HIGH-ORDER PERTURBATION THEORY AND ITS APPLICATION TO ATOMS IN STRONG FIELDS

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I. INTRODUCTION

Schrödinger invented quantum mechanical perturbation theory in the third\(^1\) of his four seminal papers of 1926 to explain the LoSurdo\(^2\)-Stark\(^3\) effect—hydrogen in an external electric field. Following an idea of Lord Rayleigh for treating vibrations, Schrödinger’s expectation was that a few terms in the power series expansion in the external field strength would be sufficient to match the experimental results. Higher-order terms could be obtained recursively from lower-order terms. This initial application of Rayleigh-Schrödinger perturbation theory (RSPT) was so straightforward and successful that it served as a paradigm for what has become a standard tool applied to countless problems in quantum physics.

Mathematically the external field in the LoSurdo-Stark effect is large, not small, and the perturbation series always diverges.\(^4,5\) There are no discrete eigenvalues in the usual sense, and after a long enough time the atom ionizes by tunnelling at a rate exponentially small \(e^{-kF}\) in the field strength \(F\). (See, for instance, Refs. 6 and 7.) Nevertheless, the perturbation series contains complete information about the energy shifts and ionization rates and with the proper technique can be (Borel or Padé-Padé) “summed” to yield this information.\(^8,9\)

Hydrogen in an electric field is one of several interrelated problems that share four common features: transformational equivalence of the unperturbed problem to a harmonic oscillator; order-by-order solvability of the perturbation series; divergence of the perturbation series; and associated exponentially small subseries. These problems include the harmonic oscillator perturbed by a potential \(x^4\) (for which the divergence of the perturbation series carried to high order was demonstrated by Bender and Wu\(^10\)), the diatomic molecule \(H_2^+\), and hydrogen in an external magnetic field (the Zeeman effect). \(H_2^+\) has the added complication of being a double-well problem with an exponentially small power series that gives the double-well splitting.\(^11,12\) The Zeeman effect has the complications of not being completely separable into one-dimensional problems and of being inherently degenerate.\(^13,14\)

This lecture begins (at the request of Professor Nicolaides) on the historical note of why the electric analog of the Zeeman effect should be called the LoSurdo-Stark effect. Next the RSPT of the LoSurdo-Stark effect is developed in some detail, with emphasis on why (in terms of the anharmonic oscillator) the terms in each order come out in closed form. The connection of the tunnelling ionization rate to the divergence rate of RSPT is briefly discussed. How to sum the series numerically leads into a discussion of Borel summability and its implications. Two additional topics touched on briefly are how to generate the RSPT for
the degenerate Zeeman-effect problem, and the anharmonic oscillator as a series in both the anharmonicity and \( \hat{a} \) as an example of how quantum mechanics can be viewed as classical mechanics plus quantum corrections.

II. HISTORICAL REMARKS CONCERNING ANTONINO LO SURDO

Much of the material on which this Section is based has been provided to the author by Professor Sandro Graffi.

Shortly before Stark, LoSurdo\(^2\) observed the electric analog of the Zeeman effect, which had been sought since the 1901 suggestion by Voigt.\(^15\) LoSurdo read Stark's announcement in the 4 December 1913 issue of Nature\(^16\) and immediately (21 December 1913) published his own account\(^2\) and a spectrum in the Rendiconti of the Accademia dei Lincei. The major experimental problem seems to have been how to obtain a sufficiently large, stable region of strong, constant electric field, which in an ordinary discharge tube is the Crooke's dark space. Stark's solution was the more complicated: he put a second anode behind a perforated cathode. LoSurdo's, on the other hand was brilliantly simple: he drew the cathodic end of the tube into a capillary, greatly elongating the dark space, which he then focused on the slit of a spectrograph.

In modern times the phenomenon is usually referred to as the the "Stark effect," with LoSurdo all but forgotten, but this was not always the case. Jammer\(^17\) indicates that the phenomenon was occasionally referred to as the "Stark-LoSurdo effect." Indeed, one can find a discussion at the 4 April 1914 meeting of the Italian Physical Society in Rome at which Garbasso formally proposed to name the new phenomenon the "Stark-LoSurdo effect." In that discussion, Garbasso's proposal was effectively killed by Corbino.\(^18\)

Additionally there is a widely stated misconception, perpetuated for instance by Jammer,\(^17\) that LoSurdo's experimental setup was inferior and did not permit quantitative measurements. In a 1932 treatise on atomic spectroscopy, Brunetti\(^19\) explicitly rebuts this misconception and remarks further on the widespread use of LoSurdo's experimental design at that time. Brunetti also comments pointedly about the question of priority:

"In the fall of the same 1913, A. LoSurdo, in a meeting of the Italian Physical Society in Pisa, showed the first photograph of the lines of the Balmer series of hydrogen split in an electric field."

A most intriguing footnote is inserted at this point: "Chi scrive era presente all'adunanza." The text then finishes:

"This was obtained during the summer of the same year in a study of the radiation emitted by the cathodic flux of a discharge tube in the Hittorf-Crookes dark space."

After the first world war, LoSurdo turned increasingly to geophysics and was a founder and director of the National Institute of Geophysics in Rome. It is surely significant that, save for one brother, LoSurdo's entire family and his fiancée were killed in the great Messina earthquake of 1908.

In summary: LoSurdo observed it first; Stark published it first; the Italian physics community was divided about naming it the Stark-LoSurdo effect; there grew a misconception that LoSurdo's experimental apparatus was only qualitative, despite widespread quantitative use by spectroscopists; LoSurdo became a pillar of Italian geophysics; and the atomic physics community forgot about LoSurdo. This author agrees with the reasons advanced by Garbasso,\(^18\) "Per la indipendenza dei due metodi [Stark's and LoSurdo's] e per la superiorità del secondo [LoSurdo's] sul primo ...," that the name of the phenomenon should include LoSurdo. In view of the facts that LoSurdo observed and publicly demonstrated the phe-
nomenon first, and that until this time LoSurdo has been slighted by history, it would seem that "LoSurdo-Stark effect," rather than "Stark-LoSurdo effect" and certainly rather than "Stark effect," is the most appropriate name for the electric analog of the Zeeman effect.

III. PERTURBATION THEORY OF THE LO SURDO-STARK EFFECT

Algorithm for nondegenerate RSPT

The working equations of RSPT are obtained by expanding the energy, wave function, and Schrödinger equation in a power series in the perturbation parameter. In the "intermediate normalization" and in a more or less standard notation, one obtains the system of equations,

\[ H = H^{(0)} + gV, \]

\[ E = E^{(0)} + gE^{(1)} + g^2E^{(2)} + \ldots, \]

\[ \psi = \psi^{(0)} + g\psi^{(1)} + g^2\psi^{(2)} + \ldots, \quad \langle \psi^{(0)} | \psi^{(N)} \rangle = \delta_{0N}, \]

\[ \left( E^{(0)} - H^{(0)} \right) \psi^{(N)} = \left( V - E^{(1)} \right) \psi^{(N-1)} - \left( E^{(2)}/E^{(0)} \right) \psi^{(N-2)} - \ldots - \left( E^{(N)}/E^{(0)} \right) \psi^{(0)}, \]

with formal solution,

\[ E^{(N)} = \langle \psi^{(0)} | V | \psi^{(N-1)} \rangle, \]

\[ \psi^{(N)} = R^{(0)} \left( V - E^{(1)} \right) \psi^{(N-1)} - \left( E^{(2)}/E^{(0)} \right) R^{(0)} \psi^{(N-2)} - \ldots - \left( E^{(N)}/E^{(0)} \right) R^{(0)} \psi^{(0)}, \]

\[ R^{(0)} = \frac{Q}{E^{(0)} - H^{(0)}} = \sum_{j} \frac{|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|}{E^{(0)} - E_j^{(0)}}, \]

Order by order solvability in closed form for the LoSurdo-Stark effect

The LoSurdo-Stark effect is one of those few cases for which the RSPT equations can be solved in closed form. The Nth-order wave function for a state with principal quantum number \( n \) is a polynomial in \( r, \sigma, y, \) and \( z \) times \( e^{-r/n} \). The series in the field strength \( F \) for the ground state energy comes out, for example,

\[ E = -\frac{1}{2} - \frac{9}{4} F^2 - \frac{3555}{64} F^4 - \frac{2512779}{512} F^6 - \ldots. \]

There is a simple way to see that the RSPT equations can in each order be solved in closed form. It involves a connection between the hydrogen atom and the harmonic oscillator. (This is a special case of a more general result; see the Appendix for details.) One begins with the Schrödinger equation in parabolic coordinates (following Schrödinger),

\[ \left[ -\sigma \frac{d^2}{d\sigma^2} + \frac{m^2 - 1}{4\sigma} + \frac{\sigma}{4} \pm \sigma^2 - \beta_\pm \right] \psi_\pm(\sigma) = 0. \]
Here $f$ (a scaled $F$) and $E$ are obtained from $F$ and the separation constants $\beta_+$ and $\beta_-$ via

$$E = -\frac{1}{2(\beta_+ + \beta_-)^2},$$

$$f = \frac{1}{4}(\beta_+ + \beta_-)^3 F.$$  

(10)

The simplifying fact is this: by the coordinate transformation,

$$\sigma = r^2, \quad \psi_\pm(\sigma) = r\Phi_\pm(r),$$

(12)

the Eqs. (9) become the Schrödinger equations for a two-dimensional, radially symmetric harmonic oscillator perturbed by $\pm 2fr^4$:

$$\left[-\frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr}\right) + \frac{m^2}{2r^2} + \frac{r^2}{2} \pm 2fr^4 - 2\beta_\pm\right]\Phi_\pm(r) = 0.$$  

(13)

That each term in the perturbation series for $\Phi_\pm$ comes out in closed form is a consequence of the vanishing of all the harmonic oscillator matrix elements $\langle n_1 | r^4 | n_2 \rangle$ except those for which $n_1 - n_2 = 4, 2, 0, -2,$ or $-4$. Quantities like $R^{(0)}(r^4 | n_2)$ that enter Eq. (6) come out to be the sum of at most five terms (where $n_0$ is the oscillator quantum number corresponding to the unperturbed state $\Phi_\pm^{(0)}$, and $a_n \ldots e_n$ are constants),

$$R^{(0)}(r^4 | n_1) = \frac{a_{n_1} | n_1 + 4 \rangle}{n_0 - n_1 - 4} + \frac{b_{n_1} | n_1 + 2 \rangle}{n_0 - n_1 - 2}$$

$$+ \frac{c_{n_1} | n_1 \rangle}{n_0 - n_1} + \frac{d_{n_1} | n_1 - 2 \rangle}{n_0 - n_1 + 2} + \frac{e_{n_1} | n_1 - 4 \rangle}{n_0 - n_1 + 4}.$$  

(14)

Divergence of RSPT and tunnelling ionization rate

Divergence of the RSPT solution is quickly apparent from the factorial growth of the computed energy coefficients $E^{(N)}$ for large $N$. Numerically one finds, for instance, that the coefficients for the ground state fit the formula (note that the odd-order coefficients are zero),

$$E^{(2N)} \sim -\frac{6}{\pi} \left(\frac{3}{2}\right)^{2N} \left[1 - \frac{107/18}{2N} + \frac{7363/648}{2N(2N-1)} + \cdots\right].$$  

(15)

Such factorial growth of RSPT coefficients was first discussed by Bender and Wu for the anharmonic oscillator. Since the LoSurdo-Stark problem is essentially a radially symmetric, two-dimensional anharmonic oscillator, the factorial growth here is the same thing.

Despite its historical role in the birth of RSPT, and unlike the case of the anharmonic oscillator, the LoSurdo-Stark effect is conceptually complicated because there are no bound states (the potential goes to $-\infty$ at $\infty$), and after a long enough time the atom will ionize by tunnelling, as is schematically indicated in Fig. 1. Calculation of the ionization rate was first attempted by Oppenheimer with a “golden rule” formula. Although the calculation was marred by numerous errors, Oppenheimer did get the exponentially small factor $e^{-2\beta r}$ that characterizes the ionization rate for the ground state. Subsequent calculations used JWKB
methods, scattering methods and complex-rotation methods, among many others, some of which were designed to obtain the ionization rate as \((-2 \times)\) the imaginary part of a complex resonance eigenvalue. That is, in the presence of the constant electric field, the bound states of hydrogen get turned into resonance eigenvalues (corresponding to outgoing-wave boundary conditions), the real part of which is the perturbed energy, and the imaginary part of which yields the ionization rate.

It is possible to obtain by quasisemiclassical methods\(^7\) a perturbation expansion for the imaginary part of the resonance eigenvalues that consists of an exponentially small factor times a power series, and which for the ground state is explicitly

\[
\text{Im} E \sim - \frac{2}{F} e^{-\frac{2}{3F}} \left[ 1 - \frac{107}{18} \left( \frac{3F}{\pi} \right)^2 + \frac{7363}{648} \left( \frac{3F}{\pi} \right)^2 + \ldots \right].
\] (16)

Note that the numerical constants in Eq. (16), \(3/2, -107/18\) and \(+7363/648\), are the same as in Eq. (15). This is because \(\text{Re} E\) and \(\text{Im} E\) are connected by a “dispersion relation” that here has the consequence,\(^{20-22}\)

\[
E^{(N)} \sim \frac{1}{2\pi} \int_0^\infty dF \, F^{-N-1} \left[ \text{Im} E_{n_1,n_2,m}(F) + (-1)^N \text{Im} E_{n_2,n_1,m}(F) \right],
\] (17)

where \(n_1\) and \(n_2\) are the parabolic quantum numbers of the unperturbed state. If Eq. (16) is put into Eq. (17) and the integral taken, the result is Eq. (15). Notice that Eq. (16) for \(\text{Im} E\) is an exponentially small subseries (vs. the RSPT series) that enters the problem and that determines the asymptotics of the RSPT expansion (via a dispersion relation).

**Numerical use of divergent RSPT: partial summation and Borel summability**

Given that the RSPT series diverges, what happens if one tries to sum it? We proceed by example for the ground state, the first few terms of which appear in Eq. (8). We take \(F = 0.04\) a.u. for concreteness.

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A plot of the partial sums of the RSPT series versus order \( N \) is given in Fig. 2. The partial sums at first start to converge, but then after order 14 diverge at an accelerating rate. The RSPT expansion is an asymptotic power series\(^{24}\) in the sense of Poincaré, which means that

\[
\left| E(F) - \sum_{N=0}^{M} E^{(N)} F^N \right| = O(F^{M+1})
\]

(18)

for all \( M \). In a manner typical of asymptotic expansions, an approximately optimal partial sum is obtained by truncating the series just before the smallest term, which for \( F=0.04 \) is the 16th order term, yielding a partial sum truncated at 14th order of \(-0.503771146\). This is the simplest way to use the RSPT expansion numerically.

The divergence is partially tamed by Padé approximants, for which the variety \([n/n]\) and \([n/n+1]\) (in \( F \)), since the odd terms in the ground state series vanish) are easily computed as continued-fraction approximants\(^{9}\) to the RSPT series. But it is clear from the residual oscillation of the Padé approximants that they do not converge to arbitrary accuracy (at least by 50th order). Note that Padé approximants work better for states in which the RSPT coefficients alternate in sign, i.e., for which \( n_2>n_1 \).

The exact complex resonance eigenvalue for \( F=0.04 \) can be obtained by a variational calculation\(^{25}\):

\[-0.503\,771\,591\,00 - i\,0.000\,001\,946\,35 \]

A partial sum or a Padé approximant of the RSPT series gives a real result, which is an approximation to \( \text{Re}E \). What about \( \text{Im}E \)? One can take partial sums of the exponentially small series (16), which is also divergent. Terms through 50th order can be found in Ref. 7, from which one obtains a value of \(-0.000\,001\,946 \). Thus one way to use the RSPT and exponentially small series is partial summation with or without Padé approximation, with the
quality of the result depending on the value of \( F \). For \( F=0.04 \), the best accuracy that can be obtained for \( \text{Re}E \) is six significant digits, and for \( \text{Im}E \) four.

Can one obtain the complex resonance \( E \) to arbitrary accuracy (at least in principle) from the RSPT series alone? The answer surprisingly is yes. This results from the Borel summability of the RSPT series to the resonance eigenvalues, proved rigorously by Graffi and Grecchi.⁴

The Borel sum (if it exists) of the series \( \sum a_nx^n \) is defined as the integral,

\[
\text{Borel sum of } \{\sum a_nx^n\} = \int_0^\infty e^{-t} B(xt) \, dt, \tag{19}
\]

where the Borel transform \( B(xt) \) is defined within a circle of convergence with nonzero radius (otherwise the procedure doesn't work) by

\[
B(xt) = \sum_{n=0}^\infty \frac{a_n}{n!} (xt)^n, \tag{20}
\]

and by analytic continuation to a neighborhood of the positive \( t \) axis outside the circle of convergence. The "standard example" of a divergent series and its Borel sum is provided by

\[
\sum a_nx^n = \sum_{n=0}^\infty (-1)^n n! x^n, \tag{21}
\]

for which the Borel transform and Borel sum are respectively,

\[
B(xt) = \frac{1}{1+xt}, \tag{22}
\]

\[
\text{Borel sum} = \int_0^\infty e^{-t} \frac{1}{1+xt} \, dt. \tag{23}
\]

To apply the Borel method numerically to the LoSurdo-Stark effect, one must evaluate \( B(xt) \) from the real RSPT series (8) and at the same time obtain its analytic continuation. One way is to use Padé approximants. In this Padé-Borel manner one calculates⁹ for the ground state at \( F=0.04 \) the resonance eigenvalue,

\[-0.503 \, 771 \, 591 \, 013 \, 7 - i \, 0.000 \, 001 \, 946 \, 349 \, 995, \]

where the accuracy is limited only by machine precision, cancellation error, and computer time, but not by divergence. Note that only the RSPT series, the first few terms of which are Eq. (8), not the imaginary series (16), went into this calculation of the complex resonance.

**Remarks about Borel summability: uniqueness; complex sums for real series**

There are two important facts connected with Borel summability. The first is uniqueness. In the sense of Poincaré many functions can have the same asymptotic power series—for instance, two functions \( f_1(x) \) and \( f_2(x) \) whose difference is \( e^{-1/2} \). Borel summation singles out a unique function that is in one-to-one correspondence with its asymptotic expansion.

The second is what happens at a boundary of a region in the interior of which the power series is Borel summable: real series can have "complex sums." To illustrate, we proceed
with the standard example (21). The phenomenon occurs when $x$ is negative, say $x = -z$. In this case, Eqs. (21)-(23) become

$$\sum a_n x^n = \sum n! z^n,$$  \hspace{1cm} (24)

$$B(x) = \frac{1}{1 - z},$$  \hspace{1cm} (25)

$$\text{Borel sum} = \int_0^\infty e^{-t} \frac{1}{1 - z} \, dt.$$  \hspace{1cm} (26)

If $z$ is real and positive, then the integral in Eq. (26) is ambiguous. Its value depends on how $z$ becomes real, from above or below, and the result is one of the two choices,

$$\int_0^\infty e^{-t} \frac{1}{1 - z} \, dt = P \int_0^\infty e^{-t} \frac{1}{1 - z} \, dt \pm i\pi \frac{e^{-1/z}}{z},$$  \hspace{1cm} (27)

where $P$ denotes principal value. Put more precisely, the Borel sum of a divergent power series on a Stokes line can be defined by analytic continuation from one side or the other, the result depending on which side the analytic continuation is from. The positive $z$ axis is such a line for Eq. (24), and it is clear in this case how a real power series gives rise to a complex sum. The real $F$ axis is similarly a Stokes line for the energy in the LoSurd-Stark problem, and this is how and why the Borel sum of the real RSPT series comes out complex.

Both of these points, uniqueness and complex sums associated with real series on Stokes lines, have important consequences whenever a function is related to its asymptotic expansion by Borel summability. The case of $H_2^+$, the hydrogen molecule-ion, is one such example.\textsuperscript{12,26-28} The energy eigenvalue has an asymptotic power series in the reciprocal of the internuclear distance $R$, which is divergent but Borel summable (although not to the energy eigenvalue). $H_2^+$ is a double-well problem with all of its states paired, symmetric with antisymmetric. The splitting between paired states is exponentially small. Computation of the exponentially small subseries in the presence of a divergent non-small power series would be conceptually if not practically difficult were it not that the divergent power series determines a unique analytic function. In the $H_2^+$ case there is in fact a hierarchy of successively exponentially smaller subseries, some of which are explicitly complex, but with the explicit imaginary parts cancelling the implicit imaginary contributions coming from the Borel sums of the divergent real series on Stokes lines.\textsuperscript{12,25}

A second important example consists of the Airy functions, which have Borel-summable asymptotic expansions.\textsuperscript{29,30} The positive $z$ axis for the Airy $Bi(z)$ function is a Stokes line. The coefficients of the large asymptotic power series associated with $Bi(z)$ are all positive and grow exponentially fast. But the Borel sum of this series is complex, the sign of the imaginary part depending on which sector the positive real axis is kept with. As a consequence, the asymptotic expansion for $Bi(z)$ also has an exponentially small imaginary subseries that cancels the imaginary contribution from the Borel sum of the real series. The Airy functions play a key role in deriving the formulas of the so-called JWKB method, and much confusion about “connection formulas” can be blamed on not taking into account these two points. The reader is referred to the references for detailed discussion.\textsuperscript{31,32}

**Padé-Padé summation method**

We mention in passing another technique\textsuperscript{8} to “sum” the RSPT series at real $F$ to obtain the complex resonances. It makes use of the analyticity of $E(F)$ for complex $F$ in the first quadrant away from the real axis and consists of two steps: (1) First the RSPT series and derivatives of the RSPT series for $E$ are summed at some point $F_{\text{intermediate}}$ in the first
quadrant via Padé approximants; (2) then the power series about $F_{\text{intermediate}}$, which is 
convergent because of analyticity, is summed at the desired final point on the real axis—
conveniently also by Padé approximants. The efficiency of the method is mildly dependent on
the choice of the intermediate point, and it is not too difficult to obtain highly accurate
complex resonance eigenvalues by this Padé-Padé method applied to the real RSPT series.

IV. PERTURBATION THEORY OF THE ZEEMAN EFFECT

Algorithm for degenerate RSPT and the Zeeman effect

As for the LoSurdo-Stark effect, RSPT for the Zeeman effect can be solved order by
order in closed form and is divergent. Unlike the LoSurdo-Stark problem, the Zeeman prob-
lem is not completely separable, and degeneracy complicates the RSPT. Since the $\phi$-depen-
dence of the wave function is $e^{im\phi}$, the Zeeman Hamiltonian can be written, in dimension-
less units, as

$$H = \left(-\frac{1}{2} \nabla^2 - \frac{1}{r} + m b \right) + \left(\frac{1}{2} b^2\right)(x^2 + y^2). \tag{28}$$

The term linear in the magnetic field strength $b$ is trivial. The natural RSPT expansion
parameter is $b^2/2$. Given that $m$ and parity are conserved, the degeneracy that is not removed
by symmetry is among those states that have the same $m$, parity, and principal quantum
number $n$. The first case is for $n=3$: namely, $3s$ and $3d_0$.

Before RSPT can be applied to a degenerate problem, the algorithm given by Eqs. (1)-
(7) needs to be modified. In particular, Eq. (6) changes, and there is the problem of the
"correct zeroth-order functions." Denote by $\psi_i^{(0)}$, $i = 1, 2, \ldots, M$, the degenerate eigenfunc-
tions that share the same energy $E^{(0)}$. Then the "correct zero order functions" satisfy

$$\left\langle \psi_i^{(0)} \right| x^2 + y^2 \left| \psi_j^{(0)} \right\rangle = E_i^{(1)} \delta_{ij}, \quad (1 \leq i, j \leq M), \tag{29}$$

where $E_i^{(1)}$ denote the first order energies. In the case of $n = 3$, $\psi_1^{(0)}$ and $\psi_2^{(0)}$ are each
linear combinations of $3s$ and $3d_0$, and the degeneracy is completely removed in first order
(in $b^2/2$). It is necessary to break the wave function in each order for the state $i$ into two
components, one $[0]$ in the space orthogonal to the degenerate $\psi_i^{(0)}$, ($j = 1, 2, \ldots, M$), and
the second $[1]$ within the degenerate subspace but orthogonal to $\psi_i^{(0)}$.

$$\psi_i^{(N)} = \psi_i^{[0]} + \psi_i^{[1]} \tag{30}$$

Equation (6) becomes an equation for the first component,

$$\psi_{[0]}^{(N)} = R_{i}^{(0)} \left( V - E_i^{(1)} \right) \psi_i^{(N-1)} - E_i^{(2)} R_{i}^{(0)} \psi_i^{(N-2)} - \cdots - E_i^{(N-1)} R_{i}^{(0)} \psi_i^{(1)}, \tag{31}$$

and there are two additional equations to fix the second component:

$$R_{i}^{(-1)} = \sum_j \left| \psi_j^{(0)} \right\rangle \left\langle \psi_j^{(0)} \right| \frac{1}{E_i^{(0)} - E_j^{(0)}}, \tag{32}$$

$$E_j^{(0)} = E_i^{(0)}, \quad j \neq i.$$
\[ \psi^{(N)}_{[1]i} = R^{-1}_{[0]} \left( V - E_{i} \right) \psi^{(N)}_{[0]i} = E^{(2)}_{R} \psi^{(N-1)}_{[0]i} \psi^{(N-1)}_{[1]i} \psi^{(N-1)}_{[1]i}. \] (33)

The first-order energy denominators in \( R^{-1} \) are characteristic of degenerate RSPT. For application to high-order RSPT for the 3s–3d case, the reader is referred to the literature.\(^{33}\) We give here only the asymptotic result (where \( C \) is a constant),

\[ E^{(N)} \sim C(-1)^{N+1} N^{15} \frac{2^{N+2}}{3^{N+1}} \frac{(2N+9/2)!}{(-1/2)!}. \] (34)

V. QUANTUM FROM CLASSICAL PERTURBATION THEORY

In this concluding section of the main paper we touch on a new twist of the perturbation theory of the anharmonic oscillator that brings out the transition from classical to quantum mechanics.\(^{34}\) The motivation is that some problems involving excited states of atoms in high fields have been amenable to solution via classical mechanics, and the possibility arises of adding quantum corrections to the classical results via the algorithm of classical canonical perturbation theory.\(^{35}\)

We begin with the Hamiltonian for an anharmonic oscillator and write the RSPT energy in a form that keeps both the \( \hbar \) and the circular frequency \( \omega \):

\[ H = \frac{1}{2} p^2 + \frac{1}{2} \omega^2 x^2 + g \omega^3 x^2, \] (35)

\[ E = \omega \left( n + \frac{1}{2} \right) \hbar \]

\[ + \omega^3 \left( n + \frac{1}{2} \right) \hbar^2 g \quad + \omega^3 \frac{\hbar^2 g}{8} \]

\[ + \omega \left( n + \frac{1}{2} \right) \hbar^3 g^3 + \omega \frac{67}{16} \left( n + \frac{1}{2} \right) \hbar^3 g^2 \]

\[ + \ldots. \] (36)

Making the identification that the classical action \( J \) for the harmonic oscillator is \( (n+1/2)\hbar \), one gets, on rearrangement and summation over powers of \( g \) (and denoting the sums \( F_0 \) and \( F_2 \), apart from the indicated factors), a series in powers of \( \hbar^2 g^2 \):

\[ E = \omega \left( n + \frac{1}{2} \right) \hbar \left[ F_0 \left( n + \frac{1}{2} \right) \hbar g \right] + \omega g \hbar^2 F_2 \left[ \left( n + \frac{1}{2} \right) \hbar g \right] + \ldots, \] (37)

\[ = \omega J \left[ F_0 \left[ J g \right] + \omega g \hbar^2 F_2 \left[ J g \right] + \ldots. \] (38)

Here the term zeroth-order in \( \hbar \) is not only the sum of the classical canonical perturbation theory, but it is identical with JWKB through first order (with \( J = (n+1/2)\hbar \)), and the term proportional to \( \hbar^2 g^2 \) is exactly the JWKB correction at that order. Thus one can obtain the semiclassical results with quantum corrections (order by order in \( \hbar^2 \)) by starting with the divergent RSPT series and rearranging terms at fixed classical action \( J \) according to order in \( \hbar \) and \( g \), and then summing the series over powers of \( g \) (whose radii of convergence are all the same and nonzero).
VI. SUMMARY

Rayleigh-Schrödinger perturbation theory can be carried out order by order in closed form for several examples of perturbed hydrogen atoms and harmonic oscillators, which are in fact transformationally equivalent. Typically the series diverge, but are asymptotic and summable by Borel or Padé-Padé methods numerically as well as in principle. Typically there is one or more exponentially small power series that may be related to the physics of the problem and that are related to the asymptotics of the RSPT series. The case of the hydrogen atom in an electric field, first observed by LoSurdo, has been examined in detail. In the case of the Zeeman effect, how to take into account degeneracy has been discussed. In the case of the harmonic oscillator perturbed by $x^4$, the RSPT series can be rearranged into a series in powers of $\hbar^2$ at constant action, and the possibility to obtain quantum results smoothly from classical results has been pointed out.

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APPENDIX: EQUIVALENCE OF RADially SYMMETRIC HARMONIC OSCILLATORS AND HYDROGEN ATOMS IN D DIMENSIONS

There is a transformational equivalence among radially symmetric harmonic oscillators and bound states of hydrogen atoms in several dimensions that is not too widely known. It seems of some pedagogical value to summarize the results here.

Consider first a radially symmetric harmonic oscillator in $D$ dimensions with force constant $k$. Its eigenfunctions can be written as a product of a radial wave function $R(r)$ and an angular function (a hyperspherical harmonic), of which the only characteristic important here is the centrifugal contribution to the radial Schrödinger equation, (where $L = 0, 1, 2, \ldots$):

$$\left[-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{D-1}{r} \frac{d}{dr}\right) + \frac{L(L+D-2)}{2r^2} + \frac{k}{2} r^2 - E\right]R(r) = 0. \quad (39)$$

By the substitution,

$$R(r) = r^{(1-D)/2} P(r), \quad (40)$$

one can eliminate the first derivative to put Eq. (39) into "Schrödinger form":

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{(L+\frac{1}{2}D-1)^2}{2r^2} - \frac{1}{4} + \frac{k}{2} r^2 - E\right]P(r) = 0. \quad (41)$$

With $m$ set equal to $L-1+D/2$, which can take on either integer or integer-plus-one-half values, the preceding equation is formally identical to that for a radially symmetric two-dimensional oscillator,

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{m^2 - 1}{4} \frac{r^2}{2r^2} + \frac{k}{2} r^2 - E\right]P(r) = 0. \quad (42)$$

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With the extension of \( m \) to half-integral values, one might say that radially symmetric harmonic oscillators in any dimension are equivalent to the (extended) two-dimensional case.

Consider next a hypothetical hydrogen atom in \( D \) dimensions with nuclear charge \( Z \). Its eigenfunctions can be written as a product of a radial wave function \( R(r) \) and an angular function as in the oscillator case, with radial wave equation

\[
\left[-\frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{D-1}{r}\frac{d}{dr}\right) + \frac{L(L+D-2)}{2r^2} - \frac{Z}{r} - E\right]R(r) = 0.
\]

(43)

The substitution (40) eliminates the first derivative:

\[
\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{(L + \frac{1}{2}D - 2)^2 - \frac{1}{4}}{2r^2} - \frac{Z}{r} - E\right]P(r) = 0.
\]

(44)

Now make the substitutions,

\[
r = \frac{1}{2}x^2, \quad P(r) = x^{1/2}\psi(x),
\]

(45)

to obtain

\[
\left[-\frac{1}{2}\frac{d^2}{dx^2} + \frac{(2L + D - 2)^2 - \frac{1}{4}}{2x^2} + \frac{(-2E)}{2}x^2 - 2Z\right]\psi(x) = 0.
\]

(46)

If one make the identifications \( m = 2L+D-2 \) (which is necessarily an integer), \( k = (-2E) \), and “energy” \( = 2Z \), then by comparing Eqs. (46) and (42), one sees that the hydrogenic radial bound-state (-2E > 0) equation is equivalent to the radially symmetric oscillator equation.

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