SYNOPSIS

Introduction

The focus of this thesis is on the fact that perturbation theory PT is not a mere tool, but some really crucial theoretical apparatus that deserves both a conceptual and computational treatment. PT [1 - 4] has its roots embedded strongly in the history of classical mechanics where it first distinguished itself as a tool for calculating planetary orbits during the time of Copernicus and Kepler, and has always been an important part of natural sciences from celestial mechanics to quantum theory, and even field theory in modern times. The theory got a dramatic expansion and evolution with the arrival of quantum mechanics. So far as the present status of PT is concerned, we start from a very simple fact: cases where a QM problem can be solved explicitly are very rare and, on the other hand, generic problems (complex systems) are difficult to handle. But, as a connecting link between these two extreme groups, there exists problems (systems) not-so-simple but close to the simple ones, and the PT machinery is then competent enough to provide a solution in “closed form” and hence these are amenable to analytic studies. Therefore, our major portion of the work is dedicated to this approach which is applied to several model systems from both static and dynamic standpoints. We have mainly concentrated on problems that allow analytical solutions of perturbative equations and avoid those that require long and tedious numerical computations. This is because, the latter might otherwise shift our focus from the core of the problem. We, however, resort to numerical results when they are necessary in order to illustrate and complement important features of the theory.

Perturbation theory still provides ample freedom for scientific thought because of its following aspects:

(i) The ability to evaluate higher order terms (made possible by modern-day computers) has stimulated a fresh interest in the convergence behavior of perturbation series.

(ii) There is yet considerable opportunity to tamper and modify the infinite perturbation series, often divergent, with new mathematical tools that are able to push them towards a far better convergence.

(iii) An effort to move out of the two major versions of traditional PT, namely RSPT and BWPT, is another area of exploration in a quantum mechanical context.
Along with the ‘no-wavefunction’ formulation [5] and a PT in terms of commutators [6], the more recent popular version, viz. the LPT [7-11], has been found to be very effective in endowing correction terms in closed forms.

Nowadays, most of the heavy computations are done by computers, but the revival of interest in PT, due in particular to problems inherited by quantum computation and quantum information, provides new situations where the PT, being analytical, presents new challenges. Not only can PT provide such precise formula, but it gives also a lot of information concerning scaling properties, asymptotic behavior and a lot of other pieces of information regarding observables that numerical computations are unable to provide.

PT can provide information even if a series diverges.

These certainly form steps in considering PT at a true conceptual level.

Outline of the work

The thesis begins with the core theory and the principal formulation, viz. the LPT, to explore some untouched areas in PT that speak of the structural aspects of the work concerned. Two new formalisms have been introduced. The first one is based on “force” [9], and we call it the FLPT. The other rests on SUSY [12 - 14].

The application part of the work is bifurcated into the analytic and the computational aspects. Two special problems have been chosen for the study. One is a non-linear perturbation [15 - 20] with a weird triple-well potential model [20]. The other [21] is concerned with a quantum-mechanical effect called the KP [22]. The latter clarifies a recent observation [23, 24] and has been studied analytically.

The computational part of PT [25 -39] has been surveyed finally. We consider two major areas. One is to cure divergence using modified PA [40] that can take care of the non-integer power law dependence of the observables in the asymptotic limit. The other [41] is to extract asymptotic response of observables from divergent perturbative series using FC [42].

Some of our works [20, 21, 42] have directly/indirectly employed what we call as related methods.

Chapter 1: In this chapter, we mainly focus on bound-state PT. Pertinence of the traditional PT theory and its status is under constant estimate because of the cumbersome integral evaluation, multiple summation and implicit series expansion that restrict their practical usage. An alternative way of solving a problem via PT in coordinate representation is LPT. By considering
the logarithmic derivative of wave-function, instead of the wave-function itself, the Schrodinger energy eigenvalue problem is transformed to a non-linear Riccati form. A subsequent perturbative formulation yields the LPT. Here, one does not need integral evaluations and infinite sums to get order corrections. Rather one has to match coefficients of certain polynomials. Our major thrust on this work is to get an ‘energy-free’ perturbative development [9] (a solely wave-function yielding recipe), as wave function alone can provide necessary information for any property sought.

Our endeavor, the FLPT, has another unique feature. It is based on force, rather than the usual potential. Role of force in traditional quantum mechanics is rarely highlighted. But, we notice here how FLPT becomes useful. The basic idea is to differentiate the Riccati equation once, thus eliminating the unknown energy, and then examining how the force-based approach is beneficial in getting wave-function correction terms. From their knowledge, energy or any other property can be easily obtained.

We start with the Schrödinger energy-eigenvalue equation in one dimension, choosing $h = 2\pi, m = \frac{1}{2}$, and a real potential $V$:

$$-\Psi_n'' + (V - E_n)\Psi_n = 0.$$ 

This equation can be rearranged into Riccati form as

$$\chi_n^2 + \chi_n' + E_n - V = 0$$

by defining the ratio $\Psi_n'' / \Psi_n = \chi_n$, where the prime refers to differentiation with respect to $x$. With $V = v_0 + \lambda \nu$, where $v_0$ is the unperturbed potential, we expand the quantities of interest, viz. $\chi$ and $E$, in terms of the perturbation parameter $\lambda$. This yields perturbation equations in the LPT framework. Here, however, we differentiate the Riccati form once more so as to get rid of energy as an unknown. Thus we arrive at

$$2\chi_n \chi_n' + \chi_n'' + F = 0$$

where $F = -dV/dx$ is the force. Note that we have thus eliminated the unknown $E_n$ from LPT.

But, we shall see that, on the basis of this equation, a perturbation theory may now be neatly developed without any problem. Let us note another point. We do not differentiate the SE directly. Had it been done, we could not have eliminated $V$ or $E_n$. The new perturbation equation has now a look rendering a classical feeling even in the quantum domain. Detailed discussion on the FLPT may be found in our article [9].
Chapter 2: In this chapter, we concentrate solely on the application of SUSY theory [12-13] to PT. The introduction of SUSY in QM has revived a fresh interest in the problem of obtaining algebraic solution of exactly soluble non-relativistic potentials. It has been argued that whenever there is a specific relation between two SUSY partner potentials, bound-state spectra and eigenfunctions can be determined by purely algebraic means by factorization of the Hamiltonians. Over the last two decades, the conceptual novelty of SUSY has been profitably employed to non-relativistic QM problems in getting a deeper insight into the reasons why certain potentials are analytically solvable and some are not, providing new approximation methods for handling potentials that are not exactly solvable. We have shown its relevance to PT [14].

To discuss the current motivation we once again look back to traditional RSPT from a slightly different standpoint. Knowledge of a perturbed eigenstate via traditional RSPT requires the knowledge of the corresponding unperturbed state. Given a solvable eigenvalue problem, perturbation theory sets out to find approximate solutions of \( E_n \) and \( \psi_n \) where RSPT tackles each stationary state \( \psi_n \) and the corresponding \( E_n \) each at a time. But here we are in search of a route that requires only the sole information of ground state but, at the same time, can compute recursively the perturbation expansion for any number of bound states thus providing the entire spectrum of the Hamiltonian. LPT along with SUSY quantum mechanics is judiciously exploited in such a pursuit. The construction of auxiliary SUSY partner Hamiltonians and their corresponding partner potentials is a simple analytic effort where the partner Hamiltonians become solvable too, thus enhancing the class of solvable potentials. This is another important feature of our present formulation. A good exposition may be found in our article [14].
Chapter 3: This chapter is focused on polynomial (non-linear) perturbation problems [15 – 19]. These are perturbations of the form of the form $V = V_0 + \lambda V_1 + \lambda^2 V_2$ and have attracted considerable attention in the context of convergence behavior of PT. So far we have been solving the Schrödinger eigenvalue equation

$$H(\lambda)\psi_\lambda(\lambda) = E_\lambda(\lambda)\psi_\lambda(\lambda)$$

by choosing linear perturbations, $H(\lambda) = H_0 + \lambda V$, with the assumption that the smallness of $V$ (perturbation) is ensured. A critical perusal of some relevant papers reveal quite a few interesting pathological polynomial perturbations where, in cases (i) the energy series converges surely, but to some wrong answer, (ii) the wave function series, though can be summed up, but cannot be normalized within the range, (iii) the energy eigenvalue series converges to the right (meaningful) answer but the wave function series diverges, and (iv) the eigenvalue series sometime converges to the right answer, but only for the positive value of the coupling constant. These pathological perturbations are seen to be highly state-dependent (or, state-specific). Since the type of potentials considered possesses a part which is more singular, divergent expansion is expected. In continuation of an earlier work [19], we construct [20] such a perturbation by choosing $V_1$ and $V_2$ in such a way that a finite Taylor-series expansion is guaranteed for a specific state and consequent state-specificity has been looked into; also a few neighboring states are scrutinized by using LPT as a tool.

In course of studying such non-linear perturbations of a HO, a particular perturbing potential has been found that deserves some attention. It is a single well at low values of coupling strength, turns to a double-well in the intermediate coupling range and finally settles into a triple-well at still higher values of the same. Another prominent observation is that the perturbation theory results are exact for both energy and wave function for the second excited state whereas such series diverges for the first. Further, the perturbed ground state acquires a pre-exponential factor, and considerably fascinating is its exponent, being same as that of the second excited state. The outcome has been analyzed with KP [22] in mind, particularly to understand how some memory effect in wave function can be sustained. A good discussion has been presented in our work [20].

Chapter 4: The main concern of this study [21] has been a renewed interest in cases that show up the KP [22]. Originally such a phenomenon is observed when potentials are sufficiently
**singular** and cannot be smoothly turned off to restore the original wave function. This implies, some sort of vestigial effect of the perturbation continues to irk the wave function. Some of the recent observations [23 - 24], however, contradicted the above popular belief to suggest that, not only singular potentials, but a PIB with various sinusoidal bottoms can show some vestigial effects being retained by quantum states similar to those of the KP.

In a brief note [21], we have analyzed the problem concerned with a box in \((0, L)\) whose flat bottom at zero potential is perturbed by the introduction of an additional potential of the form \(\lambda \cos(k \pi x / L)\) with \(k = 1, 2, 3 \ldots\) It has been claimed in one of the recent communications [23] that, other than \(k=1\), results for the perturbed ground state energy do not reduce to the parent box potential in the limit \(\lambda \rightarrow 0\) which is referred to as a kind of KP and that a node develops for the ground state for the said perturbation form at \(k = 2\). Our interest in the problem stems from the concerns outlined below: (i) So far, KP was restricted to singular nature of potential but the recent observation, if found to be true via an independent analysis, seems to contradict the belief and hence an explanation needs to be put forward. (ii) Development of node in the ground state has been another concern that requires a thorough scrutiny. (iii) There remains also an interest to know how the ground state energy of such a PIB model depends on large values of \(k\) of the above sinusoidal perturbation. Specifically, we have been eager to know if a rise in \(k\)-value causes a shift in the ground state energy by a certain factor. An independent variational analysis [21] has also been pursued to check our perturbative results.

**Chapter 5: Divergence** [27] has always been an issue that bothered PT since its inception. The major portion of our work [40] in this chapter is centered on taming the divergence [25 - 39] of various observable series using popular mathematical series accelerating tools. A divergent perturbation series is known to yield unreliable results for observables even at moderate coupling strengths. One of the most popular techniques in handling such series is to express them as rational functions, but it is often faithful only for small couplings. We outline here how one can gain considerable advantages in the large-coupling regime by properly embedding the known asymptotic scaling relations for selected observables during construction of the aforesaid PA [40]. Three new bypass routes are explored in this context: (i) PA-assisted GMA, (ii) PA of series for specific ratios of properties, and (iii) going for PA after expressing properties as functionals of energy.
Averaging methods continue to successfully handle several classes of problems with slow convergence or divergence. We notice here that a simple WGM of the form
\[
Y^*_n(N, \lambda) = \left( \frac{N}{N+1} \right)^{2/3} \left( \frac{(N+1)/N} {N} \right)^{1/3}
\]
can take proper care of the \(\lambda^{1/3}\)-dependence of a positive definite observable \(Y\) [like the energy \(E_n(\lambda)\) or kinetic energy \(\langle T \rangle_{\pi}(\lambda)\)] for the QAO problem. Further, in place of \(\langle x^4 \rangle\), if we take the series for \(\lambda \langle x^4 \rangle\) and identify it as \(Y\), then the asymptotic behavior of all these observables are endorsed on equal footing for the QAO.

Another idea is almost instinctive. We should try the PA for specific ratios of observables. For example, the ratio \(\langle T \rangle/E\) would be independent of \(\lambda\) in the \(\lambda \to \infty\) limit. Therefore, one should try diagonal PA for such a ratio. Such results, however, are not complete in the sense that, at a given \(\lambda\), if \(E\) is supplied from other sources, then only one can estimate \(\langle T \rangle\) or \(\langle x^4 \rangle\). The sort of incompleteness mentioned can be cured, we have noted, by direct application of the HFT.

A radically different approach would be to consider two observables \(F(\lambda)\) and \(G(\lambda)\) with given series expansions as follows:
\[
F(\lambda) = \sum_i f_i \lambda^i; \quad G(\lambda) = \sum_i g_i \lambda^i.
\]
It is then also possible to express \(F(\lambda)\) as a power series in \(G(\lambda)\), or vice versa. To be more precise, one needs to choose a new variable \(g_\lambda = G(\lambda) - g_0\) which is basically a shifted-\(G(\lambda)\) variable. Then one can express \(F(\lambda)\) as
\[
F(\lambda) = \sum_i f_i g_\lambda^i.
\]
This is equivalent to the parent expansion for \(F(\lambda)\), but its convergence properties may differ widely and obviously one can adopt such a strategy to gain advantage. A detailed discussion of our work on the bypass routes of curing divergence by modifying regular PA is available [40].

**Chapter 6:** This chapter pays attention to a 300 century old conventional calculus, not much popular in the scientific community. Although the application of FC [42] has attracted interest of researches in recent decades, it has a long history; indeed, the derivative of order \(\lambda^{1/2}\) had been described by Leibniz in a letter to L'Hospital in 1695. FC is the calculus of derivatives and integrals with arbitrary (real or even complex) order, which unifies and generalizes the notions of
integer order differentiation/integration, and have found many applications in recent studies to model a variety of processes from classical to quantum physics. It is believed that probably this subject translates the reality of nature better.

A major reservation, however, lies in the physical (rather geometrical) interpretation of the fractional order differentiation and integration which do not fall in the line of slope and area, but certainly awaits a broader elucidation. An interesting illustration concerning the Riemann-Liouville convention may raise the curiosity for a more general explanation. Consider, for example, the function $y = f(x) = x$. We gradually differentiate it by choosing $g = 1/4, 1/3, 1/2, 2/3$ and finally $g = 1$. The gradual change to the integer-order differentiation is shown below:

![Figure: Plot of the gradually decreasing slopes from the original function towards the integer order differentiation result ($p \to 1$) with intermediate plots ($p \to 1/4$ to $2/3$) for non-integer order differentiation.](image)

Given a power series expansion in a variable $x$ of some observable $F(x)$ that has the form

$$F(x) = \sum_j f_j x^j, x \to 0,$$

and given that $F(x)$ is an entire function of $x$ over the whole positive real axis, it is often of interest to extract the asymptotic ($x \to \infty$) behavior of $F(x)$ from a knowledge of $\{f_j\}$ up to some order. In essence, we like to estimate [41] parameters $\alpha_0$ and $\beta_0$, defined by

$$F(x) \sim \alpha_0 x^{\beta_0}, x \to \infty,$$

from the $x \to 0$ expansion. Here, $\alpha_0$ is the amplitude and $\beta_0$ is the exponent. Usually, the small-$x$ behavior is obtained from the RSPT and the large-$x$ behavior is intuitively obvious. In a few situations, however, the large-$x$ form written above stands for the leading behavior; in actuality,
it is replaced by a strong convergent expansion at very large $x$. In cases of external perturbations, the coupling parameter $x$ can be varied. Then, the problem becomes of real interest. Ready examples include variations of energy of atom under high electric or magnetic field, and the problem becomes more challenging when such series diverges. Our purpose here is to view these expansions as pure numerical series like those of anharmonic oscillator problems where divergence increases with anharmonicity.

Let us assume that the large-$x$ behavior bears no reference to any Hamiltonian origin. Sticking to the Riemann-Liouville convention [42], we define

$$D^g y^n = \frac{\Gamma(n+1)}{\Gamma(n+1-g)} y^{n-g}$$

where $g$ may be a non-integer. The above prescription now allows us to construct a function $G(x)$ of the form

$$G(x) = x^g D^g F(x)$$

that has also a power-series form like the parent $F(x)$. Indeed, we have

$$G(x) = \sum_j f_j \frac{\Gamma(j+1)}{\Gamma(j+1-g)} x^j, x \to 0,$$

and, in addition,

$$G(x) = \alpha_0 \frac{\Gamma(\beta_0 + 1)}{\Gamma(\beta_0 + 1-g)} x^{\beta_0}, x \to \infty.$$
assumption that, after a short transient, the concentration of enzyme-substrate complex remains approximately constant.

The two step model is symbolized by the reaction

\[ S + E \xrightarrow{k_1} ES \xrightarrow{k_2} P + E. \]

The coupled differential kinetic equations embody the two mass conservation equations

\[
\begin{align*}
[E]_0 &= [E] + [S] \\
[S]_0 &= [S] + [ES] + [P]
\end{align*}
\]

The purpose of the work is to survey whether (a) QSSA holds good for any substrate-enzyme ratio [49, 50], (b) steady state region is petite for large enzyme-substrate ratio, (c) initial pre-steady state region is short when QSSA is well-founded, (d) several conditions proposed from time-to-time on the validity of QSSA works sensibly in predicting the same, and (e) finally, whether any better measure for QSSA at all exists. Standard series expansion and PA are used as tools to tackle the investigation. Properly scaled variables [51] have been used. We made the choice

\[
\begin{align*}
E &= aS, \\
E &= a, \\
S &= kS, \\
E &= k, \\
t &= k_1 t.
\end{align*}
\]

Then, the principal kinetic equations may be compactly written as

\[
\begin{align*}
\frac{d\alpha}{d\tau} &= \frac{d\beta}{d\tau} + (1 - \alpha), \\
\frac{d\beta}{d\tau} &= -K_1 \beta \alpha + K_2 (1 - \alpha),
\end{align*}
\]

with initial conditions

\[
\alpha_0 = 1, \quad \beta_0 = \frac{s_0}{e_0}.
\]

The constants \( K_1 \) and \( K_2 \) are given by

\[
K_1 = k_1 e_0 / k_2, \quad K_2 = k_2 / k_1.
\]

The conservation equations read now as

\[
\alpha + \gamma = 1, \quad \beta + \gamma + \delta = \beta_0.
\]

The above system of non-linear equations can be solved analytically using the traditional power series method. Expressing the concentrations of the participating species in power series of \( r \), viz.,
\[ \alpha_r = \sum_{j=0} \alpha_j \tau^j, \beta_r = \sum_{j=0} \beta_j \tau^j, \gamma_r = \sum_{j=0} \gamma_j \tau^j, \delta_r = \sum_{j=0} \delta_j \tau^j, \]

inserting them into the differential equations and collecting equal powers of \( r \), the unknown parameters of the expansions are obtained. Note that our scaling is very different from others [51]. Moreover, to tackle the expansions at large \( r \), we construct three types of PA, \([N/N]/\), \([(N+1)/N]\) and \([N/(N+1)]\), as found useful in a variety of contexts (see, e.g. [40] and refs. quoted therein). The findings are summarized in our recent communication [53].

Typical reduced concentration profiles of the complex that emerge out of our work are shown below.

![Figure: Different types of complex concentration profiles showing (a) no QSSA and (b) QSSA for widely varying substrate-enzyme ratios.](image-url)
REFERENCES


