

# Perturbation Theory: Hydrogen and Alkali Atoms in Constant E-Field

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## Abstract

Perturbation has been widely used as a tool to approximate complex quantum systems that are slight deviations from well-known systems. Among many widely studied potentials, one perturbation is the effect of applying an electric field onto an atom known as the Stark effect. This paper contributes a qualitative summary of the graphical solution of the linear Stark effect in Hydrogen atoms of  $n=2$ .

## 1 Introduction

In quantum mechanics, perturbation theory is widely used as a tool of approximation for the wave functions and energies of systems with perturbed Hamiltonians that deviate slightly from a well-known Hamiltonian. This allows researchers to understand complex quantum systems that were once considered unsolvable. Broadly, perturbation theory is separated by the wavefunction and the Hamiltonian. First, considering the wavefunction, the theory is branched into nondegenerate perturbation theory and degenerate perturbation theory (1).. Nondegenerate perturbation theory deals with the nondegenerate parts of the Hamiltonian matrix, which include energy eigenstates have distinct eigenvalues. On the contrary, degenerate perturbation theory deals with the degenerate parts, which include independent energy eigenstates sharing the same eigenvalue. The goal for both is to derive the corrections of the energy and wavefunction to a certain order (2). In particular, this paper mainly focuses on the first two orders, but generalization from the first few orders follows the same procedure.

Alternatively, considering the Hamiltonian, perturbation theory is branched into time-independent and time-dependent perturbations. The time-independent theory deals with constant potentials whereas the time-dependent theory deals with varying potentials with respect to time. The focus for this paper is to explore theory and applications for time-independent potentials.

One of the first-studied constant potentials using perturbation theory is the affect of applying a constant electric field to an atom. This influences an atom's polarization, its charge distribution, and separates their spectral lines. More commonly, the phenomenon is named the Stark Effect. This paper aims at discussing the linear Stark Effect for hydrogen and alkali atoms. Concretely, it derives the basic magnitude of effect up to  $n=2$  in the hydrogen atom and then explore the qualitative features of the graphical solution.

With the development of the perturbation theory, many properties of complex systems can be calculated more precisely. For instance, the energy of the Hydrogen atom can be studied with many orders of accuracy, including corrections from its fine structure, the lamb shift, and hyperfine splitting. Even with the advent of numerical solutions to quantum systems using modern computational power, perturbation theory still remains a relevant method as it greatly simplifies computational complexity.

## **2 Time-Independent Perturbation Theory**

Time-dependent perturbation theory deals with time-independent Shroedinger equations and the resepective corrections of the energy eigenvalues and eigenkets. Two major formulations are the Rayleigh-Schrodinger (RS) and Brillouin-Wigner (BW) theories. This paper uses the RS formulation to derive the explicit expression for the first and second-order corrections of the perturbed states.

## 2.1 Nondegenerate Perturbation Theory

This section follows the derivation in (1). We start with setting up the known unperturbed state as

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad (1)$$

The 0 in the superscripts show their unperturbed identity. Also, this unperturbed state should have well known solutions that spans a complete set of eigenkets orthogonal to each other:

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{mn} \quad (2)$$

Then, the perturbed hamiltonian is written as the following:

$$H = H^0 + \delta H \quad (3)$$

and we formally define  $\delta H = \lambda H'$  with  $\lambda$  ranging from 0 to 1 representing a small perturbation. Then, we solve the Shrodinger equation of the perturbed hamiltonian starting with expanding both the perturbed energy and wavefunction as a power series dependent of  $\lambda$ ,

$$\psi_n = \sum_i \lambda^i \psi_n^i \quad (4)$$

$$E_n = \sum_i \lambda^i E_n^i \quad (5)$$

The perturbed Shrodinger equation then turns into,

$$(H^0 + \lambda H') \left( \sum_i \lambda^i \psi_n^i \right) = \sum_i (\lambda^i E_n^i) \left( \sum_i \lambda^i \psi_n^i \right) \quad (6)$$

Combining like terms of each power of  $\lambda$  and equating the coefficients, we can obtain the following equations for the first and second-order respectively,

$$\lambda = 1 : \quad (H^0 - E_n^0) \psi_n^1 = (H' - E_n^1) \psi_n^0 \quad (7)$$

$$\lambda = 2 : \quad (H^0 - E_n^0)\psi_n^2 = (H' - E_n^1)\psi_n^1 + E_n^2\psi_n^0 \quad (8)$$

For the first order energy correction, we take the inner product of  $\psi_n^0$  and equation (7) to obtain

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (9)$$

The above step skipped simplifying the inner product using the hermiticity of  $H^0$  and that  $\langle \psi_n^0 | \psi_n^0 \rangle = 1$  according to equation (1). Next, to obtain the correction for the wavefunction, we utilize the completeness of the unperturbed energy eigenstates. Thus,  $\psi_n^1$  can be re-expressed using the unperturbed energy states as bases,

$$\psi_n^1 = \sum_{m \neq n} \langle \psi_m^0 | \psi_n^1 \rangle \psi_m^0 \quad (10)$$

The  $m = n$  term here is omitted to ensure normalization. Concretely, to guarantee normality to the first order, we have

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + \lambda(\langle \psi_n^0 | \psi_n^1 \rangle + \langle \psi_n^1 | \psi_n^0 \rangle) = 1.$$

Since the first term already evaluates to 1, we must have  $\langle \psi_n^0 | \psi_n^1 \rangle = 0$ . Hence, omitting the  $m = n$  term by choice directly secures normalization of the perturbed wavefunction.

To find the coefficients of  $\psi_n^0$ , the inner product of  $\psi_m^0$  and equation (7) is used. This simplifies into

$$\langle \psi_m^0 | \psi_n^1 \rangle = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}. \quad (11)$$

Plugging equation (11) into equation (10), we gain the final result,

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0. \quad (12)$$

The same procedure can be applied to the second-order corrections as well. For

simplicity, here we only directly quote the second-order energy correction.

$$E_n^2 = \psi_n^1 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}. \quad (13)$$

Furthermore, this process can continue indefinitely, but the current paper only requires the first two orders.

## 2.2 Degenerate Perturbation Theory

Degeneracies emerge in many systems with symmetry such as the hydrogen atom, where multiple orthonormal energy eigenstates refer to the same eigenvalue. This causes the results derived in equation (12) and (13) take on a denominator of 0. In the case of a non-zero numerator, the equations give infinity, clearly showing a discontinuity between the unperturbed and perturbed eigenstates. The problem stems from arbitrarily choosing energy eigenstates as the basis in nondegenerate perturbation theory. These eigenstates are likely not the proper bases to determine higher-order corrections. In particular, suppose there is a N-fold degeneracy in a system with a hamiltonian  $H^0$ . The degenerate eigenstates are all linearly independent, and each eigenstate refers to the same energy. We choose from these eigenstates a set of N eigenstates  $\psi_k$  as the basis: This subsection generalizes the derivation given in (1).

$$H^0 \psi_k^0 = E^0 \psi_k^0. \quad (14)$$

Then, it can be shown that any linear combination of the N eigenstates

$$\psi^0 = \sum_{k=1}^n \alpha_k \psi_k^0 \quad (15)$$

also results in a degenerate eigenstate with the same eigenvalue by plugging this back into (14),

$$H^0 \sum_{k=1}^n \alpha_k \psi_k^0 = \sum_{k=1}^n \alpha_k E_0 \psi_k^0 = E_0 \sum_{k=1}^n \alpha_k \psi_k^0. \quad (16)$$

Hence, if we arbitrarily select  $N$  degenerate unperturbed eigenstates out of the infinite possibilities, they are unlikely to be the correct linear combinations that the perturbation will select. A serious issue with this is now we do not know the correct unperturbed wavefunction to plug in (9) and thus cannot find the first-order energy correction. Therefore, we must seek a set of good basis that corresponds to the correct linear combinations in the unperturbed system. Starting with 14, we add the common orthogonality condition,

$$\langle \psi_k^0 | \psi_n^0 \rangle = \delta_{kn}. \quad (17)$$

As the perturbation is turned on, we following the same process of expanding both the energy and wavefunction in terms of  $\lambda$  and plug them in the Shrodinger equation. This gains a similar result to equation (6),

$$(H^0 + \lambda H') \left( \sum_i \lambda^i \psi_k^i \right) = \sum_i (\lambda^i E_k^i) \left( \sum_i \lambda^i \psi_k^i \right). \quad (18)$$

It should be noted that  $E_k^0$  are the same for all  $N$  eigenstates because of the degeneracy. Furthermore, combining like terms, we gain a similar expression to equation (6) and (7) for the first and second order.

$$\lambda = 1 : \quad (H^0 - E_k^0) \psi_k^1 = (H' - E_k^1) \psi_k^0 \quad (19)$$

$$\lambda = 2 : \quad (H^0 - E_k^0) \psi_k^2 = (H' - E_k^1) \psi_k^1 + E_k^2 \psi_k^0 \quad (20)$$

Taking the inner product of  $\psi_n^0$  and equation (18), we can simplify using the fact that  $\langle \psi_n^0 | H^0 \rangle = 0$  because of  $H^0$ 's hermiticity,

$$\langle \psi_n^0 | H' | \psi_k^0 \rangle = E_k^1 \delta_{nk}. \quad (21)$$

This shows that the good basis should be chosen such that the perturbed hamiltonian matrix  $H'$  is diagonalized. Once we have obtained the good basis, the normal procedure of nondegenerate perturbation theory can be followed. However, there is one hidden assumption under this derivation. That is, the degeneracy must be lifted under perturbation. If the degeneracy is not lifted, the second order equation as in equation (19) need to be considered.

Alternatively, there is another way to find the energy corrections. We use once again the N-fold degeneracy setup in equation (13).

Instead of plugging in one basis into (18), we now plug in the general linear combination of the basis as shown in (14). Following the same procedure of taking the inner product, we get

$$\langle \psi_n^0 | H' | \psi^0 \rangle = E^1 \langle \psi_n^0 | \psi^0 \rangle. \quad (22)$$

Expanding  $\psi^0$  as a linear sum of the basis,

$$\sum_{k=1}^N \alpha_k \langle \psi_n^0 | H' | \psi_k^0 \rangle = \sum_{k=1}^N E^1 \alpha_k \delta_{kn} \quad (23)$$

$$= E^1 \alpha_n \quad (24)$$

The expectation value term is known since it is simply elements of the  $H'$  matrix with the arbitrary basis  $\psi_k^0$ . It is also convenient to define  $[H']_{kn} \equiv \langle \psi_n^0 | H' | \psi_k^0 \rangle$ . Then, we can do the inner product of every basis with equation(23) and get the following,

$$\sum_{k=1}^N ([H']_{lk} \alpha_k - E_n^1 \delta_{lk} \alpha_k) = 0. \quad (25)$$

This represents matrix multiplications, and it states that we need to find the eigenvalues and eigenstates for the  $[H']$  matrix, which is defined as  $[H']_{nk} = \langle \psi_n^0 | H' | \psi_k^0 \rangle$ . It should be noted that the size of this matrix is smaller than the complete Hilbert space containing all nondegenerate and degenerate eigenstates. Specifically, it only spans the degenerate subspace in context.

### 3 The Stark Effect

The stark effect applies time-independent perturbations to atoms experiencing a constant electric field. This section aims at solving the linear and quadratic stark effects explicitly for hydrogen and alkali atoms. Furthermore, it is going to use lithium as an example to explain the qualitative aspects of the stark effect. This section follows the derivation in (3). The unperturbed system of a hydrogen atom has the coulomb potential of

$$V^0(r) = -\frac{e^2}{r} \quad (26)$$

where  $e$  is the magnitude of the electron charge and  $r$  its distance from the nucleus. The total unperturbed hamiltonian is therefore

$$H^0 = \frac{p^2}{2m} - \frac{e^2}{r}. \quad (27)$$

For a uniform electric field in the  $z$  direction  $\mathbf{E} = E\mathbf{z}$ , the potential is

$$H' = -eEz. \quad (28)$$

This single-direction potential breaks the original rotational symmetry of the hydrogen atom with potential dependent only of  $r$ . Hence, as the perturbation is turned on, the original degenerate states will be split.



### 3.1 Linear Stark Effect in Nondegenerate states

The power of symmetry is often exploited in deriving expressions in the context of the stark effect. Assuming the unperturbed Hamiltonian commutes with the parity operator, or

$$[\pi, H^0] = 0, \quad (29)$$

it can be shown that no linear stark effect, or first order corrections, exists.

First we define the dipole moment operator as

$$\mathbf{P} = q\mathbf{x} \quad (30)$$

where  $q$  is the magnitude of the particle's charge and  $\mathbf{x}$  the position operator. Thus,

$$\langle \mathbf{P} \rangle = -e \langle \psi | \mathbf{x} | \psi \rangle. \quad (31)$$

in this case. Then, applying the results of time-independent perturbation theory, the first-order energy shift is given by

$$E^1 = \langle \psi | eEz | \psi \rangle = -\langle \mathbf{P} \rangle \cdot \mathbf{E}, \quad (32)$$

Hence, if there is no electric dipole moment, no linear stark effect exists. Furthermore, suppose  $\psi_n$  is a nondegenerate energy eigenstate of  $H^0$ . Then, according to equation (29),  $\psi_n$  must also be an eigenstate of the parity operator. Utilizing the fact that  $\pi\psi = \psi$ , we get

$$\pi\psi = \pm\psi, \quad (33)$$

showing that  $\psi$  is either odd or even. As a result,

$$\langle \mathbf{P} \rangle = -e \langle \psi | \mathbf{x} | \psi \rangle = 0. \quad (34)$$

Therefore, there is no electric dipole moment hence no linear stark effect in the first order for nondegenerate states in general as long as equation (29) holds. This also immediately means that there is no linear stark effect for the ground state of hydrogen or alkali atoms.

### 3.2 Linear Stark Effect in Excited States

#### 3.2.1 Alkali Atoms

Although alkali atoms can be modeled as a single-electron atom, it has different properties with the hydrogen atom. This subsection follows the derivation in (3). For example, the hydrogen atom has  $n^2$  degeneracies whereas alkali atoms have  $(2n+1)$ . This in turn causes there to be no linear stark effect in excited states of alkali atoms.

First, the energy level in an alkali atom is determined by two quantum numbers:  $n$  and  $l$ . Then, using equation (25), we need to compute the matrix elements of  $H'$ , or in this case

$$\langle nlm | eEz | nlm' \rangle \quad (35)$$

Here,  $n$  and  $l$  are fixed and only  $m$  and  $m'$  can change. The critical value is  $l$ , which determines the parity of the eigenstate given by the expression  $(-1)^l$ . The result is general for central potentials. Since both sides of equation (35) will have the same parity, it yields a result of 0 since  $z$  is odd. Thus, no linear Stark effect exists in alkali atoms.

#### 3.2.2 Hydrogen Atoms

Since hydrogen atoms are  $n^2$ -fold degenerate, they generate different results compared to alkali atoms in the first order corrections. In particular, now we need to compute the matrix

$$\langle nlm | eEz | nl'm' \rangle \quad (36)$$

and  $l$  is unfixed. After computing the integrals, it is seen that only  $\langle 200 | eEz | 210 \rangle$  and its conjugate  $\langle 210 | eEz | 200 \rangle$  yields a nonzero result, with

$$\langle 200 | eEz | 210 \rangle = -3a_0eE. \quad (37)$$

Solving the matrix equation as given in equation (25) shows that the eigenvalues are 0, 0, 1, -1, meaning a first order correction of energy of  $E_2$ ,  $E_2 + 3a_0eE$ , and  $E_2 - 3a_0eE$ . The corresponding good linear combinations are in turn,  $\psi_{211}$ ,  $\psi_{21-1}$ ,  $\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$ , and  $\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$  respectively. This shows that two of the original degenerate states are actually not lifted in the first order correction due to the perturbation.

### 3.2.3 Qualitative Understanding of the n=2 result

In the degenerate perturbation theory section, the result is to find a good set of basis so that the  $H'$  matrix in the degenerate subspace is diagonalized. This is exactly what the  $\frac{1}{\sqrt{2}}$  is as it corresponds to the coefficients  $\alpha_k$  in equation (15). Furthermore, features of the actual change of the electron's probability distribution can be gathered solely from knowing this linear combination.

First, since the quantum number  $l$  is 1 and 0 for the two lifted states, they have opposing parity. The  $\frac{1}{\sqrt{2}}$  coefficient also signals equal probabilities for  $\psi_{200}$  and  $\psi_{210}$ .

For the state  $\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$ , since the two eigenstates are directly added, it is shifted down in the z-axis. The opposite happens for the state  $\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$  as the relative phase difference for the two functions are now shifted for  $\pi$  radians, causing the total wavefunction to move up in the +z-direction. Furthermore, initially,  $\psi_{200}$  is rotationally symmetric while  $\psi_{210}$  is only rotationally symmetric in the z-axis. As a result, the combined function will still have rotational symmetry along the z-axis. In the work of (4), it shows simulated version of the resulting probability distribution for the two lifted states as shown in fig 1. Although such a simulation does not show the time evolution, it demonstrates many properties as described.

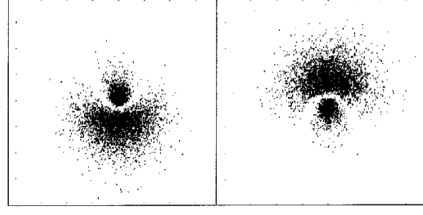


Figure 1: Fig. 1. Left:  $\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$ ; Right:  $\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$ . Adapted from (4)

## 4 Conclusion

By looking at the recurring methods applied to derive results in perturbation theory, it is possible to understand more about the qualitative aspects of the perturbed system using ideas such as rotational and parity symmetry and projecting higher order corrections to lower order subspaces. This paper starts with constructing the basic principles of time-independent perturbations and the linear Stark effect in both hydrogen and alkali atoms. From that, it analyzes the influence of a constant electric field on the  $n=2$  state of the hydrogen atom and compares it with the results from a simulation. Henceforth, certain qualitative features about the lifted energy eigenstates are summarized.

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