whittaker) functions. In a practical implementation of our symbolic-manipulation-based approach we work with a non-analyticity in the origin. A persuasive advantage is then found in the both-sidedness of our iterative localization of the energies.

Keywords:
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1 Morse potential and the molecular-spectrum paradox

Morse potential [1]

\[ V(x) = V_{(\text{Morse})}(x) = -2 \gamma_1^2 e^{-\alpha x} + \gamma_2^2 e^{-2\alpha x} \]  

say, in its special two-parametric form with \( \gamma_1 = \gamma_2 = \gamma \) (cf. Fig. 1) belongs to the family of shape-invariant interactions which make the one-dimensional Schrödinger bound-state problem

\[ -\frac{d^2}{dx^2} \psi_n(x) + V(x) \psi(x) = E_n \psi_n(x), \quad \psi_n(x) \in L^2(-\infty, \infty) \]  

solvable, in closed form, in terms of classical orthogonal polynomials. Such an exactly solvable (ES) family (which is intimately related to the supersymmetric model building, cf. [2]) is not too large. This means that potential (1) (for which the polynomial part of the exact wave functions \( \psi_n(x) \) are Laguerre polynomials) is, in the context of mathematics of differential equations, exceptional.

![Figure 1: Function (1) at \( \alpha = \gamma_1 = \gamma_2 = 1 \).](image)

Remarkably, the same potential is also exceptional from the point of view of applied quantum theory and, in particular, of molecular physics. Indeed, after an appropriate selection of parameters, model (1) offers one of the best numerical fits to the measured vibrational spectra of diatomic molecules [3]. Alas, strictly speaking, the exact solvability of the one-dimensional Schrödinger Eq. (2) with \( V(x) = V_{(\text{Morse})}(x) \) only serves, for the purposes of the fit, as an “excellent approximation” (see, e.g., pages 182-185 in Ref. [4] for more details).

In the language of mathematics such an “approximation paradox” originates from the three-dimensional nature of the realistic molecular Schrödinger equation in which the Morse potential itself only emerges in the partial-wave sequence of the so called radial Schrödinger equations

\[ -\frac{d^2}{dr^2} \psi_{n,\ell}(r) + \frac{\ell(\ell + 1)}{r^2} \psi_{n,\ell}(r) + V_{(\ell)}(r) \psi_{n,\ell}(r) = E_{n,\ell} \psi_{n,\ell}(r), \quad n, \ell = 0, 1, \ldots \]  

where [3]

\[ V_{(\ell)}(r) = V_{(\text{Morse})}(r - d) - \frac{\ell(\ell + 1)}{r^2}. \]  

(4)
Thus, the realistic molecular wave functions $\psi_{n,\ell}(r)$ only live on the half-lines of the radial coordinate $r \in (0, \infty)$ and vanish in the limit $r \to \infty$. Naturally, one has to impose the conventional boundary condition in the origin $[5]$, 

$$\psi_{n,\ell}(0) = 0.$$  

Even if we accept the trivial regularization (4) of the strongly singular centrifugal term in Eq. (3), we reveal that the power-series ansatz for wave functions does not terminate and that it cannot degenerate to a Laguerre polynomial. In other words, the molecular wave functions $\psi_{n,\ell}(r)$ of Eq. (3) cannot coincide with the exact solutions $\psi_n(x)$ of Eq. (2). Similarly, the “realistic” molecular bound-state spectrum of energies $E_{n,\ell}$ may only be determined via certain real, purely numerical roots of transcendental Eq. (5). Thus, the spectrum of the Morse-potential model of a molecule will not be given by the exact analytic formula, say, of Table Nr. 4.1 in Ref. [2].

In what follows we intend to discuss the latter paradox and we shall draw, from this discussion, a few nontrivial methodical as well as model-building consequences.

## 2 Resolution of the paradox and the new, symmetrized Morse potentials

A priori, the latter conclusions might appear rather discouraging. Fortunately, the errors caused by both of the currently accepted approximations (5) and (4) prove entirely negligible even in the most unfavorable cases in practice (cf., e.g., a compact outline of the problem in [4], p. 184). Thus, the enormous phenomenological appeal of the exactly solvable Morse potential in molecular physics may be perceived as born out of a serendipitous practical indistinguishability between the purely numerical values of the “exact” roots of the “realistic” secular Eq. (5) and the non-numerical, purely analytic values as derived from the “idealized”, ES Schrödinger Eq. (2).

Recently, a new, innovative version of the closeness between the numerical transcendental-secular-equation roots and their efficient analytic approximations has been found and used by Ishkhanyan [6]. He conjectured that such a closeness (i.e., an “excellence of approximation”) might emerge in multiple non-standard quantum eigenvalue problems on half-line. He demonstrated the feasibility of such a project via its application to the inverse square root potential $V(r) = V_0/\sqrt{r}$. He illustrated the practical appeal and the user-friendliness of such a new model-building strategy by showing that the construction may prove successful in Morse-resembling cases in which the general differential-equation solutions $\psi_{n,\ell}(r)$ entering differential Eq. (3) remain proportional to a suitable, asymptotically correct confluent hypergeometric special function.

Recently [7] we imagined that besides its usual connection with the half-line radial Schrödinger equation, boundary condition (5) may be equally well interpreted as a matching condition for all of the odd-parity bound states living on the whole real line. In other words, one can move from radial half-line Eq. (3) to the alternative, one-dimensional bound-state problem (2) in which the potential is artificially “symmetrized”, i.e., such that $V(x) = V(-x)$. In this manner, in particular,
one gets, “free of charge”, all of the odd-parity bound states in the left-right-symmetrized Morse potential

\[ V_{(\text{sym.})}(x, d) = \begin{cases} 
V_{(\text{Morse})}(-d + x), & x > 0, \\
V_{(\text{Morse})}(-d - x), & x < 0,
\end{cases} \quad d > 0 \]  

(cf. Fig. 2). In other words, after one deliberately replaces the “strongly asymmetric” function \( V_{(\text{Morse})}(x) \) of Fig. 1 by its full-line-interaction alternative of Fig. 2 the odd-parity spectrum of energies (given by the roots of Eq. (5)) remains unchanged.

\[
\begin{array}{c}
\text{Figure 2: Symmetrized descendant (6) of potential of Fig. 1 with shift } d = 1.
\end{array}
\]

The “missing”, even-parity rest of the spectrum of the new solvable model (2) + (6) will be obtained after the replacement of Eq. (5) by its alternative

\[
\lim_{x \to 0} \frac{d}{dx} \psi_{n,\ell}(x) = 0 ,
\]  

i.e., \textit{mutatis mutandis}, by the virtually equally well defined transcendental (i.e., special-function-based, confluent-hypergeometric-series-based) secular equation again.

3 Bound states

At the larger shifts \( d \) the barrier as sampled by Fig. 2 becomes very high so that the even- and odd-parity bound states will remain almost degenerate. More interesting spectra will only be obtained at the not too large, positive (or even negative, barrier-free!) values of the shift \( d \).

3.1 Analytic considerations

On the basis of the practical experience as made by molecular physicists the polynomially solvable Morse-interaction problem (1) + (2) offers a very good approximation to the non-polynomial wave functions of radial Eq. (3). While the non-polynomiality caused by the matching condition \( \psi_{n,0}(0) = 0 \) in the origin remained negligible, the advantage of having the approximate solutions in a safely analytic, non-numerical, confluent-hypergeometric-function form was decisive.
After transition to our present double-well model (2) + (6) we still can use the same formal advantages including both the quality of the existing non-numerical approximations of functions $\psi(x)$ (or bound-state energies) at $d \gg 0$, and the tractability of the general confluent-hypergeometric solutions at a fixed shift $d$ and at a variable energy $E_{\text{trial}} = -k_{\text{trial}}^2$. In the intermediate region of $ds$ the high precision of the usual approximations (based on the Stirling formula, cf., e.g., equation Nr. (70.15) in monograph [4]) will worsen so that it should certainly be systematically amended via higher-order corrections.

It is worth adding that the present introduction of an anomalous non-analyticity of the potential in the origin enables us to replace the analytic but asymmetric potential (1) by its symmetrized but non-analytic version (6) so that at least some of the formal advantages of having the traditional analytic Morse potential (as sampled, e.g., in Ref. [8]) may be lost. In parallel, the new interaction model (6) also possesses specific merits. For example, it provides a double-well shape (cf. Fig. 2) giving rise to the tunneling. The internal barrier is tunable, of a freely variable thickness.

Naturally, the similar appealing descriptive features may be found in multiple other models, the list of which would range from the purely numerical Mexican-hat-shaped quartic-polynomial potentials [9] and from the various semi-numerical square wells with two minima [10] up to the exactly solvable extreme of a pair of attractive delta-function potentials [11]. Nevertheless, a combination of the strong central repulsion with a finite height of the barrier seems to be a specific an unique phenomenological aspect of Eq. (6).

### 3.2 Numerical considerations

The most common, computation-oriented distinctive feature of model (6) with $d \gg 0$ lies, as we already emphasized, in the amazing numerical efficiency of the approximate replacement of the numerically difficult $r_0 = 0$ boundary condition $\psi_{n,\ell}(r_0) = 0$ in realistic Eq. (3) by the full line problem (2) with the Dirichlet boundary condition shifted to $r_0 \to -\infty$. After one adds the alternative boundary condition (7), one must compute higher order corrections so that the next-to-degenerate problem becomes mathematically challenging again.

Interaction (6) may be characterized by the most common specific confluent-hypergeometric versions of wave functions which are asymptotically correct (i.e., vanishing) and enter the physical boundary conditions at $r = 0$. In similar models, such an approach is most common [6]. Nevertheless, there also exists an alternative approach in which the determination of the bound-state energies would be based on the much less common (often called “regular”) specific confluent-hypergeometric versions of the wave functions $\psi^{(\text{reg.})}(x, E)$ for which we guarantee, using analytic means, the correct behavior in the origin (cf. Eqs. (5) and (7)) in advance, i.e., at any energy $E$.

One of the reasons why the use of the regular-function ansatzs $\psi^{(\text{reg.})}(x, E)$ is much less popular in practice is that their explicit representation is usually rather complicated. Thus, in their sample displayed in Fig. 3 the Whittaker-function representation of the explicit formula for $\psi^{(\text{reg.})}(x, E)$
Figure 3: The influence of errors in energy $E = -k^2$ upon the asymptotics of the (right half of the) trial-and-error ground-state regular wave functions. Potential of Eq. (6) is used with parameters $d = 1$, $\alpha = 1$, $\gamma = 1.8$. Normalization $\psi(0) = 1$ and $\psi'(0) = 0$.

Figure 4: Right half of the ground-state $\psi(x) = \psi(-x)$ with $\psi(0) = 1$ in potential $V(x) = V(-x)$ of Eq. (6) at energy $E = -k^2$, $k = 1.355765$ and parameters $d = 1$, $\alpha = 1$ and $\gamma = 1.8$. The influence of error $h = 0.000005$ is only detected at very large $x \gtrsim 7$.

which would be compatible with boundary condition (7) had to be generated via a symbolic-manipulation software. It remained too lengthy to be displayed in print. This being said, the manipulations which led to the production of Figs. 3 or 4 remained virtually trivial, fully comparable, say, with the traditional algebraic manipulations with the elementary trigonometric functions needed in the case of the piecewise-constant square wells $V(x)$.

Another, much more important specific merit of using regular special-function solutions is also well illustrated by Figs. 3, 4 and 5. Indeed, once we recall the standard oscillation theorems [12], we may “bracket” the correct root $E_n = -k_n^2$ of the necessary and sufficient asymptotic, regular-function-based boundary-condition constraint

$$L(E) = \lim_{x \to \infty} \psi^{(\text{reg.})}(x, E) = 0 \quad (8)$$

by counting the nodal zeros, i.e., in a way which immediately characterizes any preselected approximate value of the $n$–th-level parameter $k_{\text{trial}} = \sqrt{-E_{\text{trial}}}$ as giving an upper or lower bound (thus, in particular, Fig. 3 immediately informs us that, with certainty, $1.354 < k_{\text{exact}} < 1.358$).

One of the reasons why the resulting symbolic-manipulation-assisted version of the well known shooting method works much better than its standard numerical predecessors is that the special-function form of $\psi^{(\text{reg.})}(x, E)$ provides the information with a fully controlled and arbitrarily
Figure 5: Right half of the lowest excited-state $\psi(x) = -\psi(-x)$ in potential of Fig. 4 at energy $E = -k^2$ with $k = 1.268113$ and error bar $h = 0.000003$ using normalization $\psi'(0) = 1$.

preselected precision. This feature is illustrated by Figs. 4 and 5 out of which one reads, reliably, that for the potential in question we have

\[-(1.35577)^2 < E_0 < -(1.35576)^2\]

and

\[-(1.268116)^2 < E_1 < -(1.268110)^2\]

respectively.

### 3.3 Methodical considerations

Among the most popular simulations of quantum dynamics in one dimension one finds various piecewise constant potentials. The main advantage of such a choice of effective dynamics may be seen in the related piecewise trigonometric form of components $\psi^{(1,2)}(x)$ of the general, energy-dependent solutions of Eq. (2)

$$\psi_{(j)}(x) = C_{(j)}^{(1)} \psi_{(j)}^{(1)}(x) + C_{(j)}^{(2)} \psi_{(j)}^{(2)}(x), \quad x \in (a_j, a_{j+1}), \quad j = 0, 1, \ldots, K$$

such that

$$-\infty = a_0 < a_1 < \ldots < a_K < a_{K+1} = \infty.$$  \hspace{1cm} (10)

In the experimental context, typically, one has to satisfy the asymptotic boundary conditions

$$\lim_{x \to \pm \infty} \psi_n(x) = 0, \quad E = E_n < \min [V(a_0), V(a_{K+1})]$$

in order to determine the observable bound-state energies $E = E_n$ and/or the wave functions $\psi(x) = \psi_n(x) \in L^2(\mathbb{R})$. In such a setting, the pairwise matching of the logarithmic derivatives of components (9) at the boundary-points $a_j$ couples the constants $C_{(j)}^{(i)}$. Then, the construction of bound states degenerates to the search of roots of a certain algebraic secular equation resembling Eq. (8). This indicates the possible path of further generalizations of our present model.
4 Summary

The non-exact, approximative nature of the description of molecules using Morse potentials is rarely emphasized in the literature. With exceptions: The terminological inconsistency attracted our attention in our older paper [8]. We studied there the connections between the half-axis of coordinates in (3) and the full line of coordinates in (2). Successfully we regularized there the centrifugal singularity in a way based on an analytic continuation of the wave functions to the complex plane of the coordinates.

Now we addressed the same problem from an opposite point of view. Our main attention was paid to the one-dimensional phenomenological scenario and to the obvious fact that the shape of $V_{\text{Morse}}(x - d) \neq V_{\text{Morse}}(d - x)$ is so strongly asymmetric that its half-axis reinterpretation (4) provided probably its only, albeit approximative, truly useful contact with the three-dimensional real-world experiments.

In molecular physics people weakened the concept of the exact solvability when moving from the one-dimensional problem (2) to its more realistic three-dimensional generalization. In our paper we accepted such a weakened concept and we described some of its innovative model-building consequences. More explicitly, we returned to the one-dimensional setting of Eq. (2) and considered a new Morse-like potential (6). The related Schrödinger bound-state problem was discussed in some detail.

In a way inspired by the common practice in molecular physics the eigenvalue problem was characterized by the non-terminating Taylor-series representations of wave functions. In both the contexts of Eqs. (2) and (3) we considered the general solutions $\psi_n(x)$ and $\psi_{n,0}(r)$ in their respective explicit, confluent-hypergeometric-function forms. Being encouraged by Ishkhanyan [6] we decided to accept the non-ES, non-polynomial, infinite-series special-function form of wave functions as the form of bound states which can still be welcome as non-numerical and exact. Our tests of the strategy revealed an energy-bracketing behavior of the trial-and-error eigenvalues so that we believe that it offers a robust algorithm for practical computations.

In the context of physics we put main emphasis on the appeal of the double-well shapes of potentials as sampled by Fig. 2. Nevertheless, a more or less unmodified constructions of bound states seem to remain applicable even if we turn Fig. 2 upside down, yielding the single-well formula

$$V(x) = V_{\text{single well}}(x) = \begin{cases} 
-V_{\text{Morse}}(-d + x), & x > 0 \\
-V_{\text{Morse}}(-d - x), & x < 0 
\end{cases}, \quad d > 0 \quad (12)$$

in which the central attractive part becomes accompanied by certain external barriers. Although such a shape could, in principle, generate low-lying resonant states, its study already lies beyond the scope of our present paper.
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