

# Advantage of Classical Approximate Analytical Methods for Studying Rydberg States Over the Quantum Counterparts

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**Abstract:** In studies of atomic and molecular systems, approximate analytical methods play a significant role. This is because they can be used for benchmarking the results of numerical methods. Besides they offer a physical insight into the phenomena under consideration an insight impossible to achieve by numerical methods. Many approximate analytical methods were developed in such a way that each method has both the classical version and the quantum version. In the present paper we point out that for Rydberg (i.e., highly-excited) states of atomic systems, for a given analytical method, its classical version has a much broader range of validity than the corresponding quantum version. We illustrate this with two examples. The first example is the Stark effect in hydrogen atoms. The second example is hydrogen atoms in the field of high-frequency laser radiation. The advantage of classical approximate analytical methods for studying Rydberg states over the quantum counterparts is a counterintuitive result.

**Keywords:** Classical Analytical Methods, Quantum Analytical Methods, Rydberg States

## Introduction

Approximate analytical methods for studying atomic and molecular systems are important for the following reasons. First, they provide a physical insight that numerical methods lack. Second, they provide the test bench for verifying the results of numerical methods.

Let us start by discussing the standard Perturbation Theory (PT) for time-independent interactions. The overwhelming majority of textbooks on quantum mechanics create an impression that the PT is the quantum invention e.g., textbooks (Bertlmann and Friis, 2023; McIntyre, 2023; Larkoski, 2023; Nastase, 2022; Zettili, 2009; Zwiebach, 2022; Berera and Debbio, 2021; Cohen-Tannoudji *et al.*, 2020; Griffiths and Schroeter, 2018; Weinberg, 2015; Townsend, 2012) However, in reality the PT was first developed in classical mechanics by Poincaré and Magini (1899). The application of the classical PT to atomic (and some molecular) systems was presented in all detail in Born's book (Born, 1925).

Moreover, the textbooks on quantum mechanics do not present the following important facts. Namely, for Rydberg (i.e., highly excited) states of atomic and molecular systems, that is for the states for which not only the quantum PT but also the classical PT is appropriate, the region of validity of the classical PT is much broader

than the region of validity  $E_a$  of the quantum PT. In other words, Rydberg states that classical PT has a built-in advantage over quantum PT.

Indeed, the validity condition of the quantum PT is that the quantum energy correction  $\Delta E_a$  to the unperturbed energy level  $E_a^0$  must obey the condition:

$$|\Delta E_a| \ll |E_a^{(0)} - E_\beta^{(0)}| \quad (1)$$

For any level  $\alpha$  and for any level  $\beta$  different from  $\alpha$ . In distinction, the validity condition of the classical PT is that the classical energy correction  $\Delta E$  to the state of the energy  $E$  must obey the condition:

$$|\Delta E| \ll |E| \quad (2)$$

For the Rydberg states, condition (2) is much less restrictive than condition (1) for the following underlying reason. For the accurate description of the classical motion, it is sufficient to calculate the action  $S$  with a relative error much smaller than unity. In distinction, for the accurate determination of the quantum (or quasiclassical) wave function, it is necessary to calculate the action  $S$  with an absolute error much smaller than unity. Since  $S \gg 1$  for Rydberg states, then the quantum validity condition is much more restrictive than the classical validity condition.

In the present paper, first, we illustrate this by the example of the Stark effect in hydrogen atoms. The

corresponding energy corrections are well-known in the research and teaching communities.

Second, we illustrate the same thesis with a much less known example: Hydrogen atoms in the field of high-frequency laser radiation. Here "high-frequency" means that the laser frequency  $\omega$  is much greater than then any frequency  $\Omega$  characterizing the unperturbed hydrogen atom. This problem was treated not by the PT, but by the analytical method of separating rapid and slow subsystem-both in quantum and classical versions.

We emphasize that Rydberg atoms are still a hot topic for studies e.g., papers (Robicheaux *et al.*, 2024; Nguyen *et al.*, 2023; Ebadi *et al.*, 2022; Cong *et al.*, 2022; Cohen and Thompson, 2021) published in the last 3 years and references therein.

### *Comparison of the Ranges of Validity of the Quantum and Classical Perturbation Theories for the Stark Effect in Hydrogen Atoms*

The well-known quantum expression for the linear Stark effect in hydrogen in atomic units, i.e., in units where  $\hbar = e = m_e = 1$ , caused by the uniform electric field  $F$ , is e.g., the textbook (Landau *et al.*, 1965):

$$\Delta E_{nq} = 3nqF / 2, \quad q = n_1 - n_2 \quad (3)$$

where,  $n$  is the principal quantum number while  $n_1$  and  $n_2$  are the parabolic quantum numbers. Since the quantum number  $q$  (sometimes called the electric quantum number) takes the  $(2n + 1)$  values  $-(n-1), -(n-2), \dots, (n-1)$ , then the maximum value of the energy correction:

$$\max(\Delta E_{nq}) = 3n(n-1)F \quad (4)$$

For this quantum PT result to be valid, the width of this band must be much smaller than the separation between the adjacent unperturbed levels  $E_{n+1}^{(0)} - E_n^{(0)}$ . For  $n \gg 1$  (Rydberg states), this translates into:

$$3n^2F \ll 1/n^3 \quad (5)$$

Or:

$$F \ll F_{quant} \sim 1/n^5 \quad (6)$$

where,  $F_{quant}$  is the quantum critical value of the electric field.

The corresponding classical expression for the linear stark effect is e.g., book (Born, 1925):

$$\Delta E = 3J J_e F / 2 \quad (7)$$

where,  $J$  and  $J_e$  are the action variables (the generalized momenta) of the corresponding canonical action-angle variables. Here the action variable  $J$  is physically related to the conservation of the unperturbed energy and the action variable  $J_e$  is physically related to the conservation of the Runge Lenz vector  $A$  for the unperturbed system (the definition of the classical Runge-Lenz vector can be

found, e.g., in the textbook (Landau and Lifshitz, 1960). The action variable  $J_e$  takes the values:  $-J, -(J-1), J$ . (We note that  $J > 0$ ). Therefore, the maximum value of the energy correction is:

$$\max(\Delta E) = 3J^2 F / 2 \quad (8)$$

The unperturbed energy is (Poincaré and Magini 1899):

$$E = -1 / (2J^2) \quad (9)$$

So, the validity condition (2) takes the form:

$$\Delta E \leq \max(\Delta E) = 3J^2 F / 2 \ll 1 / (2J^2) \quad (10)$$

Leading to the requirement:

$$F \ll 1 / J^4 \quad (11)$$

The action variable  $J$  is the classical counterpart of the principal quantum number  $n$ , so it can be substituted by  $n$  in Eq. (11) and the validity range becomes:

$$F \ll F_{class} \sim 1/n^4 \quad (12)$$

The ratio of the classical  $F_{class}$  and quantum  $F_{quant}$  values of the critical electric fields is:

$$F_{class} / F_{quant} \sim n \quad (13)$$

Thus, for Rydberg states ( $n \gg 1$ ), the validity range of the classical energy correction is indeed by orders of magnitude broader than the validity range of the quantum energy correction.

### *Comparison of the Ranges of Validity of the Quantum and Classical Analytical Methods for Studying Hydrogen Atoms in the Field of High-Frequency Laser Radiation*

The system in point is a hydrogen atom under the linearly polarized laser field  $F(t) = F_0 \cos \omega t$  in the situation where:

$$\Omega / \omega \ll 1 \quad (14)$$

Here in the classical case,  $\Omega$  is the Kepler frequency. In the quantum case,  $\Omega$  is the maximum atomic transition frequency.

In both the quantum and classical studies of this system chapters 2 and 3 of the book (Oks, 2019), instead of the PT, the authors employed the analytical method based on the of rapid and slow subsystems. In other words, instead of using as the small parameter the relative littleness of the perturbation, the authors used the ratio  $\Omega / \omega$  as the small parameter.

The gist of this analytical method is the following. In the first step, one solves for the rapid subsystem at the frozen coordinates of the slow subsystem. In the next step, by using the solution obtained in the first step, one averages the Hamiltonian (or the Hamilton function) of the slow subsystem over the motion of the rapid

subsystem. As a result, the truncated Hamiltonian (or the Hamilton function) for the slow subsystem acquires an additional term: The effective potential. In classical mechanics, the method of effective potentials (which is how the method of separating rapid and slow subsystems is also called) was introduced in its simplest form by Kapitsa as presented in the textbook (Landau and Lifshitz, 1960). The quantum description of this method can be found in its simplest form, e.g., in the book (Galitski *et al.*, 2013).

The application of the quantum and classical methods of effective potentials to the system under consideration yielded at the first stage the following effective potential (added to the unperturbed Hamiltonian or to the unperturbed Hamilton function) in atomic units:

$$V_{eff} = [F_0^2 / (2\omega^2)^2] (1 - 3\cos^2 \theta) / r^3 \quad (15)$$

Here  $r$  and  $\theta$  are the absolute value of the radius-vector and the polar angle of the atomic electron, respectively; the  $z$ -axis being parallel to the laser field  $F$ .

This effective potential has several remarkable properties. First, it is mathematically equivalent to the effective potential for the motion of a satellite around an oblate planet (such as, e.g., the Earth) e.g., book (Beletsky, 2001). In other words, the atomic problem under consideration has the celestial analogy.

Second, any physical system described by this potential has higher than geometrical (i.e., algebraic) symmetry. While the geometrical symmetry is axial, the actual symmetry is spherical. Indeed, from the geometrical (axial) symmetry of this potential follows that only the projection  $M_z$  (but not the square  $M^2$ ) of the angular momentum is conserved. However, it turned out that  $M^2$  is also conserved—just like for the spherical symmetry. Due to this fact, the effect of this potential on the energy of the system can be calculated using the simpler, “non-degenerate” version of the PT instead of the more complicated, “degenerate” version of the PT.

As a result, the following quantum correction to the unperturbed energy has been obtained book (Oks, 2019) where  $n$ ,  $l$ , and  $m$  are the spherical quantum numbers,  $|m| \leq l \leq (n-1)$ :

$$\Delta E_{nlm} = F_0^2 / (2\omega)^2 + (F_0^2 / \omega^4) [3m^2 - l(l+1)] / [n^3 (2l+3)(l+1)(2l-1)] \quad (16)$$

for  $l > 0$  and:

$$\Delta E_{n00} = F_0^2 / (2\omega)^2 + F_0^2 / (3n^3 \omega^4) \quad (17)$$

For  $l = 0$ . The maximum value  $\max(\Delta E_{nlm}) = \Delta E_{n00}$ . For  $\omega \ll 1/n^{3/2}$ , one has:

$$\max(\Delta E_{n/m}) \approx F_0^2 / (3n^3 \omega^4) \quad (18)$$

It should be noted that for  $n \gg 1$ , the condition (14) yields  $\omega \gg 1/n^3$  so that there is a large range of laser frequencies  $1/n^3 \ll \omega \ll 1/n^{3/2}$ , for which Eq. (18) is valid.

So, for the validity of Eqs. (16-17) it is required (according to Eq. 1):

$$\max(\Delta E_{nlm}) \approx F_0^2 / (3n^3 \omega^4) \ll 1/n^3 \quad (19)$$

So that:

$$F_0 \ll F_{0,quant} \sim \omega^2 \quad (20)$$

where,  $F_{0,quant}$  is the quantum critical value of the laser field amplitude. In the classical study of the same system book (Oks, 2019); there was obtained:

$$\Delta E(J_1, J_2, J_3) = [F_0^2 / (8\omega^4)] (3J_3^2 - J_2^2) / (J_1^3 J_2^5) \quad (21)$$

Here the notations are the same as in the sect. 21 of the book (Poincaré and Magini, 1899), namely:

$$J_1 = J_r + J_\theta + J_\omega, \quad J_2 = J_\theta + J_\omega, \quad J_3 = J_\omega \quad (22)$$

where,  $J_r$ ,  $J_\theta$ , and  $J_\omega$  are the action variables corresponding to the  $r$ -,  $\theta$ - and  $\varphi$ -motions, respectively ( $|J_3| \leq J_2 \leq J_1$ ,  $J_2 > 0$ ). The validity condition (2) takes the form:

$$|\Delta E| \leq \Delta E_{max} = \Delta E(J_1, 1, 0) = F_0^2 / (4\omega^4 J_1^3) \ll 1 / (2J_1^2) \quad (23)$$

Leading to the requirement:

$$F_0 \ll J_1^{1/2} \omega^2 \quad (24)$$

The action variable  $J_1$  is the classical counterpart of the principal quantum number  $n$  so that it can be substituted by  $n$  in Eq. (24) and the validity range becomes:

$$F_0 \ll F_{0,class} \sim n^{1/2} \omega^2 \quad (25)$$

The ratio of the classical  $F_{0,class}$ , and quantum  $F_{0,quant}$  values of the critical amplitudes of the laser field is:

$$F_{0,class} / F_{0,quant} \sim n^{1/2} \quad (26)$$

Since the energy density of the laser field  $\varepsilon$  is  $F_0^2 / (8\pi)$ , then the ratio of the corresponding critical energy densities is:

$$\varepsilon_{class} / \varepsilon_{quant} \sim (F_{0,class} / F_{0,quant})^2 \sim n \quad (27)$$

Thus, for Rydberg states ( $n \gg 1$ ), the validity range of the classical energy correction is indeed by orders of magnitude broader than the validity range of the quantum energy correction.

## Conclusion

We pointed out that for Rydberg (i.e., highly-excited) states of atomic systems, for a given analytical method, its classical version has a much broader range of validity than the corresponding quantum version. We illustrated this fact with two examples.

The first example is the Stark effect in hydrogen atoms. We showed that the ratio of the classical  $F_{class}$  and quantum  $F_{quant}$  values of the critical electric fields is  $F_{class} / F_{quant} \sim n \gg 1$ .

The second example is hydrogen atoms in the field of high-frequency laser radiation. We demonstrated that the ratio of the corresponding critical energy densities is  $\epsilon_{\text{class}}/\epsilon_{\text{quant}} \sim n \gg 1$ .

Thus, for Rydberg states ( $n \gg 1$ ), the validity range of the classical analytical methods is indeed by orders of magnitude wider than the validity range of the quantum analytical methods. The advantage of classical approximate analytical methods for studying Rydberg states over the quantum counterparts is a counterintuitive result.

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## Ethics

There are no ethical issues implied by the described research.

## Conflict of Interest

The author declares no conflict of interest.

## Data Availability

All data is included in the paper.

## References

- Beletsky, V. V. (2001). *Essays on the Motion of Celestial Bodies* (1<sup>st</sup> Ed.). Springer Science & Business Media. ISBN-10: 9783764358662.
- Berera, A., & Del Debbio, L. (2021). *Quantum Mechanics*. Cambridge University Press, pp. 500. ISBN-10: 9780486784557.
- Bertlmann, R., & Friis, N. (2023). *Modern Quantum Theory: From Quantum Mechanics to Entanglement and Quantum Information* (1<sup>st</sup> Ed.). Oxford University Press. ISBN-10: 9780191506345.
- Born, M. (1925). Systeme mit einem Leuchtelektron. In *Vorlesungen über Atommechanik* (1<sup>st</sup> Ed., Vol. 2, pp. 148–281). Springer Berlin Heidelberg. [https://doi.org/10.1007/978-3-642-61898-7\\_4](https://doi.org/10.1007/978-3-642-61898-7_4)
- Cohen, S. R., & Thompson, J. D. (2021). Quantum Computing with Circular Rydberg Atoms. *PRX Quantum*, 2(3), 030322. <https://doi.org/10.1103/prxquantum.2.030322>
- Cohen-Tannoudji, C., Diu, B., & Laloë, F. (2020). *Quantum Mechanics Volume 1* (1<sup>st</sup> Ed., Vol. 1). Hermann. ISBN-10: 9782705683924.
- Cong, I., Levine, H., Keesling, A., Bluvstein, D., Wang, S.-T., & Lukin, M. D. (2022). Hardware-Efficient, Fault-Tolerant Quantum Computation with Rydberg Atoms. *Physical Review X*, 12(2), 021049. <https://doi.org/10.1103/physrevx.12.021049>
- Ebadi, S., Keesling, A., Cain, M., Wang, T. T., Levine, H., Bluvstein, D., Semeghini, G., Omran, A., Liu, J. G., Samajdar, R., Luo, X. Z., Nash, B., Gao, X., Barak, B., Farhi, E., Sachdev, S., Gemelke, N., Zhou, L., Choi, S., ... Lukin, M. D. (2022). Quantum optimization of maximum independent set using Rydberg atom arrays. *Science*, 376(6598), 1209–1215. <https://doi.org/10.1126/science.abo6587>
- Galitski, V., Karnakov, B., & Kogan, V. (2013). *Exploring Quantum Mechanics: A Collection of 700+ Solved Problems for Students, Lecturers, and Researchers* (1<sup>st</sup> Ed.). Oxford University Press. <https://doi.org/10.1093/acprof:oso/9780199232710.001.0001>
- Griffiths, D. J., & Schroeter, D. F. (2018). *Introduction to quantum mechanics*. ISBN-10: 9781118723258.
- Landau, L. D., & Lifshitz, E. M. (1960). *Mechanics: Volume 1* (1<sup>st</sup> ed., Vol. 1). Butterworth-Heinemann, 1976. ISBN-10: 9780750628969.
- Landau, L. D., Lifshitz, E. M., & E. M. (1965). *Quantum Mechanics*. Pergamon. ISBN-10: 9780486784557.
- Larkoski, A. J. (2023). *Quantum Mechanics: A Mathematical Introduction*. Cambridge University Press. ISBN-10: 9781118723258.
- McIntyre, D. H. (2023). *Quantum Mechanics: A Paradigms Approach*. Cambridge University Press. [https://physicscourses.colorado.edu/phys3220/phys3220\\_fa16/qmerrata16-2.pdf](https://physicscourses.colorado.edu/phys3220/phys3220_fa16/qmerrata16-2.pdf)
- Nastase, H. (2022). *Quantum Mechanics: A Graduate Course* (1<sup>st</sup> Ed.). Cambridge University Press. ISBN-10: 9781108985062.
- Nguyen, M.-T., Liu, J.-G., Wurtz, J., Lukin, M. D., Wang, S.-T., & Pichler, H. (2023). Quantum Optimization with Arbitrary Connectivity Using Rydberg Atom Arrays. *PRX Quantum*, 4(1), 010316. <https://doi.org/10.1103/PRXQuantum.4.010316>
- Oks, E. (2019). *Analytical Advances in Quantum and Celestial Mechanics* (2<sup>nd</sup> Ed.). IOP Publishing. <https://doi.org/10.1088/2053-2563/ab3db0>
- Poincaré, H., & Magini, R. (1899). Les méthodes nouvelles de la mécanique céleste. *Il Nuovo Cimento*, 10(1), 128–130. <https://doi.org/10.1007/bf02742713>
- Robicheaux, F., Hernández, J. V., Topçu, T., & Noordam, L. D. (2004). Simulation of coherent interactions between Rydberg atoms. *Physical Review A*, 70(4), 042703. <https://doi.org/10.1103/PhysRevA.70.042703>
- Townsend, J. S. (2012). *A modern approach to quantum mechanics* (Vol. 2). University Science Books. ISBN-10: 1891389130.
- Weinberg, S. (2015). *Lectures on quantum mechanics*. Cambridge University Press. ISBN-10: 9780486417134.
- Zettili, N. (2009). *Quantum mechanics: concepts and applications* (2<sup>nd</sup> Ed.). John Wiley & Sons, 2009. ISBN-10: 9780470026786.
- Zwiebach, B. (2022). *Mastering Quantum Mechanics: Essentials, Theory and Applications*. MIT Press. ISBN-10: 9780262046138.