Analysis of perturbative methods in quantum mechanics: Brillouin-Wigner and Dalgarno-Lewis

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Abstract

Perturbation theory in quantum mechanics (QM) is fundamental for the study of systems whose exact solution of the Schrödinger equation (SE) is not possible. Therefore, in the following work, a comparative analysis of three formulations of this time-independent theory is presented: Rayleigh–Schrödinger (RS), Brillouin–Wigner (BW), and Dalgarno–Lewis (DL). Their foundations are developed and the first corrections to the eigenfunctions and energies associated with the system's Hamiltonian are obtained. The RS and BW methods require infinite series that must be truncated, so the precision depends on the available computational resources. Additionally, BW implies a self-referential solution that requires knowing the eigenenergies iteratively. Finally, the three methods are applied to the Stark effect, finding that BW is more accurate than RS at all truncation orders. It is found that by gradually increasing the number of elements in the summations, the terms of higher orders cease to contribute.

1 Introduction

The perturbation theory in quantum mechanics (QM) is fundamental for the study of systems whose exact solution of the Schrödinger equation (SE) is not possible. Previously, its application was limited to the calculation of few low-order terms; however, with the various advances, computers have allowed evaluating higher orders, which provides the possibility that, by developing new perturbative methods, better approximations for quantum systems are achieved [1].

There are various ways to present the time-independent perturbation theory; some of these are those of Rayleigh–Schrödinger (RS), Brillouin–Wigner (BW) and Dalgarno–Lewis (DL).

Each one presents characteristics and differences that may prove more effective than the others, depending on the system to be treated. With the purpose of showing their particularities and advantages, in this work the corrections in the different orders of the energies and of the states (for time-independent perturbations) will be developed. Likewise, a discussion will be presented about the interdependence that may exist between said theories.

To evidence the effectiveness of these methods, the Stark effect problem will be analyzed, comparing the different corrections both of the energy and of the states.

2 Theoretical Framework

To develop a perturbative theory, one starts from a system for which a set of eigenfunctions and another of eigenvalues are initially known. Once this is obtained, it can be assumed that the presence of a perturbation on the initial system produces a variation in the states, which in turn generates a change in the associated eigenfunctions. Assuming that the solution to the Schrödinger equation admits a power series expansion, it is possible to find relationships between the corrections of the eigenvalues and the eigenfunctions of different orders. However, in principle, the expansion should not be restricted to a specific form. In this way, the relationships between the different corrections will be conditioned by the choice of the expansion of the solution. The quantum state Ψ that describes the system is governed by the Schrödinger equation (represented in position):

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\hat{H}\,\Psi(\mathbf{r},t). \tag{1}$$

Where $\hat{H}$ is the total Hamiltonian of the system. Usually a perturbation (through a field) is presented that allows separating the Hamiltonian into two parts. Let H^0 be the Hamiltonian of the unperturbed system and $H^1 = V$ the perturbation. Thus the complete Hamiltonian and the SE for the stationary states would be respectively

$$\hat{H}=\hat{H}^0+\lambda\hat{H}^1,\qquad \hat{H}^0\big|\varphi_n^{(0)}\big\rangle=E_n^{(0)}\big|\varphi_n^{(0)}\big\rangle. \tag{2}$$

Where λ is the perturbation parameter. The RS theory considers expansions in powers of λ for the eigenvalues and the eigenstates with respect to $\hat{H}$

$$\begin{aligned} E_n &= E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\cdots,\\ \big|\varphi_n\big\rangle &= \big|\varphi_n^{(0)}\big\rangle+\lambda\big|\varphi_n^{(1)}\big\rangle+\lambda^2\big|\varphi_n^{(2)}\big\rangle+\cdots. \end{aligned} \tag{3}$$

The Hamiltonian $\hat{H}$ must satisfy the stationary states equation, which allows finding the first corrections of the eigenvalues thus obtaining

$$E_n^{(1)}=V_{nn},\qquad E_n^{(2)}=\sum_{m\neq n}\frac{|V_{mn}|^2}{\Delta_{nm}}. \tag{4}$$

where

$$V_{mn} = \langle \varphi_m^{(0)} | \hat{H}^1 | \varphi_n^{(0)} \rangle, \qquad \Delta_{mn} = E_m^{(0)} - E_n^{(0)}. \quad (5)$$

Additionally the first corrections of the eigenstates are [2, Sec. 5.1]

$$\begin{aligned} |\varphi_n\rangle = |\varphi_n^{(0)}\rangle &+ \lambda \sum_{m\neq n} \frac{V_{mn}}{\Delta_{nm}} |\varphi_m^{(0)}\rangle \\ &+ \lambda^2 \Bigg[\sum_{m\neq n} \sum_{k\neq n} \frac{V_{mk}\, V_{kn}}{\Delta_{nm}\, \Delta_{nk}} |\varphi_m^{(0)}\rangle \\ &- \sum_{m\neq n} \frac{V_{mn}\, V_{nn}}{\Delta_{nm}^2} |\varphi_m^{(0)}\rangle \\ &- \tfrac{1}{2} \sum_{m\neq n} \frac{|V_{mn}|^2}{\Delta_{nm}^2} |\varphi_n^{(0)}\rangle \Bigg] + \mathcal{O}(\lambda^3). \end{aligned} \quad (6)$$

Although this method is useful, there are other methods that are useful when the systems to be treated have different characteristics.

2.1 Brillouin-Wigner Method

The BW method has similarities with the classical theory RS. Considering again equation (2) but in this case for the eigenstates of $\hat{H}$

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle \quad (7)$$

It can be written using (2) in the form

$$\left(E_n - \hat{H}^0\right)|\varphi_n\rangle = \lambda \hat{V}|\varphi_n\rangle \quad (8)$$

Which allows seeing the projection of the exact state onto the unperturbed state

$$\left(E_\mu - E_m^{(0)}\right)\langle \varphi_m^{(0)}|\varphi_\mu\rangle = \lambda \langle \varphi_m^{(0)}|\hat{H}^1|\varphi_\mu\rangle \quad (9)$$

Taking the normalization condition $\langle \varphi_\mu^{(0)}|\varphi_\mu\rangle = 1$ it follows that the presence of non-zero higher-order terms in perturbation theory implies that the μ-th eigenstate is not normalized to unity. Therefore, the exact eigenstate is given directly by

$$\begin{aligned} |\varphi_\mu\rangle &= \sum_m |\varphi_m^{(0)}\rangle\langle \varphi_m^{(0)}|\varphi_\mu\rangle \\ &= |\varphi_\mu^{(0)}\rangle\langle \varphi_\mu^{(0)}|\varphi_\mu\rangle + \sum_{m\neq\mu} |\varphi_m^{(0)}\rangle\langle \varphi_m^{(0)}|\varphi_\mu\rangle \\ &= |\varphi_\mu^{(0)}\rangle + \lambda \sum_{m\neq\mu} |\varphi_m^{(0)}\rangle \frac{\langle \varphi_m^{(0)}|\hat{H}^1|\varphi_\mu\rangle}{E_\mu - E_m^{(0)}} \end{aligned} \quad (10)$$

Additionally, setting $m = \mu$ in equation (7), it is found that the energy is given by

$$\begin{aligned} E_\mu &= E_\mu^{(0)} + \lambda \langle \varphi_\mu^{(0)}|\hat{H}^1|\varphi_\mu\rangle \\ &= E_\mu^{(0)} + \lambda\, V_{\mu\mu} \\ &\quad + \lambda^2 \sum_{m\neq\mu} \frac{|V_{\mu m}|^2}{E_\mu - E_m^{(0)}} \\ &\quad + \lambda^3 \sum_{\substack{j\neq\mu \\ m\neq\mu}} \frac{V_{\mu j}\, V_{jm}\, V_{m\mu}}{\left(E_\mu - E_j^{(0)}\right)\left(E_\mu - E_m^{(0)}\right)} + \cdots . \end{aligned} \quad (11)$$

These are the basic expressions regarding BW theory. It should be noted that both the state and the exact energy implicitly depend on E_μ. If this were to be expanded in a power series, as in (3), the usual expressions of RS theory would be recovered [3]. However, there is a crucial difference in the convergence behavior depending on the systems being treated. If the perturbation is small, RS theory behaves well. However, it has problems in cases where $\lambda \ll 1$ does not hold or in the case of degeneracy, since there would be convergence problems of the type $1/(E_\mu^0 - E_m^0)$ due to the singularities.

Given this problem, the question naturally arises: how is a solution found? For this, one can consider rewriting (11) as

$$f(E_n) \equiv E_n - E_n^{(0)} - K(E_n) = 0 \quad (12)$$

Where $K(E)$ represents the terms of the summation (neglecting $\mathcal{O}(\lambda^3)$). With this, it only remains to apply computational tools for the solution of these systems, which in multiple cases are nonlinear [4]

On the other hand, the previously presented methods require problematic summations which must be truncated at some point. Thus, an alternative method arises that allows suppressing the summations and the need to approximate the corrections of the different orders.

2.2 Dalgarno-Lewis Method

This method, unlike the RS method, requires another assumption about the expansion of the eigenstates. In particular (working in a position basis) it is similar to the logarithmic perturbation method (PL) [5] in which it is assumed

$$\varphi_n(x) = e^{S_n(x)}, \quad (13)$$

which implies

$$\begin{aligned} \varphi_n'(x) &= S_n'(x)\, e^{S_n(x)}, \\ \varphi_n''(x) &= \left[S_n''(x) + (S_n'(x))^2\right] e^{S_n(x)}. \end{aligned} \quad (14)$$

The stationary Schrödinger equation can be rewritten

$$-\frac{\hbar^2}{2m}\varphi_n''(x) + V(x)\,\varphi_n(x) = E_n\,\varphi_n(x), \quad (15)$$

where $V = V_0 + \lambda V_1$. By substituting (13) into (14) and replacing, one arrives at the Riccati equation

$$S_n''(x) + [S_n'(x)]^2 = \frac{2m}{\hbar^2}\left[V(x) - E\right] \quad (16)$$

An analogous solution is assumed to equation (3)

$$S_n(x) = S_n^{(0)}(x) + \lambda S_n^{(1)}(x) + \lambda^2 S_n^{(2)}(x) + \cdots \quad (17)$$

Which quickly leads to

$$\begin{aligned}&\big(S_n^{(0)''}+\lambda S_n^{(1)''}+\lambda^2 S_n^{(2)''}\big)\\&\quad+\Big[\big(S_n^{(0)'}\big)^2+2\lambda S_n^{(0)'}S_n^{(1)'}\\&\quad+\lambda^2\big(2S_n^{(0)'}S_n^{(2)'}+\big(S_n^{(1)'}\big)^2\big)\Big]\\&=\frac{2m}{\hbar^2}\big(V_0(x)+\lambda V_1(x)-E_n^{(0)}\\&\quad-\lambda E_n^{(1)}-\lambda^2E_n^{(2)}\big)+\mathcal{O}(\lambda^3).\end{aligned}$$

Which, by comparing term by term

$$\begin{aligned}\lambda^0:&\quad S_n^{(0)''}+\big(S_n^{(0)'}\big)^2=\frac{2m}{\hbar^2}\big(V_0(x)-E_n^{(0)}\big),\\\lambda^1:&\quad S_n^{(1)''}+2S_n^{(0)'}S_n^{(1)'}=\frac{2m}{\hbar^2}\big(V_1(x)-E_n^{(1)}\big),\\\lambda^2:&\quad S_n^{(2)''}+2S_n^{(0)'}S_n^{(2)'}=\frac{2m}{\hbar^2}(-E_n^{(2)})-\big(S_n^{(1)'}\big)^2.\end{aligned}\tag{18}$$

From the linear term in λ, one can assume an ansatz $S_n^0\equiv\ln\varphi_n^0$

$$S_n^{(0)''}(x)+\big(S_n^{(0)'}(x)\big)^2=\frac{\varphi_n^{(0)''}(x)}{\varphi_n^{(0)}(x)}\tag{19}$$

By comparing (18) with (17) of order 0, it is found that it is a solution. Substituting into (12)

$$\begin{aligned}\varphi_n(x)&=e^{S_n^{(0)}(x)}\,e^{\lambda S_n^{(1)}(x)+\lambda^2S_n^{(2)}(x)+\ldots}\\&=e^{S_n^{(0)}(x)}\Big[1+\big(\lambda S_n^{(1)}(x)+\lambda^2S_n^{(2)}(x)+\ldots\big)\\&\quad+\frac{1}{2}\big(\lambda S_n^{(1)}(x)+\lambda^2S_n^{(2)}(x)+\ldots\big)^2+\ldots\Big]\\&=e^{S_n^{(0)}(x)}\Big[1+\lambda S_n^{(1)}(x)\\&\quad+\lambda^2\big(S_n^{(2)}(x)+\tfrac{1}{2}S_n^{(1)2}(x)\big)+\ldots\Big]\end{aligned}\tag{20}$$

Therefore, a direct correspondence can be made $\varphi_n^{(1)}=\varphi_n^{(0)}S_n^{(1)}$. Analogously for the other orders. The following should be noted

$$\begin{aligned}H_0\varphi_n^{(1)}&=-\frac{\hbar^2}{2m}\Big(\varphi_n^{(0)''}S_n^{(1)}+2\varphi_n^{(0)'}S_n^{(1)'}+\varphi_n^{(0)}S_n^{(1)''}\Big)\\&\quad+V_0\varphi_n^{(0)}S_n^{(1)}\\&=E_n^{(0)}\varphi_n^{(0)}S_n^{(1)}-\frac{\hbar^2}{2m}\Big(2\varphi_n^{(0)'}S_n^{(1)'}+\varphi_n^{(0)}S_n^{(1)''}\Big)\\&=E_n^{(0)}\varphi_n^{(1)}-\frac{\hbar^2}{2m}\varphi_n^{(0)}\Big(S_n^{(1)''}+2S_n^{(0)'}S_n^{(1)'}\Big)\\&=E_n^{(0)}\varphi_n^{(1)}-\varphi_n^{(0)}\big(V_1-E_n^{(1)}\big).\end{aligned}$$

When rewriting it, it becomes

$$\big(H_0-E_n^{(0)}\big)\varphi_n^{(1)}(x)=\big(E_n^{(1)}-V_1(x)\big)\varphi_n^{(0)}(x).\tag{21}$$

Which can be deduced from the fundamental relation (6), thus showing that the (DL) theory is independent of the RS theory. On the other hand, it can be calculated analogously for the second order. Let

$$T=S_n^{(2)}+\frac{1}{2}\Big(S_n^{(1)}\Big)^2,$$

$$\begin{aligned}T''+2S_n^{(0)'}T'&=-\frac{\hbar^2}{2m}E_n^{(2)}-\Big(S_n^{(1)'}\Big)^2+\Big(S_n^{(1)'}\Big)^2\\&\quad+S_n^{(1)}S_n^{(1)''}+2S_n^{(0)'}S_n^{(1)}S_n^{(1)'}\\&=-\frac{\hbar^2}{2m}E_n^{(2)}+S_n^{(1)}\big(S_n^{(1)''}+2S_n^{(0)'}S_n^{(1)'}\big)\\&=-\frac{\hbar^2}{2m}E_n^{(2)}+\frac{\hbar^2}{2m}S_n^{(1)}\big(V_1-E_n^{(1)}\big).\end{aligned}$$

By performing the corresponding assignments to the corrections of the previous orders, it is found that

$$\begin{aligned}H_0\varphi_n^{(2)}&=-\frac{\hbar^2}{2m}\big(\varphi_n^{(0)''}T+2\varphi_n^{(0)'}T'+\varphi_n^{(0)}T''\big)+V_0\varphi_n^{(0)}T\\&=\left(-\frac{\hbar^2}{2m}\varphi_n^{(0)''}+V_0\varphi_n^{(0)}\right)T-\frac{\hbar^2}{2m}\big(2\varphi_n^{(0)'}T'+\varphi_n^{(0)}T''\big)\\&=E_n^{(0)}\varphi_n^{(2)}-\frac{\hbar^2}{2m}\varphi_n^{(0)}\Big(T''+2S_n^{(0)'}T'\Big)\\&=E_n^{(0)}\varphi_n^{(2)}-\frac{\hbar^2}{2m}\varphi_n^{(0)}\Big(-\frac{2m}{\hbar^2}E_n^{(2)}+\frac{2m}{\hbar^2}S_n^{(1)}(V_1-E_n^{(1)})\Big)\\&=E_n^{(0)}\varphi_n^{(2)}+E_n^{(2)}\varphi_n^{(0)}-S_n^{(1)}(V_1-E_n^{(1)})\varphi_n^{(0)}.\end{aligned}$$

Therefore, one arrives at

$$\Big(H_0-E_n^{(0)}\Big)\varphi_n^{(2)}(x)=\Big(E_n^{(1)}-V_1(x)\Big)\varphi_n^{(1)}(x)+E_n^{(2)}\varphi_n^{(0)}(x).\tag{22}$$

This in turn could be deduced from (6) by expanding in series and grouping the terms of different orders of λ, thus concluding that it is a theory exclusive of the others. The differential equation for $S_n^{(1)}$ can be rewritten (by the theory of differential equations, multiplying by the integrating factor) in the form

$$\begin{aligned}&\big[\varphi_n^{(0)}(x)\big]^2S_n^{(1)''}(x)+2\big[\varphi_n^{(0)}(x)\big]^2S_n^{(0)'}(x)S_n^{(1)'}(x)\\&\qquad=\frac{2m}{\hbar^2}\big[\varphi_n^{(0)}(x)\big]^2\big[V_1(x)-E_n^{(1)}\big]\end{aligned}$$

$$\frac{d}{dx}\Big(\big[\varphi_n^{(0)}(x)\big]^2S_n^{(1)'}(x)\Big)=\frac{2m}{\hbar^2}\big[\varphi_n^{(0)}(x)\big]^2\big[V_1(x)-E_n^{(1)}\big]$$

Therefore, upon integrating

$$\begin{aligned}S_n^{(1)'}(x)&=\frac{\big[\varphi_n^{(0)}(a)\big]^2S_n^{(1)'}(a)}{\big[\varphi_n^{(0)}(x)\big]^2}\\&\quad+\frac{2m}{\hbar^2}\frac{1}{\big[\varphi_n^{(0)}(x)\big]^2}\int_a^x\big[\varphi_n^{(0)}(x')\big]^2\big(V_1(x')-E_n^{(1)}\big)dx',\end{aligned}$$

$$\begin{aligned}S_n^{(1)}(x)&=C_1\int_b^x\frac{d\xi}{\big[\varphi_n^{(0)}(\xi)\big]^2}\\&-\frac{2m}{\hbar^2}\int_b^x\frac{1}{\big[\varphi_n^{(0)}(\xi)\big]^2}\left[\int_\xi^a\big[\varphi_n^{(0)}(x')\big]^2\big(V_1(x')-E_n^{(1)}\big)\,dx'\right]d\xi\\&\quad+C_2\end{aligned}$$

It should be kept in mind that the development of this theory can be given in terms of an operator, which is presented in [6, Cap. 14]. Its fundamental relation is

$$[F_n,H_0]\,\varphi_n\equiv(F_nH_0-H_0F_n)\,\varphi_n=\big(\hat{H}^1-E_n^{(1)}\big)\,\varphi_n.\tag{23}$$

Clearly, a form can be found for the diagonal and non-diagonal elements. Using the condition that $H_0 = H_0^\dagger$, for the diagonal elements one has

$$\begin{aligned}\langle\varphi_n^{(0)}|[F_n, H_0]|\varphi_n^{(0)}\rangle &= \langle\varphi_n^{(0)}|F_n E_n^{(0)} - E_n^{(0)} F_n|\varphi_n^{(0)}\rangle \\ &= 0 \\ &= \langle\varphi_n^{(0)}|(\hat{H}^1 - E_n^{(1)})|\varphi_n^{(0)}\rangle\end{aligned} \tag{24}$$

For non-diagonal elements ($m \neq n$), by contracting $\langle\varphi_m^{(0)}|$, from the fundamental relation one obtains

$$\begin{aligned}\langle\varphi_m^{(0)}|[F_n, H_0]|\varphi_n^{(0)}\rangle &= \langle\varphi_m^{(0)}|(\hat{H}^1 - E_n^{(1)})|\varphi_n^{(0)}\rangle \\ &= \langle\varphi_m^{(0)}|\hat{H}^1|\varphi_n^{(0)}\rangle - E_n^{(1)}\,\delta_{mn}\end{aligned} \tag{25}$$

Clearly, for the case of $m \neq n$ it would provide an equation for F_n

$$\langle\varphi_m^{(0)}|F_n|\varphi_n^{(0)}\rangle = \frac{V_{mn}}{\Delta_{nm}}. \tag{26}$$

The benefit of this equation can be shown with the following; considering the second-order change using the completeness relation.

$$\begin{aligned}E_n^{(2)} &= \sum_{m\neq n} \frac{V_{nm}V_{mn}}{\Delta_{nm}} \\ &= \sum_{m\neq n} V_{nm}\langle\varphi_m^{(0)}|F_n|\varphi_n^{(0)}\rangle \\ &= \langle\varphi_n^{(0)}|\hat{H}^1 F_n|\varphi_n^{(0)}\rangle\end{aligned}$$

This shows the use of F_n in the context of saving us infinite sums (although an integral has to be performed). Analogously, the first-order correction of the state is given by

$$\begin{aligned}|\varphi_n^{(1)}\rangle &= \sum_{m\neq n} \frac{V_{mn}}{\Delta_{nm}}\,|\varphi_m^{(0)}\rangle \\ &= \sum_{m\neq n} |\varphi_m^{(0)}\rangle\,\langle\varphi_m^{(0)}|F_n|\varphi_n^{(0)}\rangle\end{aligned}$$

As it holds that

$$\sum_{m\neq n} |\varphi_m\rangle\langle\varphi_m|F_n|\varphi_n\rangle = F_n|\varphi_n\rangle - \langle\varphi_n|F_n|\varphi_n\rangle\,|\varphi_n\rangle,$$

then the first correction is of the form

$$|\varphi_n^{(1)}\rangle = (F_n - \langle\varphi_n|F_n|\varphi_n\rangle)\,|\varphi_n\rangle.$$

Finally, it should be noted that a relation can be established between $S_n^{(1)}$ and F_n. For

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

(in position basis), and $F_n(x)$ a function of x, the commutator is written as

$$[F_n, H_0] = \left[F_n, -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right]$$

since $[F_n, V(x)] = 0$. Calculating the effect on an arbitrary function $\phi(x)$:

$$\left[F_n, -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right]\phi = -\frac{\hbar^2}{2m}\left(F_n\frac{d^2\phi}{dx^2} - \frac{d^2(F_n\phi)}{dx^2}\right).$$

Expanding the second derivative:

$$\frac{d^2(F_n\phi)}{dx^2} = \frac{d^2F_n}{dx^2}\,\phi + 2\frac{dF_n}{dx}\frac{d\phi}{dx} + F_n\frac{d^2\phi}{dx^2}.$$

Therefore:

$$[F_n, H_0]\phi = \frac{\hbar^2}{2m}\left(\frac{d^2F_n}{dx^2}\,\phi + 2\frac{dF_n}{dx}\frac{d\phi}{dx}\right).$$

Applying to $\phi = \varphi_n$:

$$[F_n, H_0]\varphi_n = \frac{\hbar^2}{2m}\left(\varphi_n\frac{d^2F_n}{dx^2} + 2\frac{dF_n}{dx}\frac{d\varphi_n}{dx}\right).$$

Equating to the right-hand side of the commutator equation (according to the text):

$$\frac{\hbar^2}{2m}\left(\varphi_n\frac{d^2F_n}{dx^2} + 2\frac{dF_n}{dx}\frac{d\varphi_n}{dx}\right) = \left(V_1(x) - E_n^{(1)}\right)\varphi_n. \tag{27}$$

Multiplying both sides by $\frac{2m}{\hbar^2}$:

$$\varphi_n\frac{d^2F_n}{dx^2} + 2\frac{dF_n}{dx}\frac{d\varphi_n}{dx} = \frac{2m}{\hbar^2}\left(V_1(x) - E_n^{(1)}\right)\varphi_n.$$

This is exactly the equation satisfied by $S_n^{(1)}$. Therefore, this will help to find corrections for different orders.

3 Problem: Stark Effect

The Stark effect constitutes a fundamental phenomenon in atomic and molecular physics, characterized by the shift and/or splitting of energy levels when a system is subjected to an external electric field [**?**]. This problem is of particular interest, as it appears in various physical contexts and allows contrasting the advantages and limitations of different perturbative methods [**?**].

The unperturbed Hamiltonian of the hydrogen atom is given by

$$H_0 = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r},$$

where atomic units are defined such that the Bohr constant takes the form

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2},$$

and energies are expressed in Hartree units.

To analyze the corrections on the ground state, the wave function in position representation is considered:

$$\psi_{100}^{(0)}(r) = \frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}. \tag{28}$$

Upon introducing a uniform electric field oriented in the z direction, the perturbation takes the form

$$H^{(1)} = Fz = Fr\cos\theta. \tag{29}$$

The first-order energy correction can be evaluated directly due to the symmetry of the perturbation and the base function, resulting in

$$E_0^{(1)} = \langle\psi_{100}^{(0)}|H'|\psi_{100}^{(0)}\rangle = F\int|\psi_{100}^{(0)}|^2 r\cos\theta\,dV = 0.$$

3.1 Rayleigh–Schrödinger Method (RS)

In the Rayleigh–Schrödinger (RS) formalism, the first correction to the ground state is expressed as

$$\psi_0^{(1)} = \sum_{n\neq 0} \frac{\langle \psi_n^{(0)} | H' | \psi_{100}^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \psi_n^{(0)},$$

where the sum is performed over all excited states ($n > 1$). For hydrogen, only states with $l = 1$ and $m = 0$ contribute, due to dipolar selection rules. Thus, it is considered that

$$\psi_{n10}^{(0)}(\vec{r}) = R_{n1}(r) Y_{10}(\theta, \phi), \quad Y_{10} = \sqrt{\tfrac{3}{4\pi}} \cos\theta.$$

The calculation of the matrix elements decomposes into an angular part and a radial part:

$$\langle \psi_{n10}(0) \mid z \mid \psi_{100}(0) \rangle = \left[\int_0^\infty R_{n1}(r) R_{10}(r)\, r^3\, dr \right] \times \left[\int Y_{10}^* \cos\theta\, Y_{00}\, d\Omega \right].$$

The angular part is evaluated as

$$\begin{aligned} \int Y_{10}^* \cos\theta\, Y_{00}\, d\Omega &= \sqrt{\frac{3}{4\pi}} \frac{1}{\sqrt{4\pi}} \int \cos^2\theta\, d\Omega \\ &= \sqrt{\frac{3}{4\pi}} \frac{1}{\sqrt{4\pi}} \cdot \frac{4\pi}{3} \\ &= \frac{\sqrt{3}}{3}. \end{aligned}$$

Regarding the radial part, defined as I_n, it is given by

$$I_n = \frac{8}{n^3} \sqrt{\frac{(n-2)!}{(n+1)!}} \int_0^\infty r^4 e^{-r(1+\frac{1}{n})} L_{n-2}^3\left(\tfrac{2r}{n}\right) dr,$$

which, after a change of variable, is rewritten as

$$I_n = \frac{n}{4} \sqrt{\frac{(n-2)!}{(n+1)!}} \int_0^\infty \rho^4 e^{-\frac{n+1}{2}} L_{n-2}^3(\rho) d\rho.$$

Thus, the first-order correction to the wave function is expressed as

$$\psi^{(1)}(r,\theta) = \frac{F\cos\theta}{\sqrt{4\pi}} \sum_{n=2}^\infty \left[\frac{I_n}{-\frac{1}{2} + \frac{1}{2n^2}} R_{n1}(r) \right].$$

3.2 Dalgarno–Lewis Method (DL)

Alternatively, the Dalgarno–Lewis (DL) technique can be employed to obtain the first-order correction directly. Due to the symmetry of the problem, a trial form is proposed $\psi^{(1)}(r,\theta) = \cos\theta\, R(r)$. Upon substituting this expression into (26), one obtains

$$\left[-\frac{1}{2} \left(\frac{1}{r^{1/2}} \frac{d}{dr} \left(r^2 R' \right) - \frac{2}{r} R \right) - \frac{1}{r} R + \frac{1}{2} R \right] = -Er \frac{e^{-r}}{\sqrt{\pi}}.$$

Assuming a solution of the form $R(r) = e^{-r}(ar^2 + br + c)$, it is deduced that $c = 0$, $b = 2a$ and $a = \frac{-E}{2\sqrt{\pi}}$. Consequently,

$$\psi^{(1)}(r,\theta) = E \frac{1}{\sqrt{\pi}} \left(\tfrac{r^2}{2} + r \right) e^{-r} \cos\theta.$$

This corresponds to the solution found in [?], obtained analytically through an approach unrelated to DL theory.

3.3 Brillouin–Wigner Method (BW)

Finally, through the Brillouin–Wigner (BW) formalism, the correction to the state is written as

$$\psi^{(1)}(r,\theta) = \frac{F\cos\theta}{\sqrt{4\pi}} \sum_{n=2}^\infty \left[\frac{I_n}{E_\mu - E_n^{(0)}} R_{n1}(r) \right],$$

where the energy E_μ is determined iteratively through

$$\begin{aligned} E_\mu &= E_0^{(0)} + F^2 \sum_{n=2}^\infty \frac{\left| \langle \psi_{100}^{(0)} \mid z \mid \psi_{n10}^{(0)} \rangle \right|^2}{E_\mu - E_n^{(0)}} \\ &= E_0^{(0)} + \frac{F^2}{3} \sum_{n=2}^\infty \frac{I_n^2}{E_\mu - E_n^{(0)}}. \end{aligned}$$

In this way, it is observed that the first-order correction can be obtained through three distinct approaches: RS, DL, and BW, whose comparison is relevant for analyzing their computational efficiency.

4 Comparison

The Brillouin–Wigner (BW) and Rayleigh–Schrödinger (RS) methods prove particularly useful when the problem at hand does not admit an exact solution. However, in the case addressed previously, an analytical solution does exist, which allows for a comparative evaluation of the efficiency of these methods in approximating perturbative corrections. Below, the behavior of the first-order correction obtained through the different approaches is analyzed.

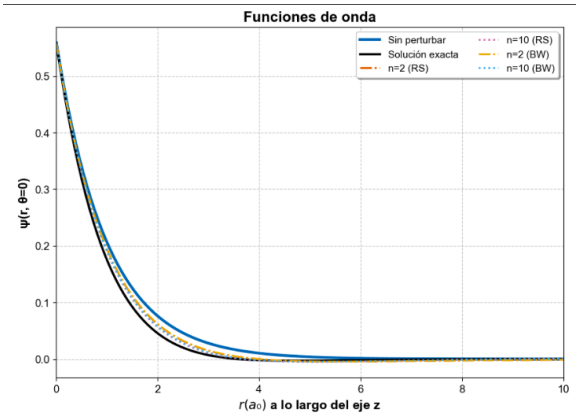

Figure 1. *Wave functions obtained with the RS, BW, and DL methods.*

In Fig. 1, it is observed that the wave functions exhibit a considerable margin of variation (including those with summation terms). However, all share the characteristic of being bounded between the exact solution [**?**] and the unperturbed solution. It then becomes necessary to analyze how the difference with respect to the exact solution behaves as the summations are extended.

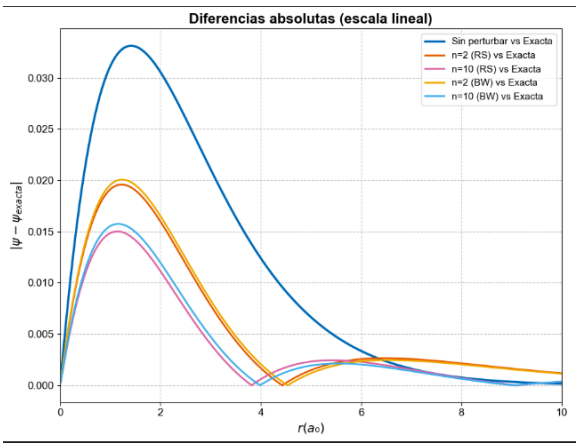

Figure 2. *Differences between the perturbative solutions and the exact solution.*

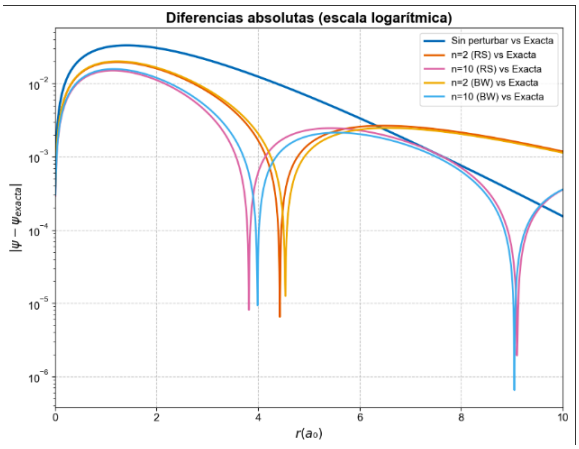

Figure 3. *Differences with respect to the exact solution on a logarithmic scale.*

From Figs. 2 and 3, it can be seen that, as the number of terms in the summations increases, the precision of the perturbative approximations improves progressively.

From this, natural questions arise: does the increase in terms in the summation imply an indefinite increase in precision?, or do the approximations tend to converge to a specific value? To answer this, the behavior of the solutions is examined as the number of included terms is increased.

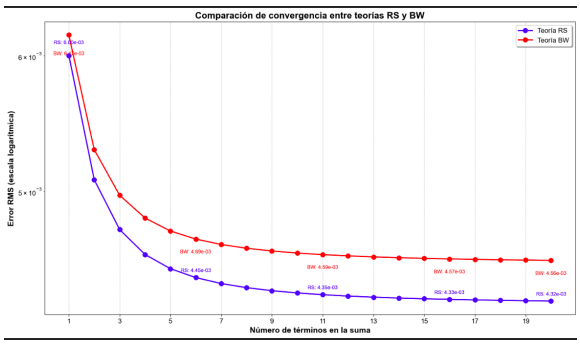

Figure 4. *Convergence behavior of the perturbative methods.*

Likewise, as the number of elements in the summation increases, the relative weight of each term in the final approximation can be analyzed.

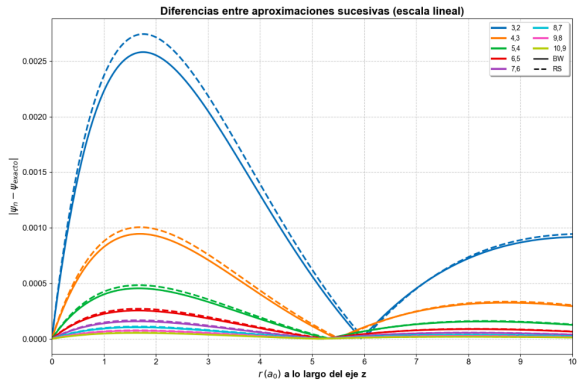

Figure 5. *Contribution of individual terms in the convergence.*

From Fig. 5, it is concluded that, as the number of terms increases, the difference with respect to the exact solution tends to converge to a defined value, which allows justifying a truncation criterion in the perturbative series.

5 Conclusions

It was found that the RS method, although the most common and systematic, requires the calculation of infinite summations over excited states, which makes it computationally expensive and dependent on a truncation that must be justified. On the other hand, the Brillouin–Wigner method, which incorporates the exact energy E_n in the denominator of its corrections, proved to be a powerful tool for potentially stronger perturbations, although it introduces an implicit dependence that must be resolved in a self-consistent manner, generally through iterative methods, showing better efficiency in terms of precision with respect to the first-order correction of the eigenstate.

Finally, the DL method stood out for its ability to obtain corrections to the states in a semi-analytical manner, completely avoiding infinite summations and replacing them with the solution of a differential equation for an operator (or function) F_n. This method demonstrated superior efficiency in the case study, delivering a closed and exact solution for the first correction of the state.

The numerical and graphical results presented confirmed that, by increasing the number of terms in the perturbative series of RS and BW, the solutions converge towards the exact result obtained through DL. This convergence validates the formal equivalence between the three theories and allows establishing truncation criteria based on the required precision.

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