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Research Article

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Time-Independent Perturbation Theory: Degeneracy Lifted to the Second Order

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Abstract

Although the fundamental principles of time-independent perturbation theory are well-established and widely applied, the case of degeneracy lifted at second order is seldom addressed explicitly in standard texts. This work fills this gap by presenting a systematic derivation of time-independent perturbation theory that accounts for the added complexity introduced by non-trivial degeneracies. We provide a general procedure and corresponding formulae for calculating state and energy corrections to any order, with degeneracy lifted to the second order. Additionally, we apply these formulae to solve a prototype problem of a dressed quark system. This work not only advances the theoretical framework but also provides practical tools for tackling complex problems in quantum physics.

Introduction

Time-independent perturbation theory, formulated within the Hamiltonian framework is a cornerstone of quantum mechanics. It has been widely used to address a variety of physical problems, ranging from atomic phenomena such as the Zeeman and Stark effects[1] to the analysis of chemical bonding and rotational–vibrational corrections in molecular physics[2]. The basic idea is to start with a simple system for which the exact solution is known and add a term representing a perturbation to the Hamiltonian. Assuming that the perturbation is small, the eigenvalues and eigenstates of the perturbed system can be expressed as asymptotic series, in which "corrections" to those of the unperturbed simple system are expanded order by order. The complicated system can therefore be studied based on knowledge of the simpler one. If the eigenvalues of the unperturbed system are degenerate, the arbitrariness in the choice of the basis within the degenerate subspace makes the naive first-order energy correction ill-defined. In such cases, standard perturbation theory must be reformulated to properly resolve the degeneracy.

It is worth noting that a variety of perturbative methods have been developed to address specific physical problems with degeneracies. In molecular spectroscopy, the contact transformation formalism—closely related to canonical Van Vleck perturbation theory[3,4]—has been widely used in the treatment of rotation–vibration energies of polyatomic molecules[5–10]. These approaches rely on near-identity unitary (canonical) transformations to eliminate interactions order by order in the perturbation parameter and to construct an effective Hamiltonian within a selected subspace. While the formalism can, in principle, be extended to arbitrary order within a recursive canonical-transformation framework, the algebraic complexity increases rapidly at higher orders. In practice, applications to vibrationally excited polyatomic molecules have been carried out up to fourth order in several studies[11,12].

In this work, we present a systematic and comprehensive derivation of time-independent perturbation theory, offering a unified treatment that extends existing works. We address the non-degenerate case, the degenerate case with degeneracy lifted to the first order, and, crucially, the degenerate case with degeneracy lifted to the second order. While time-independent perturbation theory is discussed in various quantum mechanics textbooks, providing methods for the first two cases[1,13] and introducing elementary theory for the degenerate cases[14], our derivations go further. Notably, prior work presents an insightful derivation for the second-order degenerate case under the special condition of completely unbroken first-order degeneracy and in the lowest orders[15]. Our work extends this by generalizing the second-order degenerate case to encompass a broader range of scenarios, providing a systematic and complete derivation that is valid for all orders, thereby contributing to a more comprehensive development of the subject.

Perturbation Theory of a Non-Degenerate System

Suppose that the problem Hamiltonian can be written as a summation of an unperturbed Hamiltonian H_0 and a perturbation $\lambda\delta H$. The exact solution of the Time-Independent Schrödinger Equation (TISE) with H_0 is known,

$$H_0 \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle , \quad n = 1, 2, \dots, N , \tag{1}$$

where $\left|\psi_n^{(0)}\right\rangle$ the n-th normalized eigenstate with eigenvalue $E_n^{(0)}$, with N the dimension of the problem space. Here, we consider a non-degenerate system, which means that

$$E_n^{(0)} \neq E_m^{(0)} , \quad \text{for } n \neq m . \tag{2}$$

The perturbed TISE for the n-th eigenstate becomes

$$(H_0 + \lambda\delta H) \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle . \tag{3}$$

At $\lambda = 0$, we recover the unperturbed problem as in Equation 1. We can then expect the solution to the problem to depend on λ, with the limiting case recovering the original solution as $\lambda \to 0$.

We expand the eigenvalues and eigenstates as a power series in λ*:

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \mathcal{O}(\lambda^3) = \sum_{i=0}^{\infty} E_n^{(i)}\lambda^i \ , \tag{4a}$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle\,\lambda + |\psi_n^{(2)}\rangle\,\lambda^2 + \mathcal{O}(\lambda^3) = \sum_{i=0}^{\infty} |\psi_n^{(i)}\rangle\,\lambda^i \ . \tag{4b}$$

Here and throughout the paper, we use the upper index with parenthesis "(i)" to indicate that the quantity is of the i-th order in λ. We impose a condition that all the state corrections contain no vector along the unperturbed state, without loss of generality[15],

$$\langle\psi_n^{(0)}|\psi_n^{(i)}\rangle = \delta_{i,0}\,, \quad i = 0,1,2,\dots \ , \tag{5}$$

and it follows from Equation 4b that $\langle\psi_n^{(0)}|\psi_n\rangle = 1$.

Putting Equations 4b and 4a back to Equation 3, we get

$$H_0\,|\psi_n^{(0)}\rangle + \sum_{i=1}^{\infty}\left[H_0\,|\psi_n^{(i)}\rangle + \delta H\,|\psi_n^{(i-1)}\rangle\right]\lambda^i = E_n^{(0)}\,|\psi_n^{(0)}\rangle + \sum_{i=1}^{\infty}\lambda^i\sum_{j=0}^{i} E_n^{(j)}\,|\psi_n^{(i-j)}\rangle \ . \tag{6}$$

The equation holds only if it is satisfied at each order of λ. Therefore, we have,

$$H_0\,|\psi_n^{(0)}\rangle = E_n^{(0)}\,|\psi_n^{(0)}\rangle \ , \tag{7}$$

at $i = 0$, and

$$H_0\,|\psi_n^{(i)}\rangle + \delta H\,|\psi_n^{(i-1)}\rangle - \sum_{j=0}^{i} E_n^{(j)}\,|\psi_n^{(i-j)}\rangle = 0 \ , \tag{8}$$

for $i = 1, 2, \dots$, from which one can solve for the perturbed wavefunction and energy.

The First Order Correction

To obtain first order correction to the eigenvalue $E_n^{(1)}$, we project Equation 8 with index $i = 1$ on the eigenstate $\langle\psi_n^{(0)}|$,

$$\langle\psi_n^{(0)}|H_0|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\delta H|\psi_n^{(0)}\rangle - E_n^{(0)}\,\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle - E_n^{(1)}\,\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 0 \ . \tag{9}$$

The first and third terms cancel out and we end up with,

$$E_n^{(1)} = \langle\psi_n^{(0)}|\delta H|\psi_n^{(0)}\rangle \ . \tag{10}$$

It means that the diagonal matrix elements of δH gives the 1st order energy correction, as illustrated in Figure 1. Let us define $\delta H_{m,n} \equiv \langle\psi_m^{(0)}|\delta H|\psi_n^{(0)}\rangle$. To obtain the first order correction to the eigenstate, we write the first order correction in terms of the unperturbed basis states,

$$|\psi_n^{(1)}\rangle = \sum_m |\psi_m^{(0)}\rangle\,\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = \sum_{m\neq n} c_m^{(n)(1)}\,|\psi_m^{(0)}\rangle \ , \tag{11}$$

in which we have applied the condition in Equation 5. To find the coefficients $c_m^{(n)(1)}$, we project Equation 8 with index $i = 1$ on the eigenstate $\langle\psi_m^{(0)}|$ where $m \neq n$,

$$\langle\psi_m^{(0)}|H_0|\psi_n^{(1)}\rangle + \langle\psi_m^{(0)}|\delta H|\psi_n^{(0)}\rangle - E_n^{(0)}\,\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle - E_n^{(1)}\,\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = 0 \ . \tag{12}$$

* Here and throughout the paper, we assume that the relevant eigenvalues and eigenstates admit an analytic continuation in λ in a neighborhood of $\lambda = 0$. In exceptional cases (e.g., in the presence of intruder states), such a continuation may fail to exist.

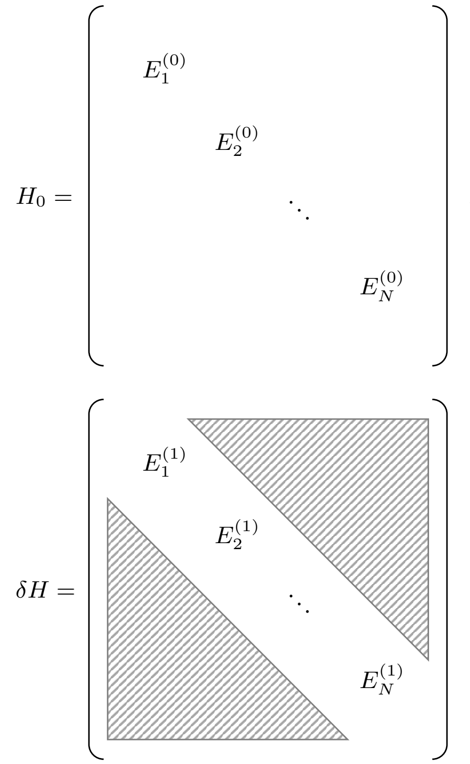

Figure 1. Matrix representations of the Hamiltonian operator H_0 and δH in the unperturbed basis for a non-degenerate system. The diagonal matrix elements of the perturbation δH gives the first order energy correction.

The last term vanishes by orthogonality,

$$c_m^{(n)(1)}(E_m^{(0)} - E_n^{(0)}) = -\,\langle\psi_m^0|\delta H|\psi_n^0\rangle \,. \tag{13}$$

For non-degenerate systems, it follows that

$$c_m^{(n)(1)} = -\frac{\delta H_{m,n}}{E_m^{(0)} - E_n^{(0)}} \ . \tag{14}$$

Higher Order Correction

We can generalize the aforementioned procedure for higher order corrections, for which we obtain a recursive relation. We first find the corrections to the energy by projecting Equation 8 to $|\psi_n^{(0)}\rangle$,

$$\langle\psi_n^{(0)}|H_0|\psi_n^{(i)}\rangle + \langle\psi_n^{(0)}|\delta H|\psi_n^{(i-1)}\rangle - \sum_{j=1}^{i-1} E_n^{(j)}\,\langle\psi_n^{(0)}|\psi_n^{(i-j)}\rangle - E_n^{(0)}\,\langle\psi_n^{(0)}|\psi_n^{(i)}\rangle = E_n^{(i)}\,\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle \ , \tag{15}$$

The first and forth terms cancel out by seeing that $|\psi_n^{(0)}\rangle$ is the eigenstate of H_0 with eigenvalue $E_n^{(0)}$. The third term vanishes by orthogonality. We therefore have

$$E_n^{(i)} = \langle\psi_n^{(0)}|\delta H|\psi_n^{(i-1)}\rangle\,, \qquad i = 1, 2, \dots \ . \tag{16}$$

This means that the i-th order energy correction can be determined by knowing the $(i-1)$-th order state correction. In particular, the second order correction is

$$E_n^{(2)} = \sum_{m\neq n}\frac{|\delta H_{m,n}|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{17}$$

Now, we expand the i-th order eigenstates in terms of the unperturbed basis states,

$$|\psi_n^{(i)}\rangle = \sum_m c_m^{(n)(i)}\,|\psi_m^{(0)}\rangle \ . \tag{18}$$

The orthonormal condition of the unperturbed states gives $c_m^{(n)(0)} = \delta_{m,n}$ and the condition of the state correction given by Equation 5 can be written as $c_n^{(n)(i)} = 0$ when $i \geq 1$.

We project Equation 8 on the eigenstate $\langle \psi_k^{(0)} |$ with $k \neq n$,

$$c_k^{(n)(i)}(E_k^{(0)} - E_n^{(0)}) + \sum_m c_m^{(n)(i-1)} \langle \psi_k^{(0)} | \delta H | \psi_m^{(0)} \rangle - \sum_{j=1}^{i-1} E_n^{(j)} c_k^{(n)(i-j)} = 0 \; . \tag{19}$$

The $j = i$ term vanishes due to state orthogonality. We have a recursive relation for the coefficient $c_k^{(n)(i)}$ at different order i. For a non-degenerate system, where $E_k^{(0)} \neq E_n^{(0)}$ for $k \neq n$, one can solve for $c_k^{(n)(i)}$ as

$$c_k^{(n)(i)} = \frac{1}{E_k^{(0)} - E_n^{(0)}} \left[- \sum_m c_m^{(n)(i-1)} \delta H_{k,m} + \sum_{j=1}^{i-1} E_n^{(j)} c_k^{(n)(i-j)} \right] \; . \tag{20}$$

Perturbation of a Degenerate System, Degeneracy Lifted to the First Order

Now we consider perturbation theory in a degenerate case, where for the initial Hamiltonian there are more than one eigenstates having the same eigenvalue. The procedure for non-degenerate systems as described in the first section no longer fully applies, as Equations 17 and 20 can become singular with $E_k^0 - E_n^0 = 0$ $(k \neq n)$ in the denominator.

Without loss of generality, suppose there is a g-fold degeneracy in the unperturbed Hamiltonian, i.e., there are g eigenstates of H_0 with the same eigenvalue $E_D^{(0)\dagger}$. We denote these states by $\{|D; m^{(0)}\rangle\}$ with $m = 1, 2, ..., g$, and their spanned subspace by D. The Hilbert space can be written as $\mathcal{H} = D \oplus \mathbb{V}_\perp$, in which $\mathbb{V}_\perp$ is the non-degenerate subspace orthogonal to D and one can calculate its perturbation by using the non-degenerate perturbation procedure as explained in the first section.

Note that due to the degeneracy, any linear combination of $\{|D; m^{(0)}\rangle\}$ is also an eigenstate of H_0 with eigenvalue $E_D^{(0)}$. To compute the state and energy correction in powers of λ, as in Equations 4a and 4b, we need to use the correct unperturbed state that the corresponding perturbed state approaches in the limit $\lambda \to 0$. Let us denote the states of the subspace D after perturbation as $\{|D; n\rangle\}$ with $n = 1, 2, ..., g$, which in general do not belong to D but in the limit of $\lambda \to 0$ become $\{|D; n^{(0)}\rangle\}$. For this reason, we will refer to the states $\{|D; n^{(0)}\rangle\}$ as the "good basis". The set $\{|D; n^{(0)}\rangle\}$ is a basis of D, which however are not necessarily the same with $\{|D; m^{(0)}\rangle\}$. As such, we have

$$|D; n\rangle = |D; n^{(0)}\rangle + |D; n^{(1)}\rangle \lambda + |D; n^{(2)}\rangle \lambda^2 + \mathcal{O}(\lambda^3) \; , \tag{21a}$$

$$E_{D;n} = E_D^{(0)} + E_{D;n}^{(1)} \lambda + E_{D;n}^{(2)} \lambda^2 + \mathcal{O}(\lambda^3) \; . \tag{21b}$$

We have imposed the orthonormal condition Equation 5 on $\{|D; n^{(i)}\rangle\}$, in the same manner as for $\{|\psi_n^{(i)}\rangle\}$ in the discussion of the non-degenerate system. Note that Equations 6-8, which are obtained by rearranging the Schrödinger equation order by order in λ, also apply to these states upon making the replacements $E_n \to E_{D;n}$, $E_n^{(i)} \to E_{D;n}^{(i)}$, $|\psi_n\rangle \to |D; n\rangle$, and $|\psi_n^{(i)}\rangle \to |D; n^{(i)}\rangle$.

[†] In cases with multiple degenerate subspaces, say D_1, D_2, . . ., each having a different eigenvalue $E_{D_1}^{(0)}$, $E_{D_2}^{(0)}$, . . ., one can apply the procedure described in this section to each subspace.

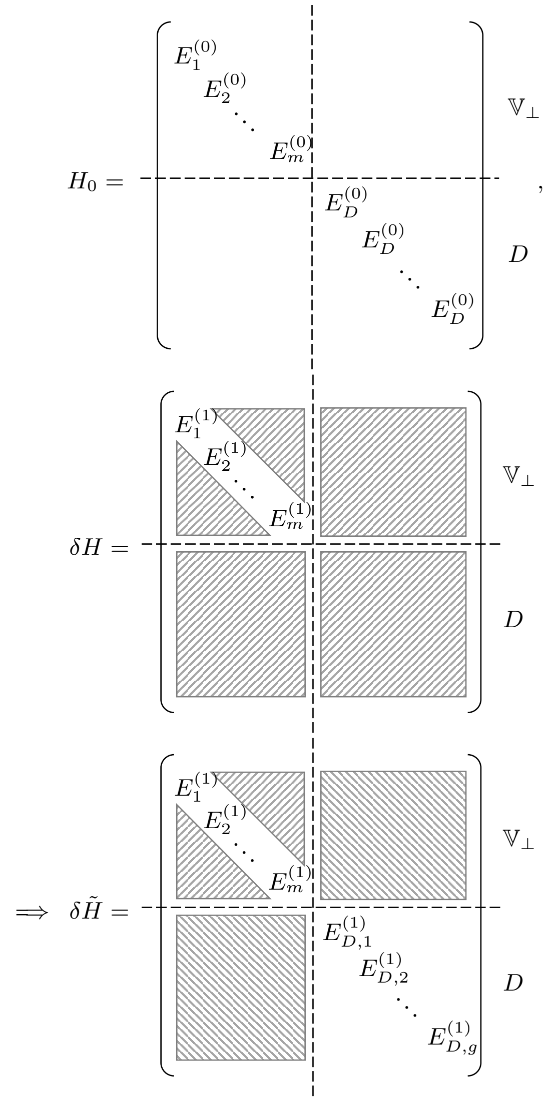

Figure 2. Matrix representations of the Hamiltonian operator for a system with degeneracy, with $\mathbb{V}_\perp$ denoting the non-degenerate subspace and D the degenerate subspace. From top to bottom: H_0 in the unperturbed basis, δH in the unperturbed basis, and $\delta\tilde{H}$, the matrix representation of δH in the "good basis" where it is diagonal in D.

First Order Equation

We project Equation 8 (with the replacement $E_n^{(i)} \to E_{D;n}^{(i)}$ and $|\psi_n^{(i)}\rangle \to |D; n^{(i)}\rangle$) for the case $i = 1$, onto $\langle D; l^{(0)}|$, an arbitrary state from the set $\{|D; n^{(0)}\rangle\}$ that we are looking for,

$$\langle D; l^{(0)} | H_0 | D; n^{(1)} \rangle + \langle D; l^{(0)} | \delta H | D; n^{(0)} \rangle - E_D^{(0)} \langle D; l^{(0)} | D; n^{(1)} \rangle - E_{D;n}^{(1)} \langle D; l^{(0)} | D; n^{(0)} \rangle = 0 \; . \tag{22}$$

The first and third terms cancel out and we end up with

$$E_{D;n}^{(1)} \delta_{n,l} = \langle D; l^{(0)} | \delta H | D; n^{(0)} \rangle \; . \tag{23}$$

This means that the basis $\{|D; n^{(0)}\rangle\}$ diagonalizes δH in D, and $E_{D;n}^{(1)}$s are the eigenvalues, as illustrated in Figure 2. For simplicity, let us define $\delta H_{D;l,D;n} \equiv \langle D; l^{(0)} | \delta H | D; n^{(0)} \rangle$, such that $E_{D;n}^{(1)} = \delta H_{D;n,D;n}$.

To continue, we project the same first order TISE, onto a state in the $\mathbb{V}_\perp$

subspace, $\langle\psi_p^{(0)}|$,

$$\langle\psi_p^{(0)}|H_0|D;n^{(1)}\rangle + \langle\psi_p^{(0)}|\delta H|D;n^{(0)}\rangle - E_D^{(0)}\langle\psi_p^{(0)}|D;n^{(1)}\rangle - E_{D;n}^{(1)}\langle\psi_p^{(0)}|D;n^{(0)}\rangle = 0\ . \quad (24)$$

The last term vanishes due to orthogonality, and we are left with

$$\langle\psi_p^{(0)}|D;n^{(1)}\rangle = -\frac{\delta H_{p,D;n}}{E_p^{(0)} - E_D^{(0)}}\ , \quad (25)$$

in which we have defined $\delta H_{p,D;n} \equiv \langle\psi_p^{(0)}|\delta H|D;n^{(0)}\rangle$ for convenience. Note that we only get the part of the first order state in the $\mathbb{V}_\perp$ subspace, and that in D is still missing,

$$|D;n^{(1)}\rangle = \sum_{p\notin D}|\psi_p^{(0)}\rangle\langle\psi_p^{(0)}|D;n^{(1)}\rangle + \sum_{l\in D, l\neq n}|D;l^{(0)}\rangle\langle D;l^{(0)}|D;n^{(1)}\rangle\ . \quad (26)$$

Second Order Equation

We project the second order TISE, i.e., Equation 8 with index $i=2$, onto $\langle D;l^{(0)}|$,

$$\langle D;l^{(0)}|(H_0 - E_D^{(0)})|D;n^{(2)}\rangle - \langle D;l^{(0)}|(E_{D;n}^{(1)} - \delta H)|D;n^{(1)}\rangle - E_{D;n}^{(2)}\langle D;l^{(0)}|D;n^{(0)}\rangle = 0\ . \quad (27)$$

The first term vanishes immediately. Substituting Equation 26 and performing some simplifications, we arrive at

$$(E_{D;n}^{(1)} - E_{D;l}^{(1)})\langle D;l^{(0)}|D;n^{(1)}\rangle - \sum_{p\notin D}\delta H_{D;l,p}\langle\psi_p^{(0)}|D;n^{(1)}\rangle + E_{D;n}^{(2)}\delta_{l,n} = 0\ . \quad (28)$$

We already know the second term from Equation 25. We take $l\neq n$ to extract the remaining information in $|D;n^{(1)}\rangle$. Here, we assume that the degeneracy is completely resolved so that $E_{D;n}^{(1)} \neq E_{D;l}^{(1)}$ when $l\neq n$. Therefore,

$$\langle D;l^{(0)}|D;n^{(1)}\rangle = \sum_{p\notin D} -\frac{\delta H_{D;l,p}\delta H_{p,D;n}}{(E_{D;n}^{(1)} - E_{D;l}^{(1)})(E_p^{(0)} - E_D^{(0)})}\ . \quad (29)$$

We obtain the first order state correction with Equations 25, 26, and 29. We take $l=n$ in Equation 28 and obtain the second order energy correction as

$$E_{D;n}^{(2)} = \sum_{p\notin D} -\frac{|\delta H_{p,D;n}|^2}{E_p^{(0)} - E_D^{(0)}}\ . \quad (30)$$

To complete the calculation at the second order equation, we project the second-order TISE onto a state in the $\mathbb{V}_\perp$ subspace, $\langle\psi_p^{(0)}|$,

$$\langle\psi_p^{(0)}|(H_0 - E_D^{(0)})|D;n^{(2)}\rangle - \langle\psi_p^{(0)}|(E_{D;n}^{(1)} - \delta H)|D;n^{(1)}\rangle - E_{D;n}^{(2)}\langle\psi_p^{(0)}|D;n^{(0)}\rangle = 0\ . \quad (31)$$

The last term vanishes due to state orthogonality, and the first order corrections are already known. We therefore get the second order state correction in the $\mathbb{V}_\perp$ subspace,

$$\langle\psi_p^{(0)}|D;n^{(2)}\rangle = \frac{1}{E_p^{(0)} - E_D^{(0)}}\Big[E_{D;n}^{(1)}\langle\psi_p^{(0)}|D;n^{(1)}\rangle - \sum_{q\notin D}\delta H_{p,q}\langle\psi_q^{(0)}|D;n^{(1)}\rangle - \sum_{l\in D, l\neq n}\delta H_{p,D;l}\langle D;l^{(0)}|D;n^{(1)}\rangle\Big]\ . \quad (32)$$

Higher Order Corrections

Let us generalize the aforementioned procedure for higher-order corrections. Note that for states in the $\mathbb{V}_\perp$ subspace, the results shown in the first section apply directly. The i-th order eigenstates, expressed in terms of the unperturbed basis states, can be written as:

$$|D;n^{(i)}\rangle = (\mathrm{P}_{\mathbb{V}_\perp} + \mathrm{P}_D)|D;n^{(i)}\rangle = \sum_{p\notin D}|\psi_p^{(0)}\rangle c_p^{(D;n)(i)} + \sum_{l\in D}|D;l^{(0)}\rangle c_{D;l}^{(D;n)(i)}\ , \quad (33)$$

in which $c_p^{(D;n)(i)} \equiv \langle\psi_p^{(0)}|D;n^{(i)}\rangle$ and $c_{D;l}^{(D;n)(i)} \equiv \langle D;l^{(0)}|D;n^{(i)}\rangle$. The orthonormal condition of the unperturbed states gives $c_{D;l}^{(D;n)(0)} = \delta_{l,n}$ and the condition of the state correction given by Equation 5 can be written as $c_{D;n}^{(D;l)(i)} = 0$ for $l=n$ when $i\geq 1$.

From the i-th order TISE, one can express $E_{D;n}^{(i)}$, $c_p^{(D;n)(i)}$s and $c_{D;l}^{(D;n)(i-1)}$s (for $i\geq 2$ in the last case) in terms of lower-order results, as shown in the first and second order equations. We now proceed with the i-th order equation, given by Equation 8,

$$H_0|D;n^{(i)}\rangle + \delta H|D;n^{(i-1)}\rangle - \sum_{j=0}^{i}E_{D;n}^{(j)}|D;n^{(i-j)}\rangle = 0\ , \quad (34)$$

and continue from here.

- Projection onto $\mathbb{V}_\perp$
  Projecting Equation 34 onto a state in the $\mathbb{V}_\perp$ subspace, $\langle\psi_p^{(0)}|$, gives

  $$(E_p^{(0)} - E_D^{(0)})\langle\psi_p^{(0)}|D;n^{(i)}\rangle + \langle\psi_p^{(0)}|\delta H|D;n^{(i-1)}\rangle - \sum_{j=1}^{i-1}E_{D;n}^{(j)}\langle\psi_p^{(0)}|D;n^{(i-j)}\rangle = 0\ . \quad (35)$$

  Expanding the state correction with Equation 33, we get

  $$c_p^{(D;n)(i)} = -\frac{1}{E_p^{(0)} - E_D^{(0)}}\Big[\sum_{q\notin D}\delta H_{p,q}c_q^{(D;n)(i-1)} + \sum_{l\in D}\delta H_{p,D;l}c_{D;l}^{(D;n)(i-1)} - \sum_{j=1}^{i-1}E_{D;n}^{(j)}c_p^{(D;n)(i-j)}\Big]\ . \quad (36)$$

  All terms on the right-hand side are known from lower-order equations.
- Projection onto D
  Projecting Equation 34 onto a state in the D subspace, $\langle D;l^{(0)}|$, gives

  $$\langle D;l^{(0)}|\delta H|D;n^{(i-1)}\rangle - \sum_{j=1}^{i-1}E_{D;n}^{(j)}\langle D;l^{(0)}|D;n^{(i-j)}\rangle - E_{D;n}^{(i)}\langle D;l^{(0)}|D;n^{(0)}\rangle = 0\ . \quad (37)$$

  In the case of $l=n$, we have

  $$E_{D;n}^{(i)} = \langle D;n^{(0)}|\delta H|D;n^{(i-1)}\rangle\ . \quad (38)$$

  In the case of $l\neq n$, we have

  $$c_{D;l}^{(D;n)(i-1)} = \frac{1}{E_{D;l}^{(1)} - E_{D;n}^{(1)}}\Big[\sum_{j=2}^{i-1}E_{D;n}^{(j)}c_{D;l}^{(D;n)(i-j)} - \sum_{p\notin D}\delta H_{D;l,p}c_p^{(D;n)(i-1)}\Big]\ . \quad (39)$$

We summarize the general procedure for the perturbative theory of a degenerate system whose degeneracy is resolved at first order as follows:

i) Identify the degenerate subspace D in the basis of unperturbed eigenstates of H_0. Diagonalize δH in this subspace, and use its eigenstates as the new unperturbed states, with the eigenvalues giving the first-order state correction.

ii) Calculate the perturbation correction to states whose unperturbed states are in the degenerate subspace using Equations 36, 38, and 39.

iii) Calculate the perturbation correction to states whose unperturbed states are in the non-degenerate subspace using Equations 16 and 20.

Perturbation of a Degenerate System, Degeneracy Lifted to the Second Order

When the degeneracy is not fully resolved in first order, the method in the previous fails, as Equation 29 becomes singular. In this case, we cannot determine the correct zeroth-order basis states from the first-order perturbation alone. This section addresses the scenario where the degeneracy is partially or not resolved at first order but is completely resolved at second order.

We consider a system with a g-fold degeneracy on a subspace D. We carry on the setup that the full Hilbert space of the problem can be written as $\mathcal{H} = D \oplus V_\perp$. The subspace D is spanned by the unperturbed eigenstates $\{|D; n^{(0)}\rangle\}$ ($n = 1, 2, \ldots, g$) (with unperturbed eigenvalue $E_D^{(0)}$) that already diagonalize the perturbation δH in D. Their first order corrections, as can be obtained by Equation 23, are $\{E_{D_1}^{(1)}, E_{D_2}^{(1)}, \ldots, E_{D_B}^{(1)}\}$ where $B < g$; note that in the scenario of $B = g$ the degeneracy is completely broken at first order and the problem is solved according to the previous procedure. We now express D as a direct sum of the subspaces with different first order correction, $D = \bigoplus_{I=1}^{B} D_I$, where D_I is the subspace spanned by the unperturbed eigenstates that have the same first order energy correction $E_{D_I}^{(1)}$. The dimensions of D_I is N_I such that $\sum_{I=1}^{B} N_I = g$. For convenience, let us denote the unperturbed basis states $\{|D; n^{(0)}\rangle\}$ that are in the D_I subspace with the subscript I as $\{|D_I; n_I^{(0)}\rangle\}$ ($n_I = 1, 2, \ldots, N_I$). For a subspace D_I with $N_I > 1$, any linear combination of $\{|D; n^{(0)}\rangle\}$ is still a H_0 eigenstate with eigenvalue $E_D^{(0)}$, and our goal here is to find the "good basis" that the corresponding perturbed state approaches in the limit $\lambda \to 0$.

Let us denote the "good basis" by $\{|D_I; \alpha_I^{(0)}\rangle\}$ ($\alpha_I = 1, 2, \ldots, N_I$), for which we use Greek letters as the state index to distinguish those of the original basis. We can write the α_I-th state of the D_I subspace as a linear combination of the original basis states,

$$|D_I; \alpha_I^{(0)}\rangle = \sum_{n_I=1}^{N_I} v_{n_I}^{\alpha_I} |D_I; n_I^{(0)}\rangle \ . \tag{40}$$

Here, $v_{n_I}^{\alpha_I} \equiv \langle D_I; n_I^{(0)} | D_I; \alpha_I^{(0)}\rangle$. Note that δH remains diagonal in D in the "good basis". We can expand the corresponding perturbed state and energy in powers of λ,

$$\begin{aligned} |D_I; \alpha_I\rangle =& |D_I; \alpha_I^{(0)}\rangle + |D_I; \alpha_I^{(1)}\rangle \lambda + |D_I; \alpha_I^{(2)}\rangle \lambda^2 \\ &+ \mathcal{O}(\lambda^3) \ , \end{aligned} \tag{41a}$$

$$E_{D_I;\alpha_I} = E_D^{(0)} + E_{D_I}^{(1)} \lambda + E_{D_I;\alpha_I}^{(2)} \lambda^2 + \mathcal{O}(\lambda^3) \ . \tag{41b}$$

As before, we apply the orthogonality condition on $\{|D_I; \alpha_I^{(i)}\rangle\}$ as defined in Equation 5. The eigenvalue equation, as of Equation 8, for $|D_I; \alpha_I^{(i)}\rangle$, becomes

$$\mathcal{O}(1) : (H_0 - E_D^{(0)}) |D_I; \alpha_I^{(0)}\rangle = 0 \ , \tag{42a}$$

$$\mathcal{O}(\lambda) : (H_0 - E_D^{(0)}) |D_I; \alpha_I^{(1)}\rangle = (E_{D_I}^{(1)} - \delta H) |D_I; \alpha_I^{(0)}\rangle \ , \tag{42b}$$

$$\begin{aligned} \mathcal{O}(\lambda^2) : (H_0 - E_D^{(0)}) |D_I; \alpha_I^{(2)}\rangle =& (E_{D_I}^{(1)} - \delta H) |D_I; \alpha_I^{(1)}\rangle \\ &+ E_{D_I;\alpha_I}^{(2)} |D_I; \alpha_I^{(0)}\rangle \ , \end{aligned} \tag{42c}$$

$$\begin{aligned} \mathcal{O}(\lambda^3) : (H_0 - E_D^{(0)}) |D_I; \alpha_I^{(3)}\rangle =& (E_{D_I}^{(1)} - \delta H) |D_I; \alpha_I^{(2)}\rangle \\ &+ E_{D_I;\alpha_I}^{(2)} |D_I; \alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(3)} |D_I; \alpha_I^{(0)}\rangle \ , \end{aligned} \tag{42d}$$

(42e)

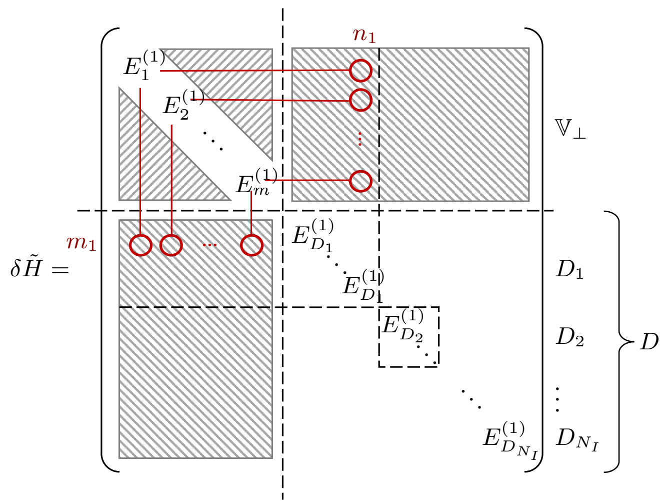

Figure 3. For a system with degeneracy lifted to the second order, diagonalizing the perturbation δH in the $E^{(0)}$-degenerate subspace D does not completely break the degeneracy (c.f. Figure 2), and we have $D = D_1 \oplus D_2 \oplus \ldots \oplus D_{N_I}$, where D_I's are $E^{(1)}$-degenerate subspaces. The "good basis" diagonalizes $\boldsymbol{\Delta}_{D_I}^{(2)}$ as defined in Equation 51. The red circles denote the matrix elements involved in calculating $\Delta_{D_1}^{(2)}|_{m_1,n_1}$ as an example.

First Order Equation

From the first order equation, we obtain the first order energy correction $E_{D_I}^{(1)} = \delta H_{D_I;\alpha_I, D_I;\alpha_I}$, similar to Equation 23, and the first order state correction in $\mathbb{V}_\perp$, analogous to Equation 25, which is:

$$\langle \psi_p^{(0)} | D_I; \alpha_I^{(1)}\rangle = -\frac{\delta H_{p,D_I;\alpha_I}}{E_p^{(0)} - E_D^{(0)}} = -\frac{\sum_{n_I=1}^{N_I} v_{n_I}^{\alpha_I} \delta H_{p,D_I;n_I}}{E_p^{(0)} - E_D^{(0)}} \ . \tag{43}$$

We have defined $\delta H_{p,D_I;\alpha_I} \equiv \langle \psi_p^{(0)} | \delta H | D_I; \alpha_I^{(0)}\rangle$ and similarly, $\delta H_{p,D_I;n_I} \equiv \langle \psi_p^{(0)} | \delta H | D_I; n_I^{(0)}\rangle$ for convenience. Note that $|D_I; n_I^{(0)}\rangle$ is just $|D; n^{(0)}\rangle$ in Equation 25 with the subspace index I written out.

Second Order Equation

In the second order equation, unlike before, we must account for the remaining degeneracy after the first order perturbation. Instead of Equation 26, we project $|D_I;\alpha_I^{(1)}\rangle$ onto three subspaces, $\mathbb{V}_\perp$, $D-D_I$, and D_I,

$$|D_I;\alpha_I^{(1)}\rangle = (\mathrm{P}_{\mathbb{V}_\perp} + \mathrm{P}_{D-D_I} + \mathrm{P}_{D_I})\,|D_I;\alpha_I^{(1)}\rangle = \sum_{p\notin D} |\psi_p^{(0)}\rangle\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle + \sum_{J\neq I}\sum_{n_J=1}^{N_J} |D_J;n_J^{(0)}\rangle\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle + \sum_{n_I=1}^{N_I} |D_I;n_I^{(0)}\rangle\,\langle D_I;n_I^{(0)}|D_I;\alpha_I^{(1)}\rangle\ . \tag{44}$$

The projection onto $D-D_I$ gives us part of the first order state correction. Written explicitly, projecting Equation 42c onto $\langle D_J;n_J^{(0)}|$ with $J\neq I$, we get

$$\langle D_J;n_J^{(0)}|(H_0-E_D^{(0)})\,|D_I;\alpha_I^{(2)}\rangle = \langle D_J;n_J^{(0)}|\,(E_{D_I}^{(1)}-\delta H)\,|D_I;\alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(2)}\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(0)}\rangle\ . \tag{45}$$

The first and second terms vanish, and by using Equation 44 we obtain

$$E_{D_I}^{(1)}\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle = \sum_{p\notin D}\delta H_{D_J;n_J,p}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle + \delta H_{D_J;n_J,D_J;n_J}\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle\ . \tag{46}$$

Together with Equation 43, we have:

$$\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle = \sum_{p\notin D} -\frac{\delta H_{D_J;n_J,p}\delta H_{p,D_I;\alpha_I}}{\left(E_{D_I}^{(1)}-E_{D_J}^{(1)}\right)\left(E_p^{(0)}-E_D^{(0)}\right)}\ . \tag{47}$$

This result is similar to Equation 29, and recovers the latter when $N_I=1$.

Next, we project Equation 42c onto D_I,

$$\langle D_I;n_I^{(0)}|(H_0-E_D^{(0)})\,|D_I;\alpha_I^{(2)}\rangle = \langle D_I;n_I^{(0)}|\,(E_{D_I}^{(1)}-\delta H)\,|D_I;\alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(2)}\,\langle D_I;n_I^{(0)}|D_I;\alpha_I^{(0)}\rangle\ . \tag{48}$$

The first term vanishes, and we recognize $v_{n_I}^{\alpha_I}$ in the last term. Applying Equation 44, we obtain:

$$\sum_{p\notin D}\delta H_{D_I;n_I,p}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle - E_{D_I;\alpha_I}^{(2)}v_{n_I}^{\alpha_I} = 0\ . \tag{49}$$

In the above equation, we used that that δH is diagonal in D and $E_{D_I}^{(1)} = \delta H_{D_I;n_I,D_I;n_I}$. Together with Equation 43, we have

$$-\sum_{p\notin D}\delta H_{D_I;n_I,p}\frac{\sum_{m_I=1}^{N_I} v_{m_I}^{\alpha_I}\delta H_{p,D_I;m_I}}{E_p^{(0)}-E_D^{(0)}} - E_{D_I;\alpha_I}^{(2)}v_{n_I}^{\alpha_I} = 0\ . \tag{50}$$

We rewrite the above equation by defining the second-order perturbation operator $\mathbf{\Delta}_{D_I}^{(2)}$, with matrix elements

$$\Delta_{D_I}^{(2)}|_{n_I,m_I} = \langle D_I;n_I^{(0)}|\mathbf{\Delta}_{D_I}^{(2)}|D_I;m_I^{(0)}\rangle \equiv -\sum_{p\notin D}\frac{\delta H_{D_I;n_I,p}\delta H_{p,D_I;m_I}}{E_p^{(0)}-E_D^{(0)}}\ . \tag{51}$$

Physically, this is the energy fluctuation of an initial state in D_I going through any intermediate states in $\mathbb{V}_\perp$ and back to D_I. It is structurally analogous to the second-order off-diagonal elements of the contact-transformed Hamiltonian in Darling-Dennison resonances in hydroxyl stretching polyads[16–18].

Equation 50 becomes

$$\sum_{m_I=1}^{N_I}\left[\Delta_{D_I}^{(2)}|_{n_I,m_I} - E_{D_I;\alpha_I}^{(2)}\delta_{n_I,m_I}\right]v_{m_I}^{\alpha_I} = 0\ , \tag{52}$$

which is clearly an eigenvalue equation of vectors $\boldsymbol{v}^{\alpha_I} \equiv \{v_1^{\alpha_I}, v_2^{\alpha_I},\ldots,v_{n_I}^{\alpha_I}\}$, with $\alpha_I = 1,2,\ldots,N_I$. We therefore find the "good basis" by solving $\boldsymbol{v}^{\alpha_I}$ as the eigenvectors of $\mathbf{\Delta}_{D_I}^{(2)}$, and in the meantime, we obtain the second order energy correction $E_{D_I;\alpha_I}^{(2)}$ as the eigenvalues. We illustrate the relation of $\mathbf{\Delta}_{D_I}^{(2)}$ and the δH matrix in Figure 3. Lastly, we project Equation 42c onto $\mathbb{V}_\perp$,

$$\langle\psi_p^{(0)}|\,(H_0-E_D^{(0)})\,|D_I;\alpha_I^{(2)}\rangle = \langle\psi_p^{(0)}|\,(E_{D_I}^{(1)}-\delta H)\,|D_I;\alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(2)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(0)}\rangle\ . \tag{53}$$

The last term vanishes by orthogonality. Decomposing the first order state by Equation 44, we get

$$\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle = \frac{1}{E_p^{(0)}-E_D^{(0)}}\Bigg\{E_{D_I}^{(1)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle - \sum_{q\notin D}\delta H_{p,q}\,\langle\psi_q^{(0)}|D_I;\alpha_I^{(1)}\rangle - \sum_{J\neq I}\sum_{n_J=1}^{N_J}\delta H_{p,D_J;n_J}\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle - \sum_{n_I=1}^{N_I}\delta H_{p,D_I;n_I}\,\langle D_I;n_I^{(0)}|D_I;\alpha_I^{(1)}\rangle\Bigg\}\ . \tag{54}$$

The first three terms on the right-hand side of the equation are known from Equations 43 and 47. This gives a relation between two unknowns, but we have exhausted the second-order equation. Next, we proceed with the third order equation.

Third Order Equation

We first project Equation 42d onto D_I, and now that we have found the "good basis", we use $\langle D_I;\beta_I^{(0)}|$. This gives us

$$\langle D_I;\beta_I^{(0)}|(H_0-E_D^{(0)})\,|D_I;\alpha_I^{(3)}\rangle = \langle D_I;\beta_I^{(0)}|\,(E_{D_I}^{(1)}-\delta H)\,|D_I;\alpha_I^{(2)}\rangle + E_{D_I;\alpha_I}^{(2)}\,\langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(3)}\,\langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(0)}\rangle\ . \tag{55}$$

The terms on the left-hand side cancel out. In the case $\beta_I=\alpha_I$, we get, after applying the orthogonality condition of $|D_I;\alpha_I^{(i)}\rangle$ with respect to $|D_I;\alpha_I^{(0)}\rangle$ as defined in Equation 5,

$$E_{D_I;\alpha_I}^{(3)} = \langle D_I;\alpha_I^{(0)}|\,\delta H\,|D_I;\alpha_I^{(2)}\rangle = \sum_{p\notin D}\delta H_{D_I;\alpha_I,p}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle\ . \tag{56}$$

We get to the second equation by noting that δH is diagonal in D.

In the case $\beta_I\neq\alpha_I$, the last term of Equation 55 vanishes by state orthogonality, and we have

$$0 = \langle D_I;\beta_I^{(0)}|\,(E_{D_I}^{(1)}-\delta H)\,|D_I;\alpha_I^{(2)}\rangle + E_{D_I;\alpha_I}^{(2)}\,\langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(1)}\rangle\ . \tag{57}$$

We decompose the second-order state correction in the above equation as

$$\begin{aligned} |D_I;\alpha_I^{(2)}\rangle &= \sum_{p\notin D} |\psi_p^{(0)}\rangle\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle \\ &\quad + \sum_{J\neq I}\sum_{\gamma_J=1}^{N_J} |D_J;\alpha_J^{(0)}\rangle\,\langle D_J;\alpha_J^{(0)}|D_I;\alpha_I^{(2)}\rangle \\ &\quad + \sum_{\gamma_I\neq\alpha_I} |D_I;\gamma_I^{(0)}\rangle\,\langle D_I;\gamma_I^{(0)}|D_I;\alpha_I^{(2)}\rangle\ . \end{aligned} \tag{58}$$

The first component will survive in Equation 57; the second component will not contribute due to state orthogonality and δH being diagonal in D; the third component will not contribute by seeing $\delta H \to E_{D_I}^{(1)}$ in D_I. As a result, we have

$$\sum_{p\notin D} \delta H_{D_I;\beta_I,p}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle = E_{D_I;\alpha_I}^{(2)}\,\langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(1)}\rangle\ . \tag{59}$$

Combining with Equation 54, we get

$$\begin{aligned} E_{D_I;\alpha_I}^{(2)}\,\langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(1)}\rangle &= \sum_{p\notin D}\delta H_{D_I;\beta_I,p}\frac{1}{E_p^{(0)}-E_D^{(0)}} \\ &\times\Bigg\{E_{D_I}^{(1)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle - \sum_{q\notin D}\delta H_{p,q}\,\langle\psi_q^{(0)}|D_I;\alpha_I^{(1)}\rangle \\ &- \sum_{J\neq I}\sum_{n_J=1}^{N_J}\delta H_{p,D_J;n_J}\,\langle D_J;n_J^{(0)}|D_I;\alpha_I^{(1)}\rangle \\ &- \sum_{\gamma_I\neq\alpha_I}\delta H_{p,D_I;\gamma_I}\,\langle D_I;\gamma_I^{(0)}|D_I;\alpha_I^{(1)}\rangle\Bigg\}\ . \end{aligned} \tag{60}$$

Note that in writing the last term, we have switched the summation to the "good basis". Recall that we already know the first three terms on the right-hand side by Equations 43 and 47. Let us examine the last term,

$$\begin{aligned} -\sum_{p\notin D}&\frac{\delta H_{D_I;\beta_I,p}\delta H_{p,D_I;\gamma_I}}{E_p^{(0)}-E_D^{(0)}} \\ &= \langle D_I;\beta_I^{(0)}|\boldsymbol{\Delta}_{D_I}^{(2)}|D_I;\gamma_I^{(0)}\rangle = E_{D_I;\beta_I}^{(2)}\delta_{\beta_I,\gamma_I}\ , \end{aligned} \tag{61}$$

in which we recognize the $\boldsymbol{\Delta}_{D_I}^{(2)}$ operator, as in Equation 51, and recall that it is diagonal in the "good basis". By assuming that the degeneracy is completely resolved at second order, i.e., $E_{D_I;\alpha_I}^{(2)} \neq E_{D_I;\beta_I}^{(2)}$ for $\alpha_I \neq \beta_I$, we can write Equation 60 as

$$\begin{aligned} \langle D_I;\beta_I^{(0)}|D_I;\alpha_I^{(1)}\rangle &= \frac{1}{E_{D_I;\alpha_I}^{(2)}-E_{D_I;\beta_I}^{(2)}}\sum_{p\notin D}\frac{\delta H_{D_I;\beta_I,p}}{E_p^{(0)}-E_D^{(0)}} \\ &\times\Bigg\{-E_{D_I}^{(1)}\frac{\delta H_{p,D_I;\alpha_I}}{E_p^{(0)}-E_D^{(0)}} + \sum_{q\notin D}\frac{\delta H_{p,q}\delta H_{q,D_I;\alpha_I}}{E_q^{(0)}-E_D^{(0)}} \\ &+ \sum_{J\neq I}\sum_{n_J=1}^{N_J}\sum_{q\notin D}\frac{\delta H_{p,D_J;n_J}\delta H_{D_J;n_J,q}\delta H_{q,D_I;\alpha_I}}{\left(E_{D_I}^{(1)}-E_{D_J}^{(1)}\right)\left(E_q^{(0)}-E_D^{(0)}\right)}\Bigg\}\ . \end{aligned} \tag{62}$$

Up to this point, we complete the derivation of the first order state correction. One can write out the full expression by putting Equations 43, 44, 47, and 62 together. It is then straightforward to get the second order state correction that comes from outside D (i.e., $\mathbb{V}_\perp$) as in Equation 54 and the third order energy correction as in Equation 56.

We next project Equation 42d onto $D - D_I$, using the "good basis" $\langle D_J;\beta_J^{(0)}|$ $(J \neq I)$,

$$\begin{aligned} \langle D_J;\beta_J^{(0)}|\,(H_0 - E_D^{(0)})\,|D_I;\alpha_I^{(3)}\rangle &= \langle D_J;\beta_J^{(0)}|\,(E_{D_I}^{(1)} - \delta H)\,|D_I;\alpha_I^{(2)}\rangle \\ + E_{D_I;\alpha_I}^{(2)}\,\langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(1)}\rangle &+ E_{D_I;\alpha_I}^{(3)}\,\langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(0)}\rangle\ . \end{aligned} \tag{63}$$

The terms on the left-hand side cancel out, and the last term on the right vanishes due to orthogonality. Therefore,

$$\begin{aligned} 0 = \langle D_J;\beta_J^{(0)}|\,(E_{D_I}^{(1)} - \delta H)\,|D_I;\alpha_I^{(2)}\rangle \\ + E_{D_I;\alpha_I}^{(2)}\,\langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(1)}\rangle\ . \end{aligned} \tag{64}$$

By the state decomposition given in Equation 58, we obtain a second component of the second order state correction

$$\begin{aligned} \langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(2)}\rangle = \frac{-1}{E_{D_I}^{(1)}-E_{D_J}^{(1)}}\Bigg\{E_{D_I;\alpha_I}^{(2)}\,\langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(1)}\rangle \\ - \sum_{p\notin D}\delta H_{D_J;\beta_J,p}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle\Bigg\}\ . \end{aligned} \tag{65}$$

Finally, we project Equation 42d onto $\mathbb{V}_\perp$ with $\langle\psi_p^{(0)}|$,

$$\begin{aligned} \langle\psi_p^{(0)}|\,(H_0 - E_D^{(0)})\,|D_I;\alpha_I^{(3)}\rangle = \langle\psi_p^{(0)}|\,(E_{D_I}^{(1)} - \delta H)\,|D_I;\alpha_I^{(2)}\rangle \\ + E_{D_I;\alpha_I}^{(2)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle + E_{D_I;\alpha_I}^{(3)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(0)}\rangle\ , \end{aligned} \tag{66}$$

and arrives at

$$\begin{aligned} \langle\psi_p^{(0)}|D_I;\alpha_I^{(3)}\rangle &= \frac{1}{E_p^{(0)}-E_D^{(0)}}\Bigg\{E_{D_I}^{(1)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(2)}\rangle \\ &+ E_{D_I}^{(2)}\,\langle\psi_p^{(0)}|D_I;\alpha_I^{(1)}\rangle - \sum_{q\notin D}\delta H_{p,q}\,\langle\psi_q^{(0)}|D_I;\alpha_I^{(2)}\rangle \\ &- \sum_{J\neq I}\sum_{\beta_J=1}^{N_J}\delta H_{p,D_J;\beta_J}\,\langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(2)}\rangle \\ &- \sum_{\gamma_I\neq\alpha_I}\delta H_{p,D_I;\gamma_I}\,\langle D_I;\gamma_I^{(0)}|D_I;\alpha_I^{(2)}\rangle\Bigg\}\ . \end{aligned} \tag{67}$$

This equation contains two unknowns: the left-hand side and the last term on the right-hand side. Since the third-order equation is exhausted, we need to go to the next order to solve for them.

Higher Order Corrections

We can generalize the aforementioned procedure for higher order corrections, for which we will obtain a recursive relation of the corrections. Note that for states in the non-degenerate subspace, the formulas obtained before apply directly, and here we make the derivation for the states in the degenerate subspace D. The i-th order eigenstates in terms of the unperturbed basis states can be written as,

$$\begin{aligned} |D_I;\alpha_I^{(i)}\rangle &= (\mathrm{P}_{\mathbb{V}_\perp} + \mathrm{P}_{D-D_I} + \mathrm{P}_{D_I})\,|D_I;\alpha_I^{(i)}\rangle \\ &= \sum_{p\notin D}|\psi_p^{(0)}\rangle\,c_p^{(D_I;\alpha_I)(i)} \\ &+ \sum_{J\neq I}\sum_{\beta_J=1}^{N_J}|D_J;\beta_J^{(0)}\rangle\,c_{D_J;\beta_J}^{(D_I;\alpha_I)(i)} \\ &+ \sum_{\gamma_I=1}^{N_I}|D_I;\gamma_I^{(0)}\rangle\,c_{D_I;\gamma_I}^{(D_I;\alpha_I)(i)}\ . \end{aligned} \tag{68}$$

in which $c_\psi^{(D_I;\alpha_I)(i)} \equiv \langle\psi|D_I;\alpha_I^{(i)}\rangle$. From the i-th order TISE, we can get $E_{D_I;\alpha_I}^{(i)}$, $c_p^{(D_I;\alpha_I)(i-1)}$, $c_{D_I;\beta_I}^{(D_I;\alpha_I)(i-2)}(\beta_I \neq \alpha_I)$, $c_{D_J;\beta_J}^{(D_I;\alpha_I)(i-1)}(I \neq J)$ in terms of lower order results, and a relation between $c_p^{(D_I;\alpha_I)(i)}$ and $c_{D_I;\beta_I}^{(D_I;\alpha_I)(i-1)}(\beta_I \neq \alpha_I)$ [which will be solved with the $(i+1)$-th order equation]. We have shown this with the eigenvalue equations up to the third order. We proceed with the $i(\geq 3)$-th order equation,

$$H_0 \left|D_I;\alpha_I^{(i)}\right\rangle + \delta H \left|D_I;\alpha_I^{(i-1)}\right\rangle - \sum_{j=0}^{i} E^{(j)}_{D_I;\alpha_I} \left|D_I;\alpha_I^{(i-j)}\right\rangle = 0 \,. \quad (69)$$

- Projection onto D_I
Projecting Equation 69 onto a state in the D_I subspace, $\langle D_I;\gamma_I^{(0)}|$, gives

$$\langle D_I;\gamma_I^{(0)}|\delta H|D_I;\alpha_I^{(i-1)}\rangle - \sum_{j=1}^{i-1} E^{(j)}_{D_I;\alpha_I} \langle D_I;\gamma_I^{(0)}|D_I;\alpha_I^{(i-j)}\rangle - E^{(i)}_{D_I;\alpha_I} \langle D_I;\gamma_I^{(0)}|D_I;\alpha_I^{(0)}\rangle = 0 \,. \quad (70)$$

In the case of $\gamma_I = \alpha_I$, we have

$$E^{(i)}_{D_I;\alpha_I} = \langle D_I;\alpha_I^{(0)}|\delta H|D_I;\alpha_I^{(i-1)}\rangle \,. \quad (71)$$

In the case of $\gamma_I \neq \alpha_I$, after expanding the state correction with Equation 68, we get

$$\sum_{p\notin D} \delta H_{D_I;\gamma_I,p} c_p^{(D_I;\alpha_I)(i-1)} - E^{(2)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-2)}_{D_I;\gamma_I} - \sum_{j=3}^{i-1} E^{(j)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-j)}_{D_I;\gamma_I} = 0 \,. \quad (72)$$

The unknown terms at the current order are $c_p^{(D_I;\alpha_I)(i-1)}$ and $c^{(D_I;\alpha_I)(i-2)}_{D_I;\gamma_I}$. We will solve it in combination with the $(i-1)$-th order Equation 74

- Projection onto $\mathbb{V}_\perp$
Projecting Equation 69 onto $\mathbb{V}_\perp$ gives

$$(E_p^{(0)} - E_D^{(0)}) \langle \psi_p^{(0)}|D_I;\alpha_I^{(i)}\rangle + \langle \psi_p^{(0)}|\delta H|D_I;\alpha_I^{(i-1)}\rangle - \sum_{j=1}^{i-1} E^{(j)}_{D_I;\alpha_I} \langle \psi_p^{(0)}|D_I;\alpha_I^{(i-j)}\rangle = 0 \,, \quad (73)$$

Expanding the state correction with Equation 68, we get

$$\begin{aligned} c_p^{(D_I;\alpha_I)(i)} = &-\frac{1}{E_p^{(0)} - E_D^{(0)}} \Bigg[\sum_{q\notin D} \delta H_{p,q} c_q^{(D_I;\alpha_I)(i-1)} \\ &+ \sum_{J\neq I} \sum_{\beta_J=1}^{N_J} \delta H_{p,D_J;\beta_J} c^{(D_I;\alpha_I)(i-1)}_{D_J;\beta_J} \\ &+ \sum_{\gamma_I=1}^{N_I} \delta H_{p,D_I;\gamma_I} c^{(D_I;\alpha_I)(i-1)}_{D_I;\gamma_I} \\ &- \sum_{j=1}^{i-1} E^{(j)}_{D_I;\alpha_I} c_p^{(D_I;\alpha_I)(i-j)} \Bigg] \,. \end{aligned} \quad (74)$$

All terms except $c_p^{(D_I;\alpha_I)(i)}$ and $c^{(D_I;\gamma_I)(i-1)}_{D_I;\beta_I}$ are known from lower order equations. These two terms will be solved together with Equation 72 of the $(i+1)$-th order TISE.

- Combination with the $(i-1)$-th order equation
Plugging the $(i-1)$-th order of Equation 74 into the first term of Equation 72 (which is obtained at the i-th order) gives

$$\begin{aligned} &\sum_{p\notin D} \frac{\delta H_{D_I;\gamma_I,p}}{E_p^{(0)} - E_D^{(0)}} \Bigg[\sum_{q\notin D} \delta H_{p,q} c_q^{(D_I;\alpha_I)(i-2)} \\ &+ \sum_{J\neq I} \sum_{\beta_J=1}^{N_J} \delta H_{p,D_J;\beta_J} c^{(D_I;\alpha_I)(i-2)}_{D_J;\beta_J} \\ &+ \sum_{\rho_I=1}^{N_I} \delta H_{p,D_I;\rho_I} c^{(D_I;\alpha_I)(i-2)}_{D_I;\rho_I} \\ &- \sum_{j=1}^{i-2} E^{(j)}_{D_I;\alpha_I} c_p^{(D_I;\alpha_I)(i-1-j)} \Bigg] + E^{(2)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-2)}_{D_I;\gamma_I} \\ &+ \sum_{j=3}^{i-1} E^{(j)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-j)}_{D_I;\gamma_I} = 0 \,. \end{aligned} \quad (75)$$

We simplify third term in the bracket by recognizing the $\mathbf{\Delta}^{(2)}_{D_I}$ operator, as in Equation 61, and obtain

$$\begin{aligned} c^{(D_I;\alpha_I)(i-2)}_{D_I;\gamma_I} = &\frac{1}{E^{(2)}_{D_I;\gamma_I} - E^{(2)}_{D_I;\alpha_I}} \Bigg\{ \sum_{p\notin D} \frac{\delta H_{D_I;\gamma_I,p}}{E_p^{(0)} - E_D^{(0)}} \\ &\times \Bigg[\sum_{q\notin D} \delta H_{p,q} c_q^{(D_I;\alpha_I)(i-2)} \\ &+ \sum_{J\neq I} \sum_{\beta_J=1}^{N_J} \delta H_{p,D_J;\beta_J} c^{(D_I;\alpha_I)(i-2)}_{D_J;\beta_J} \\ &- \sum_{j=1}^{i-2} E^{(j)}_{D_I;\alpha_I} c_p^{(D_I;\alpha_I)(i-1-j)} \Bigg] \\ &+ \sum_{j=3}^{i-1} E^{(j)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-j)}_{D_I;\gamma_I} \Bigg\} \,. \end{aligned} \quad (76)$$

Substituting into Equation 74, we obtain $c_p^{(D_I;\alpha_I)(i-1)}$.

- Projection onto $D_J (J \neq I)$
Projecting Equation 69 onto a state in the D_J subspace, $\langle D_J;\beta_J^{(0)}|$, gives

$$\langle D_J;\beta_J^{(0)}|\delta H|D_I;\alpha_I^{(i-1)}\rangle = \sum_{j=1}^{i-1} E^{(j)}_{D_I;\alpha_I} \langle D_J;\beta_J^{(0)}|D_I;\alpha_I^{(i-j)}\rangle \,, \quad (77)$$

Expanding the state correction with Equation 68, we get

$$\begin{aligned} c^{(D_I;\alpha_I)(i-1)}_{D_J;\beta_J} = &\frac{1}{E^{(1)}_{D_I} - E^{(1)}_{D_J}} \\ &\times \Bigg[\sum_{p\notin D} \delta H_{D_J;\beta_J,p} c_p^{(D_I;\alpha_I)(i-1)} \\ &- \sum_{j=2}^{i-1} E^{(j)}_{D_I;\alpha_I} c^{(D_I;\alpha_I)(i-j)}_{D_J;\beta_J} \Bigg] \end{aligned} \quad (78)$$

We summarize the general procedure for the perturbative theory of a degenerate system with degeneracy resolved at second order:

i) Identify the degenerate subspace D in the basis of unperturbed eigenstates of H_0. Diagonalize δH in D, and take the eigenstates as the trial unperturbed states in this subspace.

ii) Identify the remaining degeneracy in the trial basis space by writing $D = D_1 \oplus D_2 \oplus \cdots$, such that different D_Is have different δH eigenvalues and each D_I subspace is degenerate in δH.

iii) In each D_I subspace, construct the second-order perturbation matrix $\boldsymbol{\Delta}^{(2)}_{D_I}$, according to Equation 51. Then solve its secular equation, Equation 52, by diagonalization and take the eigenstates as the correct unperturbed states.

iv) Calculate the perturbation correction to the states whose unperturbed states are in the degenerate subspace D according to Equations 71, 74, 76, and 78.

v) Calculate the perturbation correction to the states whose unperturbed states are in the non-degenerate subspace according to Equations 16 and 20.

If the degeneracy is not fully removed in second order, one has to proceed to higher orders. In some cases, as in the problem discussed in the next section, the degeneracy may persist in all orders. In such scenarios, symmetries of the Hamiltonian can be used to decompose the Hilbert space into decoupled subspaces, where the degeneracy exists between subspaces, not within them. Perturbation theory can then be applied to each subspace separately.

Application: Dressed Quark Prototype

We now apply time-independent perturbation theory to the dressed quark in Quantum Chromodynamics (QCD). In the QCD Hamiltonian formalism, a dressed quark is represented by the eigenstate in the expanded Fock space $|q\rangle + |qg\rangle + \cdots$ with the quantum numbers of a single quark. Here, we extract a prototype from the more extensively studied dressed quark scattering problem in high-energy nuclear physics[19].

Consider a simplified Hilbert space of $|q\rangle + |qg\rangle$, where the $|q\rangle$ sector contains the two spin states of the quark, $s_q = \pm 1/2$, and the $|qg\rangle$ sector contains the four quark-gluon spin states, $\{s_q, s_g\} = \{+1/2, +1\}, \{+1/2, -1\}, \{-1/2, +1\}$, and $\{-1/2, -1\}$. All other quantum numbers, including color and momentum (total for quark-gluon states), are chosen to be the same, allowing quark and quark-gluon states to couple through the $q \leftrightarrow qg$ vertex interaction. The resulting Hamiltonian is given by $H = H_0 + \lambda \delta H$, with

$$H_0 = \text{diag}\{a, a, b, b, b, b\}\,,$$
$$\delta H = \begin{bmatrix} 0 & 0 & u^R & v^R & w & 0 \\ 0 & 0 & 0 & -w & v^L & u^L \\ u^L & 0 & 0 & 0 & 0 & 0 \\ v^L & -w & 0 & 0 & 0 & 0 \\ w & v^R & 0 & 0 & 0 & 0 \\ 0 & u^R & 0 & 0 & 0 & 0 \end{bmatrix}\,. \tag{79}$$

The unperturbed Hamiltonian H_0 is degenerate in the $|q\rangle$ and the $|qg\rangle$ sectors, with $a, b > 0$, denoting the kinetic energy of the quark and the quark-gluon states respectively. The perturbation δH is the interaction for the gluon emission and absorption, and its structure is extracted from the vertex interaction such that $u^{R/L} = ue^{\pm i\theta_u}$, $v^{R/L} = ve^{\pm i\theta_v}$, and $u, v, w > 0$.

The unperturbed eigenstates and eigenvalues are,

$$\begin{aligned} E^{(0)}_{1,m} &= a\,, \ (m = 1, 2), & |v^{(0)}_{1,1}\rangle &= [1, 0, 0, 0, 0, 0]^T\,, \\ & & |v^{(0)}_{1,2}\rangle &= [0, 1, 0, 0, 0, 0]^T\,, \\ E^{(0)}_{2,p} &= b\,, \ (p = 1, 2, 3, 4), & |v^{(0)}_{2,1}\rangle &= [0, 0, 1, 0, 0, 0]^T\,, \\ & & |v^{(0)}_{2,2}\rangle &= [0, 0, 0, 1, 0, 0]^T\,, \\ & & |v^{(0)}_{2,3}\rangle &= [0, 0, 0, 0, 1, 0]^T\,, \\ & & |v^{(0)}_{2,4}\rangle &= [0, 0, 0, 0, 0, 1]^T\,. \end{aligned} \tag{80}$$

There are two degenerate subspaces: $\mathbb{V}_1$ spanned by $v^{(0)}_{1,m}$, and $\mathbb{V}_2$ spanned by $v^{(0)}_{2,p}$. Since δH is already diagonal within each subspace, the degeneracy remains unbroken at first order and we need to treat the degeneracy at second order. We write out the second-order energy fluctuation operator according to Equation 51. For the subspace $\mathbb{V}_1$,

$$\boldsymbol{\Delta}^{(2)}_{\mathbb{V}_1} = -\frac{1}{b-a}\begin{bmatrix} \Delta^2 & 0 \\ 0 & \Delta^2 \end{bmatrix}\,, \tag{81}$$

where we define $\Delta^2 \equiv u^2 + v^2 + w^2$. It is already diagonal, which means that the original basis is already the good basis in $\mathbb{V}_1$, and the diagonal elements are the second order energy correction,

$$\begin{aligned} &E^{(2)}_{1,1} = E^{(2)}_{1,2} = -\frac{1}{b-a}\Delta^2\,, \\ &\{|\psi^{(0)}_{1,1}\rangle\,, |\psi^{(0)}_{1,2}\rangle\} = \{|v^{(0)}_{1,1}\rangle\,, |v^{(0)}_{1,2}\rangle\}\,. \end{aligned} \tag{82}$$

For the subspace $\mathbb{V}_2$,

$$\boldsymbol{\Delta}^{(2)}_{\mathbb{V}_2} = \frac{1}{b-a}\begin{bmatrix} u^2 & u^L v^R & u^L w & 0 \\ u^R v^L & v^2 + w^2 & 0 & -u^L w \\ u^R w & 0 & v^2 + w^2 & u^L v^R \\ 0 & -u^R w & u^R v^L & u^2 \end{bmatrix}\,. \tag{83}$$

By diagonalizing $\boldsymbol{\Delta}^{(2)}_{\mathbb{V}_2}$, we find the good basis and the second-order energy correction simultaneously,

$$\begin{aligned} E^{(2)}_{2,1} &= 0, & |\psi^{(0)}_{2,1}\rangle &= \frac{1}{\Delta u}[0, 0, -u^L v^R, u^2, 0, wu^R]^T\,, \\ E^{(2)}_{2,2} &= 0, & |\psi^{(0)}_{2,2}\rangle &= \frac{1}{\Delta u}[0, 0, -wu^L, 0, u^2, -v^L u^R]^T\,, \\ E^{(2)}_{2,3} &= \frac{\Delta^2}{b-a}, & |\psi^{(0)}_{2,3}\rangle &= \frac{1}{\Delta}[0, 0, u^L, v^L, w, 0]^T\,, \\ E^{(2)}_{2,4} &= \frac{\Delta^2}{b-a}, & |\psi^{(0)}_{2,4}\rangle &= \frac{1}{\Delta}[0, 0, 0, -w, v^R, u^R]^T\,. \end{aligned} \tag{84}$$

Note that the degeneracy is not completely broken at second order. Let us write out the Hamiltonian in the good basis $\{|\psi^{(0)}_{n,m}\rangle\}$,

$$\tilde{H}_0 = \text{diag}\{a, a, b, b, b, b\}\,,$$
$$\delta\tilde{H} = \begin{bmatrix} 0 & 0 & 0 & 0 & \Delta & 0 \\ 0 & 0 & 0 & 0 & 0 & \Delta \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \Delta & 0 & 0 & 0 & 0 & 0 \\ 0 & \Delta & 0 & 0 & 0 & 0 \end{bmatrix}\,. \tag{85}$$

The system decouple into three blocks as $\tilde{H}_0 = \tilde{H}_{0,1} \oplus \tilde{H}_{0,2} \oplus \tilde{H}_{0,3}$ and $\delta\tilde{H} = \delta\tilde{H}_1 \oplus \delta\tilde{H}_2 \oplus \delta\tilde{H}_3$, with

$$\begin{aligned}
\mathbb{V}_{Q,1} &= \{|\psi^{(0)}_{1,1}\rangle, |\psi^{(0)}_{2,3}\rangle\}, \quad \tilde{H}_{0,1} = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}, \delta\tilde{H}_1 = \begin{bmatrix} 0 & \Delta \\ \Delta & 0 \end{bmatrix}, \\
\mathbb{V}_{Q,2} &= \{|\psi^{(0)}_{1,2}\rangle, |\psi^{(0)}_{2,4}\rangle\}, \quad \tilde{H}_{0,2} = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}, \delta\tilde{H}_2 = \begin{bmatrix} 0 & \Delta \\ \Delta & 0 \end{bmatrix}, \\
\mathbb{V}_{qge} &= \{|\psi^{(0)}_{2,1}\rangle, |\psi^{(0)}_{2,2}\rangle\}, \quad \tilde{H}_{0,3} = \begin{bmatrix} b & 0 \\ 0 & b \end{bmatrix}, \delta\tilde{H}_3 = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}.
\end{aligned} \tag{86}$$

We proceed the perturbation calculations separately for each block. The subspaces $\mathbb{V}_{Q,1}$ and $\mathbb{V}_{Q,2}$ have identical structures, reflecting the degeneracy of spin-up and spin-down dressed quarks. Applying nondegenerate perturbation theory via Equations 16 and 20, we obtain the solution for each subspace. For $\mathbb{V}_{Q,1}$,

$$\begin{aligned}
E_{1,1}(\lambda) &= a + \lambda^2 \frac{\Delta^2}{a-b} + \lambda^4 \frac{\Delta^4}{(b-a)^3} - \lambda^5 \frac{2\Delta^6}{(b-a)^5} + O(\lambda^8), \\
|\psi_{1,1}(\lambda)\rangle &= |\psi^{(0)}_{1,1}\rangle - \lambda \frac{\Delta}{b-a} |\psi^{(0)}_{2,3}\rangle + \lambda^3 \frac{\Delta^3}{(b-a)^3} |\psi^{(0)}_{2,3}\rangle \\
&\quad - \lambda^5 \frac{2\Delta^5}{(b-a)^5} |\psi^{(0)}_{2,3}\rangle + O(\lambda^7), \\
E_{2,3}(\lambda) &= b + \lambda^2 \frac{\Delta^2}{b-a} + \lambda^4 \frac{\Delta^4}{(a-b)^3} - \lambda^5 \frac{2\Delta^6}{(a-b)^5} + O(\lambda^8), \\
|\psi_{2,3}(\lambda)\rangle &= |\psi^{(0)}_{2,3}\rangle - \lambda \frac{\Delta}{a-b} |\psi^{(0)}_{1,1}\rangle + \lambda^3 \frac{\Delta^3}{(a-b)^3} |\psi^{(0)}_{1,1}\rangle \\
&\quad - \lambda^5 \frac{2\Delta^5}{(a-b)^5} |\psi^{(0)}_{1,1}\rangle + O(\lambda^7).
\end{aligned} \tag{87}$$

The result is the same for $\mathbb{V}_{Q,2}$ if we swap indices "1,1"→"1,2" and "2,3"→"2,4". The subspace $\mathbb{V}_{qge}$ is perturbation-free, so the unperturbed eigenstates are the exact solution,

$$\begin{aligned}
E_{2,1}(\lambda) &= b, \qquad |\psi_{2,1}(\lambda)\rangle = |\psi^{(0)}_{2,1}\rangle, \\
E_{2,2}(\lambda) &= b, \qquad |\psi_{2,2}(\lambda)\rangle = |\psi^{(0)}_{2,2}\rangle.
\end{aligned} \tag{88}$$

For comparison, we find the exact solutions of the full Hamiltonian H by diagonalization. The eigenvector space splits into three degenerate subspaces with the following eigenvalues and eigenstates:

$$\begin{aligned}
E_1 &= \frac{1}{2}(a+b-\eta), \\
|\phi_{1,1}\rangle &= \frac{1}{N_-}[b-a+\eta, 0, -2\lambda u^L, -2\lambda v^L, -2\lambda w, 0]^T, \\
|\phi_{1,2}\rangle &= \frac{1}{N_-}[0, b-a+\eta, 0, 2\lambda w, -2\lambda v^R, -2\lambda u^R]^T, \\
E_2 &= \frac{1}{2}(a+b+\eta), \\
|\phi_{2,1}\rangle &= \frac{1}{N_+}[a-b+\eta, 0, 2\lambda u^L, 2\lambda v^L, 2\lambda w, 0]^T, \\
|\phi_{2,2}\rangle &= \frac{1}{N_+}[0, a-b+\eta, 0, -2\lambda w, 2\lambda v^R, 2\lambda u^R]^T, \\
E_3 &= b, \\
|\phi_{3,1}\rangle &= \frac{1}{\Delta u}[0, 0, -u^L v^R, u^2, 0, w u^R]^T, \\
|\phi_{3,2}\rangle &= \frac{1}{\Delta u}[0, 0, -w u^L, 0, u^2, -v^L u^R]^T.
\end{aligned} \tag{89}$$

Here, we define the quantities $\eta \equiv \sqrt{(a-b)^2 + 4\lambda^2\Delta^2}$ and $N_\pm \equiv \sqrt{(a-b\pm\eta)^2 + 4\lambda^2\Delta^2}$ to reduce the clutter in the algebra. In comparison with the perturbative results we obtained: $\phi_{1,1}$ and $\phi_{1,2}$ are $\psi_{1,1}$ and $\psi_{1,2}$ upon normalization, $\phi_{2,1}$ and $\phi_{2,2}$ are $\psi_{2,3}$ and $\psi_{2,4}$ upon normalization, and $\phi_{3,1}$ and $\phi_{3,2}$ are just $\psi_{2,1}$ and $\psi_{2,2}$. The eigenvalues also agree, seeing that $E_1 = E_{1,1} = E_{1,2}$, $E_2 = E_{2,3} = E_{2,4}$ and $E_3 = E_{2,1} = E_{2,2}$. Although diagonalizing the full Hamiltonian is feasible here due to the relatively small problem size, for higher-dimensional cases—such as those involving multiple momentum and color modes—perturbation theory offers valuable insights to reduce complexity and simplify calculations.

In this problem, the full Hamiltonian remains degenerate at all perturbation orders. Such degeneracy implies the existence of a symmetry operator **S** that commutes with H. Consequently, the Hamiltonian becomes block-diagonal in the **S** eigenspace, allowing each block to be solved independently. Here, the **S** operator is essentially the quark spin projection operator (containing the relative orbital angular momentum between the quark and the gluon). By diagonalizing $\boldsymbol{\Delta}^2$ using the second-order degenerate perturbation theory, we effectively block-diagonalize the Hamiltonian $\tilde{H}$.

Conclusion

In this work, we have presented a systematic derivation of time-independent perturbation theory for systems in which degeneracy is lifted at second order. By carefully analyzing the structure of the perturbative expansion, we established a general procedure for computing energy and state corrections to arbitrary order within this framework. The resulting formulae clarify how higher-order effects generate effective couplings within an initially degenerate subspace and provide a transparent interpretation of the associated second-order operator.

When degeneracy persists at first order but is lifted at second order, the perturbative structure acquires additional subtleties that are not fully addressed in standard treatments. By organizing the expansion consistently and making explicit the role of intermediate states outside the degenerate subspace, we obtain expressions that are systematic and directly applicable to practical calculations. Beyond the prototype dressed quark example considered here, this formalism may apply to a wide range of degenerate or near-degenerate systems encountered in molecular spectroscopy, atomic and nuclear structure, condensed matter physics, and effective Hamiltonian approaches in quantum field theory. As an illustration, in the hydrogen atom the unperturbed energies depend only on the principal quantum number n; a perturbation preserving rotational symmetry at first order may split the l degeneracy while leaving m degenerate, with a second-order symmetry-breaking term lifting the remaining m degeneracy—precisely the type of scenario addressed here.

We hope that the formulation presented here will serve both as a pedagogical clarification and as a practical tool for tackling complex perturbative problems in quantum physics.

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