Explicit Solution for the Wavefunction and Energy in Degenerate Rayleigh–Schrödinger Perturbation Theory*

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The Rayleigh–Schrödinger perturbation series for the energy and wavefunction are derived for the case that the zeroth-order state is degenerate. The solution, embodied in four "rules," is a generalization of the nondegenerate formulas of Huby and Brueckner. The derivation consists of redefining the unperturbed Hamiltonian and the perturbation (in a particular way) so as to remove the degeneracy, then rearranging the terms in the nondegenerate series in the new perturbation according to the order in the old perturbation. The "choice" of "correct" zeroth-order functions falls out in a natural way, as do the components of the wavefunction in the degenerate unperturbed subspace. The solution given here is not directly related to the degenerate problems solved previously by Kato and by Bloch, in that their solutions do not lead directly to the Rayleigh–Schrödinger series for the energy and wavefunction. The present solution is more related to the one given by Hirschfelder (both being solutions of the same problem), but it differs in not involving the recursively defined operators $Q_i^{(n)}$, in being expressed in terms of quantities directly related to the unperturbed Hamiltonian and the perturbation, and in the method of derivation. (An explicit representation of Hirschfelder's $Q_i^{(n)}$ is given in Appendix C.)

I. INTRODUCTION

Degenerate Rayleigh–Schrödinger perturbation theory ex[redacted]udes opacity. Standard quantum mechanics texts usually treat only the lowest orders, and then only if the degeneracy is completely removed in first or second order. In contrast with the nondegenerate case, no specific procedures for obtaining the higher-order energies and wavefunctions are given. Indeed, a general, recursive solution has only recently been worked out by Hirschfelder,[1] and a general approach, based on repeated application of the partitioning technique discussed by Löwdin,[2] has been outlined by Choi.[3]

The purpose of this paper is to derive an explicit, nonrecursive solution to the Rayleigh–Schrödinger perturbation problem for a state degenerate in zeroth order. The *form* of the solution is a generalization of the nondegenerate formal solution of Huby[4] and Brueckner.[5] The philosophy of the derivation embodies the spirit of perturbation theory itself—the deduction of the unknown as a perturbation of the known. By a suitable redefinition of the unperturbed Hamiltonian and the perturbation, the degenerate problem is recast as a nondegenerate problem. The terms in the known solution of the nondegenerate problem are then rearranged to give a solution of the degenerate problem. A feature of the approach is that the "correct zeroth-order functions" fall out in a natural way, and no extra effort need be expended to obtain the components of the perturbed wavefunction in the space spanned by the degenerate zeroth-order functions.

Some years ago Kato[6] derived a Rayleigh–Schrödinger expansion for the projection operator P onto the subspace of the perturbed functions that are degenerate in zeroth order. Later Bloch[7] derived a simpler expansion for an operator U, defined by

$$PP_0=UP_0PP_0, \tag{1}$$

$$UP_0=U, \tag{2}$$

where P_0 is the projection operator onto the space of unperturbed degenerate functions. Both approaches lead to energies and wavefunctions via secular equations involving the expansions for P or U, correct through, say, the nth order. One is *not* led to a series expansion (in the perturbation) for the wavefunction and energy.[8] Thus these projection-operator approaches do not lead to the Rayleigh–Schrödinger expansions for the wavefunction and energy. In this paper, "Rayleigh–Schrödinger expansion" is always used in the sense, "power series expansion in the perturbation."

Hirschfelder's approach[1] does lead directly to the Rayleigh–Schrödinger expansions for the energy and the wavefunction. Hirschfelder's solution is cast in terms of certain operators, denoted $Q_{n-2}^{(n)}$. The $Q_{n-2}^{(n)}$ are the apex of a recursively defined heirarchy of operators $Q_i^{(n)}$. The base of the heirarchy, the $Q_0^{(n)}$, are recursively defined from the perturbation and the perturbed energies of orders $\leq n$. Hirschfelder's derivation involves inductively replacing the Rayleigh–Schrödinger version of the Schrödinger equation by equations involving $Q_0^{(n)}$, then $Q_1^{(n)}$, then $\cdots Q_{n-2}^{(n)}$. The present approach differs from Hirschfelder's in that no such intermediate $Q_i^{(n)}$ operators need be defined, most quantities are expressed directly in terms of the perturbation and unperturbed Hamiltonian, and the solution is obtained directly from the nondegenerate solution. Some of the concepts and definitions introduced by Hirschfelder, however, play a key role here, and an explicit, nonrecursive recipe for Hirschfelder's $Q_i^{(n)}$ drops out of the present approach.

The final results of Choi's approach[3] are also the Rayleigh–Schrödinger expansions for the energy and wavefunction. However, use of his methods requires first the definition of "effective Hamiltonians" $\mathcal{H}_l$ and resolvents T_l, then the expansion of $\mathcal{H}_l$ and T_l in powers of V. These expansions are carried out in Choi's paper[3] for the first few orders of three special cases, but they are not given explicitly for the general case. Moreover, there are extensive cancellations in Choi's method that are not discussed by Choi. The equivalent terms here are already cancelled and do not contribute to the final expressions.

The paper is organized as follows: Section II contains the statement of the problem. In Sec. III, the method of solution is first outlined; the solution is derived for the special case of complete removal of the degeneracy in first order, then for the general case in which removal of the degeneracy occurs in several orders. A few examples are given in Sec. IV. The general solution is summarized in four "rules" (Sec. III.F.7), which begin after Eq. (100) and end slightly beyond Eq. (105). In Appendix A, the "choice" of "correct" zeroth-order functions is shown to harbor a subtlety. Some auxiliary operators, which aid in the application of the four rules, and which are reminiscent of Hirschfelder's $Q_i^{(n)}$, appear in Appendix B. The explicit recipe for the $Q_i^{(n)}$ is given in Appendix C. In addition, a simple proof of Huby's nondegenerate rules is given in Sec. III.C.

II. DEFINITIONS

This section, which seems unavoidable, consists almost entirely of definitions.

A. Definition of the Problem

Let H, $H^{(0)}$, and V denote the complete Hamiltonian, the unperturbed Hamiltonian, and the perturbation:

$$H=H^{(0)}+V. \tag{3}$$

Let ψ_0 be an eigenfunction of H with energy E_0, which reduces to the eigenfunction $|0\rangle$ of $H^{(0)}$ with energy $E_0^{(0)}$ when $V\rightarrow 0$:

$$(H-E_0)\psi_0=0, \tag{4}$$

$$(H^{(0)}-E_0^{(0)})\,|\,0\rangle=0, \tag{5}$$

$$\lim_{V\rightarrow 0}\psi_0=|\,0\rangle. \tag{6}$$

The *subscript*, which labels the *state*, should not be confused with the *superscript*, which labels the *order*. Both ψ_0 and E_0 are to be expanded[9] in a power series in the strength of V,

$$\psi_0=|\,0\rangle+\chi^{(1)}+\chi^{(2)}+\cdots, \tag{7}$$

$$E_0=E_0^{(0)}+E_0^{(1)}+E_0^{(2)}+\cdots. \tag{8}$$

The equations for the $\chi^{(n)}$ are simplified by use of the "intermediate normalization":

$$\langle 0\,|\,0\rangle=1 \tag{9}$$

$$=\langle 0\,|\,\psi_0\rangle, \tag{10}$$

$$\langle 0\,|\,\chi^{(n)}\rangle=0 \qquad (n=1,2,\cdots). \tag{11}$$

Equations (3)–(11) yield the Rayleigh–Schrödinger version of the Schrödinger equation,

$$(E_0^{(0)}-H^{(0)})\chi^{(n)}=V\chi^{(n-1)}-\sum_{k=1}^{n-1}E_0^{(k)}\chi^{(n-k)}-E_0^{(n)}\,|\,0\rangle. \tag{12}$$

In the nondegenerate case, $|\,0\rangle$ is a nondegenerate eigenfunction of $H^{(0)}$ and is assumed known. The problem is to solve Eq. (12) for $E_0^{(n)}$ and $\chi^{(n)}$.

Here we are interested in the case that $E_0^{(0)}$ is a g-fold degenerate level of $H^{(0)}$ $(2\leq g<\infty)$. Let $|\,k\rangle$ $(k=0,1,2,\cdots,g-1)$ denote the degenerate members of the $E_0^{(0)}$ level and ψ_k the corresponding perturbed eigenfunctions. Then like Eqs. (5), (6), and (8), we have

$$(H^{(0)}-E_0^{(0)})\,|\,k\rangle=0 \qquad (k=0,1,2,\cdots,g-1), \tag{13}$$

$$\lim_{V\rightarrow 0}\psi_k=|\,k\rangle \qquad (k=0,1,2,\cdots,g-1), \tag{14}$$

$$E_k=E_0^{(0)}+E_k^{(1)}+E_k^{(2)}+\cdots \qquad (k=0,1,2,\cdots,g-1), \tag{15}$$

and also,

$$\langle k\,|\,l\rangle=\delta_{kl}. \tag{16}$$

Although the state labeled "0" is the one of primary interest, some quantities involving its $(g-1)$ partners inadvertently pop up. The subspace spanned by the $|\,k\rangle$ $(k=0,1,\cdots,g-1)$ is assumed known, but generally which vectors are the $|\,k\rangle$ specified by Eqs. (6) and (14) is not known. Moreover, unlike the nondegenerate case, $\chi^{(n)}$ cannot be completely determined from the nth order Eq. (12), because $(E_0^{(0)}-H^{(0)})$ annihilates the components along $|\,k\rangle$ $(k=1,2,\cdots,g-1)$. Both the "choice" of the $|\,k\rangle$ and the matrix elements $\langle k\,|\,\chi^{(m)}\rangle$ can eventually be obtained from repeated use of the orthogonality of the left-hand side of Eq. (12) to the degenerate functions, but the path[1] is neither simple nor straight. The problem then in the degenerate case is to solve Eq. (12) for $|\,0\rangle$, the $E_0^{(n)}$, and the $\chi^{(n)}$, and the quagmire is the determination of $|\,0\rangle$ and the matrix elements $\langle k\,|\,\chi^{(n)}\rangle$, $(k=1,2,\cdots,g-1)$.

B. Classification of Zeroth-Order States by the Order in Which Their Degeneracy with ψ_0 is Removed

It is useful to characterize the degenerate functions by the order in which their degeneracy with ψ_0 is removed. Following Hirschfelder,[1] we define the class C_n as the set of all states $|\,k\rangle$ whose degeneracy is *first* removed from ψ_0 in the nth order. Thus,

$$C_1=\{|\,k\rangle\,|\,E_k^{(0)}=E_0^{(0)} \quad (\text{i.e., } 1\leq k\leq g-1), \text{ and } E_k^{(1)}\neq E_0^{(1)}\}, \tag{17}$$

$$C_2=\{|\,k\rangle\,|\,E_k^{(0)}=E_0^{(0)},\,E_k^{(1)}=E_0^{(1)},\,E_k^{(2)}\neq E_0^{(2)}\}, \tag{18}$$

and, in general,

$$C_n=\{|\,k\rangle\,|\,E_k^{(i)}=E_0^{(i)}\ (i\leq n-1),\,E_k^{(n)}\neq E_0^{(n)}\}. \tag{19}$$

If we let $|\,k\rangle$ for $k\geq g$, denote the eigenfunctions of $H^{(0)}$ with unperturbed energy $\neq E_0^{(0)}$, then we can also write

$$C_0=\{|\,k\rangle\,|\,k=g,\,g+1,\cdots\}. \tag{20}$$

Note[1] that $|\,0\rangle$ belongs to no class. Note also that a given state $|\,k\rangle$ is classified according to its behavior with respect to ψ_0, and not with respect to any of the other ψ_l.

We explicitly assume that ψ_0 is a nondegenerate eigenfunction of H. Then each of the $g-1$ states $|k\rangle$ $(1\leq k\leq g-1)$ belongs to some class, and the number of nonvacuous classes is finite $(\leq g-1)$. The generalization to the case that ψ_0 itself is degenerate because of symmetry is straightforward but will not be discussed here.

III. SOLUTION OF THE DEGENERATE PROBLEM

A. Approach and First Step

A logical way to avoid the degenerate problem but stay within the realm of perturbation theory would be to redefine $H^{(0)}$ so as to remove the degeneracy. If the new $\mathcal{H}^{(0)}$ differed from the old $H^{(0)}$ by terms proportional to various powers of V, one might be able to rearrange the (new) nondegenerate series to obtain the (old) degenerate series. Of the infinity of possible redefinitions, one seems to be the least arbitrary and the most reasonable, and it turns out to be essentially the only redefinition that makes the rearrangement of the series tractable. (See, however, Appendix A.) The redefinition is *to shift the energy of each state* $|k\rangle$ $(k=1, 2,\cdots, g-1)$ *in the new zeroth-order Hamiltonian* $\mathcal{H}^{(0)}$ *by an amount equal to its lowest-order nonvanishing energy splitting with respect to* ψ_0. The shift for $|k\rangle$ belonging to class C_i would be $(E_k^{(i)}-E_0^{(i)})$. Accordingly, define $\mathcal{H}^{(0)}$ and $\mathcal{V}$ by

$$\mathcal{H}^{(0)}=H^{(0)}+\sum_{i\geq 1}\sum_{k\epsilon C_i}|k\rangle(E_k^{(i)}-E_0^{(i)})\langle k|, \tag{21}$$

$$\mathcal{V}=V-\sum_{i\geq 1}\sum_{k\epsilon C_i}|k\rangle(E_k^{(i)}-E_0^{(i)})\langle k|. \tag{22}$$

Note that the index i enumerates the class, k the states in C_i. The number of nonzero terms is $g-1$.

[In Eqs. (21) and (22), and subsequently throughout the paper, $k\in C_i$ is consistently used in place of the more cumbersome $|k\rangle\in C_i$ that Eqs. (17)–(20) would seem to dictate.]

B. Chicken or Egg. "Correct" Zeroth-Order Functions. Notation

There is a slight difficulty with the redefinitions of Eqs. (21) and (22): the "correct" zeroth-order functions and the $(E_k^{(i)}-E_0^{(i)})$ are not known in advance. It is *essential* that $|0\rangle$ be the correct zeroth-order function specified by Eq. (6) so that

$$\lim_{\mathcal{V}\to 0}\psi_0=\lim_{V\to 0}\psi_0, \tag{23}$$

$$=|0\rangle. \tag{24}$$

For $k\neq 0$, *until demonstrated otherwise, the* $|k\rangle$ *in Eqs. (21) and (22) are to be regarded as arbitrary (but orthonormal) functions in the g-dimensional degenerate subspace, and the* $(E_k^{(i)}-E_0^{(i)})$ *as arbitrary quantities proportional to the* ith *power of the strength of* V. During the derivation, $|0\rangle$ turns out to be an eigenfunction of certain operators (a property that operationally determines $|0\rangle$). The other $|k\rangle$ are chosen to be eigenfunctions of some of the operators, and the $E_k^{(i)}$ *defined* as the corresponding eigenvalues, *for convenience*. At the end the $E_k^{(i)}$ so defined are shown to be the $E_k^{(i)}$ appearing in Eq. (15). The $|k\rangle$, so specified, are *consistent* with Eq. (14) in the following sense: If $k\in C_i$ and $l\in C_i$, then $|k\rangle$ and $|l\rangle$ will not have been distinguished from each other if $E_k^{(i)}=E_l^{(i)}$. This remaining indeterminency has no consequence for ψ_0. Particular linear combinations of the $|k\rangle$ that share a common value for $E_k^{(i)}$ will satisfy Eq. (14), but any orthonormal linear combinations are "correct" for ψ_0 [cf. Eqs. (21) and (22)].

It would be more precise to use new symbols in Eqs. (21) and (22) and to replace them by $|k\rangle$ and $(E_k^{(i)}-E_0^{(i)})$ only after they were shown to have those meanings. The concomitant explanation, however, seems so involved, that clarity would probably be the price of precision. Consequently, we have decided to use the notation that is consistent with the ultimate (although not initial) significance of the quantities, with the caveat to reread the paragraph preceding this one.

C. Nondegenerate Formulas of Huby and Brueckner

By construction, $E_0^{(0)}$ is a nondegenerate level of $\mathcal{H}^{(0)}$. Any of the several explicit nondegenerate formulas[4–7,10] can be used to evaluate E_0 and ψ_0 as power series in the strength of $\mathcal{V}$. In the present context, the solution of Huby[4] and Brueckner[5] is the easiest to deal with. Denote the nth-order energy and wavefunction with respect to $\mathcal{V}$ by $\mathcal{E}_0^{(n)}$ and $X^{(n)}$. Then $\mathcal{E}_0^{(n)}$ and $X^{(n)}$ are constructed according to two rules given by Huby,[4] slightly corrupted here for notational consistency.

The rules, which involve the reduced resolvent operator $\mathcal{R}$,

$$\mathcal{R}=(1-|0\rangle\langle 0|)/(E_0^{(0)}-\mathcal{H}^{(0)}), \tag{25}$$

are:

Nondegenerate Rule 1 (Huby). To find $\mathcal{E}_0^{(n)}$ first write down the basic matrix element,

$$\langle 0|\mathcal{V}(\mathcal{R}\mathcal{V})^{n-1}|0\rangle. \tag{26}$$

Add to this basic matrix element all other expressions that can be obtained from it by inserting any number of bra-ket brackets around the $\mathcal{V}$ factors other than the first or the last. The bra and ket of a pair may be separated by any number of link factors

$$\mathcal{V}\mathcal{R}\mathcal{V}\mathcal{R}\cdots\mathcal{V}, \tag{27}$$

and brackets may lie within brackets, but one bra-ket pair may not straddle another, and no brackets may touch. The sign $(-1)^\nu$ is attached to the expressions, where ν is the number of bra-ket pairs inserted in it. Each bra-ket pair signifies the expectation value of the enclosed operator in the state $|0\rangle$,

$$\langle\mathcal{V}\cdots\mathcal{V}\rangle\equiv\langle 0|\mathcal{V}\cdots\mathcal{V}|0\rangle. \tag{28}$$

Nondegenerate Rule 2 (Huby). To find $X^{(n)}$, first write down the basic function,

$$(\mathcal{R}\mathcal{V})^n \mid 0\rangle. \tag{29}$$

Add to this all expressions that can be obtained from it by inserting any number of bra-ket pairs around the $\mathcal{V}$ factors other than the last (furthest right). The rules for arranging and interpreting the brackets, and for the sign, are the same as those in Rule 1.

Huby proved these rules from Bloch's formulas.[7] An alternative proof follows inductively from Eqs. (12) (with $\mathcal{V}$ and $\mathcal{H}^{(0)}$ replacing V and $H^{(0)}$). The rules are trivially true for $\mathcal{E}_0^{(1)}$, $\mathbf{X}^{(1)}$, and $\mathcal{E}_0^{(2)}$. Then, assuming the rules true through $\mathbf{X}^{(n-1)}$ and $\mathcal{E}_0^{(n)}$, we solve Eq. (12) for $\mathbf{X}^{(n)}$,

$$\mathbf{X}^{(n)} = \mathcal{R}\mathcal{V}\mathbf{X}^{(n-1)} - \sum_{k=1}^{n-1} \mathcal{R}\mathcal{E}_0^{(k)}\mathbf{X}^{(n-k)}, \tag{30}$$

and note that $\mathcal{R}\mathcal{V}\mathbf{X}^{(n-1)}$ consists of all terms obtained with Rule 2, except those with a bra to the left of the first $\mathcal{V}$, and that $\mathcal{R}\mathcal{E}_0^{(k)}\mathbf{X}^{(n-k)}$ consists of all terms obtained with Rule 2 for which the ket partner of the bra to the left of the first $\mathcal{V}$ lies $k\mathcal{V}$'s to the right. Rule 1 for $\mathcal{E}_0^{(n+1)}$ follows immediately from the formula,

$$\mathcal{E}_0^{(n+1)} = \langle 0 \mid \mathcal{V} \mid \mathbf{X}^{(n)}\rangle. \tag{31}$$

Explicitly, the first few $\mathbf{X}^{(n)}$ and $\mathcal{E}_0^{(n)}$ are

$$\mathbf{X}^{(1)} = \mathcal{R}\mathcal{V} \mid 0\rangle, \tag{32}$$

$$\mathbf{X}^{(2)} = \mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}\mathcal{V} \mid 0\rangle, \tag{33}$$

$$\mathbf{X}^{(3)} = \mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}\mathcal{V} \mid 0\rangle - \mathcal{R}\langle\mathcal{V}\mathcal{R}\mathcal{V}\rangle\mathcal{R}\mathcal{V} \mid 0\rangle, \tag{34}$$

$$\mathcal{E}_0^{(1)} = \langle 0 \mid \mathcal{V} \mid 0\rangle, \tag{35}$$

$$\mathcal{E}_0^{(2)} = \langle 0 \mid \mathcal{V}\mathcal{R}\mathcal{V} \mid 0\rangle, \tag{36}$$

$$\mathcal{E}_0^{(3)} = \langle 0 \mid \mathcal{V}\mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}\mathcal{V} \mid 0\rangle, \tag{37}$$

$$\mathcal{E}_0^{(4)} = \langle 0 \mid \mathcal{V}\mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}(\mathcal{V} - \langle\mathcal{V}\rangle)\mathcal{R}\mathcal{V} \mid 0\rangle - \langle 0 \mid \mathcal{V}\mathcal{R}\langle\mathcal{V}\mathcal{R}\mathcal{V}\rangle\mathcal{R}\mathcal{V} \mid 0\rangle. \tag{38}$$

D. Decomposition of $\mathcal{R}$

The $\mathbf{X}^{(n)}$ and $\mathcal{E}_0^{(n)}$, given in terms of $\mathcal{V}$ and $\mathcal{R}$, can be re-expressed in terms of $H^{(0)}$- and V-related quantities by substituting the definition of $\mathcal{V}$ [Eq. (22)] and a suitable formula for $\mathcal{R}$ [Eq. (40) below]. One obtains for $\mathcal{R}$ from Eqs. (25) and (21),

$$\mathcal{R} = \sum_{i\geq 0}\sum_{k\in C_i} \frac{\mid k\rangle\langle k \mid}{E_0^{(i)} - E_k^{(i)}}, \tag{39}$$

$$= \sum_{i\geq 0} R^{(-i)}, \tag{40}$$

where the partial reduced resolvent $R^{(-i)}$ for the Class C_i,

$$R^{(-i)} \equiv \sum_{k\in C_i} \frac{\mid k\rangle\langle k \mid}{E_0^{(i)} - E_k^{(i)}}, \tag{41}$$

defined originally by Hirschfelder,[1] is proportional to the $(-i)$th power of V,

$$R^{(-i)} \sim V^{-i}. \tag{42}$$

The number of nonzero terms in Eq. (40) is finite $(\leq g)$.

Note that when Eqs. (22) and (40) for $\mathcal{V}$ and $\mathcal{R}$ are substituted into $\sum_n \mathbf{X}^{(n)}$ and $\sum_n \mathcal{E}_0^{(n)}$, because of the negative orders in $\mathcal{R}$, there appear to be terms of arbitrary negative order in V and an infinite number of terms of any given order. In fact, the elimination of nonpositive orders and the elimination of all but a finite number of terms of each positive order result in the determination of the $\mid k\rangle$ and $E_k^{(i)}$.

The orthonormality of the unperturbed functions [Eq. (16)] results in some immediate simplification in using Eqs. (22) and (40):

$$\mathcal{V}R^{(0)} = VR^{(0)}, \tag{43}$$

$$\mathcal{V} \mid 0\rangle = V \mid 0\rangle, \tag{44a}$$

or equivalently,

$$\cdots\mathcal{V}\rangle = \cdots V\rangle, \tag{44b}$$

$$\cdots R^{(-i)}\langle V\cdots V\rangle R^{(-j)}\cdots = 0 \qquad (i\neq j). \tag{45}$$

E. Special Case. All Degeneracy Lifted in First Order

The special case of complete removal of degeneracy in first order illustrates the principles involved in the general case, but the details are simpler.

1. Determination of $\mid 0\rangle$

The correct zeroth-order function $\mid 0\rangle$ is intimately connected with the nonoccurrence of nonpositive powers of V in the rearranged series. By assumption, the i in Eqs. (22) and (40) takes on the maximum value 1:

$$\mathcal{V} = V - \sum_{k\in C_1} \mid k\rangle(E_k^{(1)} - E_0^{(1)})\langle k \mid, \tag{46}$$

$$\mathcal{R} = R^{(0)} + R^{(-1)}. \tag{47}$$

We put Eqs. (46) and (47) into Eq. (32) for $\mathbf{X}^{(1)}$ and use Eq. (44) to obtain

$$\mathbf{X}^{(1)} = R^{(0)}V \mid 0\rangle + R^{(-1)}V \mid 0\rangle. \tag{48}$$

The term $R^{(-1)}V \mid 0\rangle$ is zeroth order with respect to V and should not contribute to ψ_0 [cf. Eqs. (23) and (24)]. The simplest way for $R^{(-1)}V \mid 0\rangle$ not to contribute to ψ_0 is for it to vanish,[11]

$$R^{(-1)}V \mid 0\rangle = 0, \tag{49}$$

which, because of Eq. (41), is equivalent to

$$\langle k \mid V \mid 0\rangle = 0 \qquad (k = 1, 2, \cdots, g-1). \tag{50}$$

That is, the zeroth-order (with respect to V) contribution to $\mathbf{X}^{(1)}$ *vanishes if, and only if,* $\mid 0\rangle$ *is an eigenfunction of the truncated matrix of V in the subspace spanned by the degenerate functions* $\{\mid k\rangle \mid 0 \leq k \leq g-1\}$.

2. *Choice of* $|k\rangle$. *Definition of* $E_k^{(1)}$. *Cancellation of Terms*

The next important result appears in the simplification of $X^{(3)}$. We substitute Eqs. (46) and (47) into Eq. (34) and use Eqs. (43)-(45), and (49) to obtain

$$X^{(3)}=\{R^{(0)}(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$-R^{(0)}\langle VR^{(0)}V\rangle R^{(0)}V\mid 0\rangle\}$$
$$+\{R^{(0)}VR^{(-1)}VR^{(0)}V\mid 0\rangle$$
$$+R^{(-1)}VR^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle\}$$
$$+R^{(-1)}(\mathcal{V}-\langle V\rangle)R^{(-1)}VR^{(0)}V\mid 0\rangle. \quad (51)$$

Note in passing that the terms in the first set of braces in Eq. (51) are identical in form with the nondegenerate result, and that the terms in the second set of braces are second order in V and contribute to $\chi^{(2)}$. We focus now on the combination $R^{(-1)}(\mathcal{V}-\langle V\rangle)R^{(-1)}$ appearing in the last term. With Eqs. (41) and (46) we obtain

$$R^{(-1)}(\mathcal{V}-\langle V\rangle)R^{(-1)}$$
$$=\sum_{k\epsilon C_1}\sum_{l\epsilon C_1}\frac{|k\rangle[\langle k\mid V\mid l\rangle-\delta_{kl}(E_k^{(1)}-E_0^{(1)}+\langle V\rangle)]\langle l|}{(E_0^{(1)}-E_k^{(1)})(E_0^{(1)}-E_l^{(1)})}. \quad (52)$$

Considerable simplification results from choosing the remaining $(g-1)$ degenerate functions $|k\rangle$ to "diagonalize" V, i.e.,

$$\langle k\mid V\mid l\rangle=\delta_{kl}E_k^{(1)} \qquad [0\leq(k,l)\leq g-1], \quad (53)$$

with the eigenvalues *defining* the $E_k^{(1)}$ in Eqs. (21) and (22). Then

$$R^{(-1)}(\mathcal{V}-\langle V\rangle)R^{(-1)}=0, \quad (54)$$

and the last term in Eq. (51) vanishes.

The cancellation expressed in Eq. (54) is a two-part key to the success of the rearrangement approach. One part is the simplicity of going from $\mathcal{V}$ and $\mathcal{R}$ to V, $R^{(0)}$ and $R^{(-1)}$: The $\mathcal{V}$ always becomes V [Eqs. (43) and (44)]; terms with two consecutive $R^{(-1)}$ are dropped [Eq. (54)]. The second, perhaps more profound part is that only a finite number of terms can contribute to each order in V. In a given term in the re-expression of $X^{(n)}$ and $\mathcal{E}_0^{(n)}$, no more than half of the $R^{(-i)}$ can be $R^{(-1)}$, the rest being $R^{(0)}$, so that the lowest order terms in $X^{(n)}$ and $\mathcal{E}_0^{(n)}$ are approximately of order $n/2$. More precisely, $\chi^{(n)}$ receives contributions from $X^{(n)}$, $X^{(n+1)}$, $\cdots$, $X^{(2n)}$, but not from $X^{(i)}$ with $i>2n$, and $E_0^{(n)}$ receives contributions from $\mathcal{E}_0^{(n)}$, $\mathcal{E}_0^{(n+1)},\cdots$, $\mathcal{E}_0^{(2n-2)}$, but not from $\mathcal{E}_0^{(n+i)}$ with $i>n-2$.

This second consequence of Eq. (54) is important enough to look at another way: Any $R^{(-1)}$ appearing in $X^{(n)}$ or $\mathcal{E}_0^{(n)}$ necessarily appears with a second-order factor immediately to the right,

$$\cdots R^{(-1)}VR^{(0)}V\cdots, \quad (55)$$

$$\cdots R^{(-1)}VR^{(0)}\langle V\cdots\rangle\cdots, \quad (56)$$

or

$$\cdots R^{(-1)}\langle VR^{(0)}V\cdots\rangle\cdots, \quad (57)$$

so that the order of a given term is at least equal to the number of $R^{(-1)}$.

3. *Rule for Expressing* $X^{(n)}$ *and* $\mathcal{E}_0^{(n)}$ *in terms of* V, $R^{(0)}$, *and* $R^{(-1)}$. *Illustrations*

The results of the preceeding section are conveniently summarized by two rules (which apply only when degeneracy is completely removed in first order):

Zeroth-order-functions rule. The "correct" zeroth-order functions $|k\rangle$ diagonalize V in the g-dimensional subspace of degenerate functions, the corresponding eigenvalues being the $E_k^{(1)}$.

Rule for expressing $X^{(n)}$ *and* $\mathcal{E}_0^{(n)}$ *in terms of* V, $R^{(0)}$, *and* $R^{(-1)}$. In the expressions obtained with Nondegenerate Rules 1 and 2:

(a) Replace $\mathcal{R}$ by $(R^{(0)}+R^{(-1)})$.

(b) Omit terms having two $R^{(-1)}$ separated by a single $\mathcal{V}$, which vanish because of the cancellation of Eq. (54).

(c) Replace $\mathcal{V}$ by V.

(d) Omit terms of the form

$$\cdots R^{(0)}\langle V\cdots V\rangle R^{(-1)}\cdots$$

and

$$\cdots R^{(-1)}\langle V\cdots V\rangle R^{(0)},$$

which vanish by orthogonality.

(e) Omit terms of the form

$$\cdots R^{(-1)}V\rangle\cdots$$

and

$$\cdots\langle VR^{(-1)}\cdots,$$

which vanish because of the "diagonal" nature of V.

By way of example, the above rules applied to $X^{(1)}$, $X^{(2)}$, $X^{(3)}$, $\mathcal{E}_0^{(1)}$, $\mathcal{E}_0^{(2)}$, $\mathcal{E}_0^{(3)}$, and $\mathcal{E}_0^{(4)}$ [Eqs. (32)-(38)] yield

$$X^{(1)}=R^{(0)}V\mid 0\rangle, \quad (58)$$

$$X^{(2)}=R^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle+R^{(-1)}VR^{(0)}V\mid 0\rangle, \quad (59)$$

$$X^{(3)}=\{R^{(0)}(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$-R^{(0)}\langle VR^{(0)}V\rangle R^{(0)}V\mid 0\rangle\}$$
$$+\{R^{(-1)}VR^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$+R^{(0)}VR^{(-1)}VR^{(0)}V\mid 0\rangle\}, \quad (60)$$

$$\mathcal{E}_0^{(1)}=\langle 0\mid V\mid 0\rangle, \quad (61)$$

$$\mathcal{E}_0^{(2)}=\langle 0\mid VR^{(0)}V\mid 0\rangle, \quad (62)$$

$$\mathcal{E}_0^{(3)}=\langle 0\mid VR^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle, \quad (63)$$

$$\mathcal{E}_0^{(4)}=\langle 0\mid VR^{(0)}(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$-\langle 0\mid VR^{(0)}\langle VR^{(0)}V\rangle R^{(0)}V\mid 0\rangle$$
$$+\langle 0\mid VR^{(0)}VR^{(-1)}VR^{(0)}V\mid 0\rangle. \quad (64)$$

4. Rearrangement. Significance of $E_k^{(1)}$

Since [cf. Eqs. (23) and (24)]

$$\mathbf{X}^{(1)}+\mathbf{X}^{(2)}+\cdots=\chi^{(1)}+\chi^{(2)}+\cdots \quad (65)$$

and

$$\mathcal{E}_0^{(1)}+\mathcal{E}_0^{(2)}+\cdots=E_0^{(1)}+E_0^{(2)}+\cdots, \quad (66)$$

we can apply the re-expression rule, add the $\mathbf{X}^{(i)}$ or $\mathcal{E}_0^{(i)}$ together, and collect terms according to their power of V to obtain the $\chi^{(n)}$ and $E_0^{(n)}$. The results for $\chi^{(1)}$, $\chi^{(2)}$, $E_0^{(1)}$, $E_0^{(2)}$, and $E_0^{(3)}$, which follow from Eqs. (58)–(66) [with a contribution from $\mathbf{X}^{(4)}$ slipped into $\chi^{(2)}$], are

$$\chi^{(1)}=R^{(0)}V\mid 0\rangle+R^{(-1)}VR^{(0)}V\mid 0\rangle, \quad (67)$$

$$\chi^{(2)}=R^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle+R^{(0)}VR^{(-1)}VR^{(0)}V\mid 0\rangle$$
$$+R^{(-1)}VR^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$+R^{(-1)}(VR^{(0)}V-\langle VR^{(0)}V\rangle)R^{(-1)}VR^{(0)}V\mid 0\rangle, \quad (68)$$

$$E_0^{(1)}=\langle 0\mid V\mid 0\rangle, \quad (69)$$

$$E_0^{(2)}=\langle 0\mid VR^{(0)}V\mid 0\rangle, \quad (70)$$

$$E_0^{(3)}=\langle 0\mid VR^{(0)}(V-\langle V\rangle)R^{(0)}V\mid 0\rangle$$
$$+\langle 0\mid VR^{(0)}VR^{(-1)}VR^{(0)}V\mid 0\rangle. \quad (71)$$

Finally, there is one loose end to tie up—the double meaning of $E_k^{(1)}$ and $|k\rangle$. Equations (53) and (69) show that the first-order energy $E_0^{(1)}$ is indeed the same as the eigenvalue of the truncated matrix of V corresponding to the $|0\rangle$. That $E_k^{(1)}$ [Eq. (53)] is the first-order energy corresponding to ψ_k follows from interchanging the roles of 0 and k and applying perturbation theory to ψ_k. This interchange also confirms the "correctness" of the $|k\rangle$ $(k>0)$ to the extent discussed in Sec. II.B.

F. General Case

1. Over-all View

The logic of the general case parallels that of the C_1-only case. The "correct" zeroth order $|k\rangle$ guarantee the vanishing terms proportional to nonpositive powers of V and, with the "definitions" of the $E_k^{(i)}$, guarantee that a given $\chi^{(n)}$ or $E_0^{(n)}$ receives contributions from only a finite number of $\mathbf{X}^{(N)}$ or $\mathcal{E}_0^{(N)}$.

To establish the conditions that determine the "correct" $|k\rangle$, we proceed heuristically to develop the conditions that eliminate the most obvious terms proportional to nonpositive powers of V. In $\mathbf{X}^{(1)}$ the vanishing of $\sum_{i\geq 1}R^{(-i)}V\mid 0\rangle$ leads to the condition that V be "diagonal." The Class C_1 is identified, and $R^{(-1)}$ is completely determined. In $\mathbf{X}^{(2)}+\mathbf{X}^{(3)}+\cdots$, the sum of all terms of the form $R^{(-i)}$ $(i\geq 2)$ times an expression second order in V, involving necessarily $R^{(0)}$ and possibly $R^{(-1)}$, must vanish. The resulting condition identifies the Class C_2 and completely determines $R^{(-2)}$. This aufbau process is continued, so that at the nth stage, the vanishing of the sum of all terms in $\mathbf{X}^{(n)}+\mathbf{X}^{(n+1)}+\cdots$ of the form $R^{(-i)}$ $(i\geq n)$ times an expression nth-order in V, involving also $R^{(-j)}$ $(j<n)$, leads to the identification of the Class C_n and the determination of $R^{(-n)}$. The state $|0\rangle$ is what is left after its $(g-1)$ partners have been assigned to classes.

The conditions determining the C_n and $R^{(-n)}$ are seen to preclude *all terms* proportional to nonpositive powers of V from the series $\sum_{i\geq 1}\mathbf{X}^{(i)}$ and $\sum_{i\geq 1}\mathcal{E}_0^{(i)}$, and to make finite the number of terms of a given order of V in each series. Thus the heuristic procedure will have been justified.

2. Class C_1. "Diagonalization" of V

The first step is essentially the C_1-only case. The result is the separation of Class C_1 from the degenerate subspace. Put Eq. (40) for $\mathcal{R}$ into Eq. (30) for $\mathbf{X}^{(1)}$. Via Eq. (44), one obtains

$$\mathbf{X}^{(1)}=R^{(0)}V\mid 0\rangle+\sum_{i\geq 1}R^{(-i)}V\mid 0\rangle. \quad (72)$$

Require that the $|k\rangle$ be chosen so that V is diagonal in the subspace spanned by $\{|k\rangle, 0\leq k\leq g-1\}$, and denote the eigenvalues by $E_k^{(1)}$:

$$\langle k\mid V\mid l\rangle=\delta_{kl}E_k^{(1)}, \qquad 0\leq(k,l)\leq g-1. \quad (73)$$

Then, as in the C_1-only case, the unwanted terms in $\mathbf{X}^{(1)}$ vanish:

$$R^{(-i)}V\mid 0\rangle=0 \qquad (i\geq 1). \quad (74)$$

The states for which $E_k^{(1)}\neq E_0^{(1)}$ belong to C_1, but the ones (other than $|0\rangle$) for which $E_k^{(1)}=E_0^{(1)}$ belong to higher classes. Thus, Eq. (73) *identifies* C_1, defines the $E_0^{(1)}$ and $E_k^{(1)}$, and completely determines $R^{(-1)}$. The cancellation law that follows from Eq. (73) and the definition of $\mathcal{V}$ [Eq. (22)] has a slightly more general form than in the C_1-only case [Eq. (54)]:

$$R^{(-i)}(\mathcal{V}-\langle V\rangle)R^{(-j)}=0 \quad (i=j=1;\text{ or } i\neq j,\ i\geq 1, j\geq 1). \quad (75)$$

3. Class C_2. "Diagonalization" of $VR^{(0)}V$

Substitute Eq. (40) for $\mathcal{R}$ and Eq. (22) for $\mathcal{V}$ into $\mathbf{X}^{(2)}+\mathbf{X}^{(3)}+\cdots$, and consider all terms that have $R^{(-i)}$ $(i\geq 2)$ followed by a second-order expression in V involving $R^{(0)}$ and possibly $R^{(-1)}$, but not $R^{(-j)}$ $(j>1)$. In fact, Eqs. (74) and (75) preclude $R^{(-1)}$ from entering such an expression of order lower than three. The only term not vanishing because of Eqs. (43)–(45) and (73)–(75) comes entirely from $\mathbf{X}^{(2)}$ and is

$$\sum_{i\geq 2}R^{(-i)}VR^{(0)}V\mid 0\rangle. \quad (76)$$

By the same reasoning as in the C_1-only case, for these unwanted terms to vanish, $|0\rangle$ must be an eigenfunction of the truncated $VR^{(0)}V$ matrix. Similarly [cf. Eqs. (52)–(54)], for simplicity one is lead to the *condition* on the $|k\rangle$ $(|k\rangle\notin C_1)$ that $VR^{(0)}V$ is diagonal in the degenerate subspace with the C_1 subspace removed, with the eigenvalues *defining* the $E_k^{(2)}$,

$$\langle k\mid VR^{(0)}V\mid l\rangle=\delta_{kl}E_k^{(2)}$$
$$[0\leq(k,l)\leq g-1,\ k\notin C_1,\ l\notin C_1]. \quad (77)$$

The states for which $E_k^{(2)}\neq E_0^{(2)}$ constitute the Class C_2; the ones (other than $|0\rangle$) for which $E_k^{(2)}=E_0^{(2)}$ belong to higher classes yet undetermined. In addition to determining $R^{(-2)}$ and implying the vanishing of Eq. (76),

$$R^{(-i)}VR^{(0)}V|0\rangle=0 \qquad (i\geq 2), \qquad (78)$$

Eq. (77), with the definition of $\mathcal{V}$ [Eq. (22)], also leads to a cancellation between terms in $\mathbf{X}^{(n)}$ or $\mathcal{E}_0^{(n)}$ with terms in $\mathbf{X}^{(n+1)}$ or $\mathcal{E}_0^{(n+1)}$:

$$\cdots R^{(-2)}(\mathcal{V}-\langle V\rangle)R^{(-2)}\cdots+\cdots R^{(-2)}\times(VR^{(0)}V-\langle VR^{(0)}V\rangle)R^{(-2)}\cdots$$
$$=\sum_{k\in C_2}\cdots R^{(-2)}|k\rangle[E_k^{(1)}-(E_k^{(2)}-E_0^{(2)})-E_0^{(1)}+E_k^{(2)}-E_0^{(2)}]\langle k|R^{(-2)}\cdots, \qquad (79)$$
$$=0. \qquad (80)$$

{To derive Eqs. (79) and (80), use is made of the definitions of $R^{(-2)}$ [Eq. (41)], the diagonal nature of $\mathcal{V}$ [Eqs. (22) and (73)], the orthogonality of the $|k\rangle$ [Eq. (16)], the diagonal nature of $VR^{(0)}V$ [Eq. (72)], the definitions of $E_l^{(1)}$ and $E_l^{(2)}$ [Eqs. (73) and (78)], and the equality of $E_k^{(1)}$ with $E_0^{(1)}$ for $k\in C_2$.} A slightly more general result is easily obtained:

$$R^{(-i)}(\mathcal{V}-\langle V\rangle+VR^{(0)}V-\langle VR^{(0)}V\rangle)R^{(-j)}=0$$
$$(i=j=2;\text{ or } i\neq j,\ i\geq 2,\ j\geq 2). \qquad (81)$$

A main consequence of Eqs. (78) and (81) is that $R^{(-2)}$ must be separated from the nearest $|0\rangle$, $\langle 0|$, or $R^{(-i)}$ $(i\geq 2)$ by a factor of at least third order in V.

4. Class C_3. "Diagonalization" of $VR^{(0)}(V-\langle V\rangle)\times R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V$

One finds three terms in $\mathbf{X}^{(3)}+\mathbf{X}^{(4)}+\cdots$, having $R^{(-1)}$ $(i\geq 3)$ separated from $|0\rangle$ by an expression third order in V involving no $R^{(-j)}$ $(j\geq 3)$, that do not already vanish because of Eqs. (43)–(45), (73)–(75), (78), and (81). Two come from $\mathbf{X}^{(3)}$ and one from $\mathbf{X}^{(4)}$. The sum is made to vanish,

$$R^{(-i)}[VR^{(0)}VR^{(0)}V-VR^{(0)}\langle V\rangle R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V]|0\rangle=0 \qquad (i\geq 3), \qquad (82)$$

by the requirement on the $|k\rangle$ $(0\leq k\leq g-1,\ k\notin C_1,\ k\notin C_2)$, that

$$\langle k|VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V|l\rangle$$
$$=\delta_{kl}E_k^{(3)}, \quad [0\leq(k,l)\leq g-1,\text{ both } k \text{ and } l\notin C_1,\notin C_2]. \qquad (83)$$

Equation (83) *defines* $E_k^{(3)}$ $(k\in C_i,\ i\geq 3$ or $k=0)$, identifies Class C_3, determines $R^{(-3)}$, and leads to the cancellation between terms in $\mathbf{X}^{(n)}$ or $\mathcal{E}_0^{(n)}$ with terms in $\mathbf{X}^{(n+2)}$ or $\mathcal{E}_0^{(n+2)}$:

$$\cdots R^{(-i)}[\mathcal{V}-\langle V\rangle+VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V-\langle VR^{(0)}(V-\langle V\rangle)R^{(0)}V\rangle-\langle VR^{(0)}VR^{(-1)}VR^{(0)}V\rangle]R^{(-j)}\cdots=0$$
$$(i=j=3;\text{ or } i\neq j,\ i\geq 3,\ j\geq 3). \qquad (84)$$

5. Class C_n. "Diagonalization" of $\mathcal{H}^{(n)}$

The aufbau procedure leads inductively to the following general result. Denote the sum of all terms in $\mathbf{X}^{(n)}+\mathbf{X}^{(n+1)}+\cdots$ of the form $R^{(-i)}$ $(i\geq n)$ times an expression nth order in V, possibly involving various $R^{(-j)}$ $(j<n)$, by

$$R^{(-i)}\mathcal{H}^{(n)}|0\rangle \qquad (i\geq n). \qquad (85)$$

(An explicit rule for obtaining $\mathcal{H}^{(n)}$ is given in Sec. III.F.7.) Require that the $|k\rangle$ $(k\in C_i,\ i\geq n)$ and $|0\rangle$ satisfy

$$\langle k|\mathcal{H}^{(n)}|l\rangle=\delta_{kl}E_k^{(n)} \qquad (k,l=0\text{ or }\in C_i,\ i\geq n), \qquad (86)$$

which also *defines* the $E_k^{(n)}$. Then

$$R^{(-i)}\mathcal{H}^{(n)}|0\rangle=0 \qquad (i\geq n). \qquad (87)$$

The states for which $E_k^{(n)}\neq E_0^{(n)}$ belong to Class C_n; the others (except for $|0\rangle$) belong to higher classes. Equation (86) determines C_n, $R^{(-n)}$, and leads to the cancellation law between terms in $\mathbf{X}^{(N)}$ or $\mathcal{E}_0^{(N)}$ with terms in $\mathbf{X}^{(N+n-1)}$ or $\mathcal{E}_0^{(N+n-1)}$:

$$R^{(-i)}(\mathcal{V}-\langle V\rangle+\mathcal{H}^{(n)}-\langle\mathcal{H}^{(n)}\rangle)R^{(-j)}=0$$
$$(i=j=n;\text{ or } i\neq j,\ i\geq n,\ j\geq n). \qquad (88)$$

An immediate consequence of Eqs. (87) and (88) is that the lowest-order $\mathcal{H}^{(j)}$ that $R^{(-n)}$ can enter is $\mathcal{H}^{(n+2)}$, via the term,

$$\mathcal{H}^{(n+1)}R^{(-n)}\mathcal{H}^{(n+1)}. \qquad (89)$$

One need continue the procedure until n coincides with the order at which degeneracy with ψ_0 is completely removed. However, in a formal sense, the sentence that includes Eq. (85) defines $\mathcal{H}^{(n)}$ for arbitrarily large n.

Note that the first few $\mathcal{H}^{(n)}$ are obviously Hermitian:

$$\mathcal{H}^{(1)}=V, \qquad (90)$$
$$\mathcal{H}^{(2)}=VR^{(0)}V, \qquad (91)$$
$$\mathcal{H}^{(3)}=VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V. \qquad (92)$$

The Hermiticity of the general $\mathcal{H}^{(n)}$ is proved in the next subsection.

6. Cancellation of All Terms Proportional to Nonpositive Powers of V. Hermiticity of $\mathcal{H}^{(n)}$

We now prove the assertion: The conditions given above for the correct $|k\rangle$ and the $E_k^{(i)}$ prevent the occurrence of *all* terms proportional to nonpositive powers of V in $\sum_{i\geq 1}\mathbf{X}^{(i)}$ and $\sum_{i\geq 1}\mathcal{E}_0^{(i)}$, and the number of terms of a given order in V in either series is finite.

The proof is inductive. The assertion is trivially true for all terms involving no $R^{(-i)}$ $(i\geq 1)$. Consider terms involving $R^{(0)}$ and $R^{(-1)}$. The remarks straddling Eqs. (55)–(57) apply to the general case: Because of Eq. (74) and the cancellation law [Eq. (75)], terms in $\sum_{i\geq 1}\mathbf{X}^{(i)}$ and $\sum_{i\geq 1}\mathcal{E}_0^{(i)}$ involving $R^{(0)}$ and $R^{(-1)}$, but no $R^{(-i)}$ $(i>1)$, have orders greater than or equal to the number of $R^{(-1)}$. Moreover, $\chi^{(n)}$ receives no contributions from

$\mathbf{X}^{(j)}$ ($j>2n$), and $E_0^{(n)}$ receives no contributions from $\mathcal{E}_0^{(j)}$ ($j>2n-2$). The assertion is thus true for all terms involving no $R^{(-i)}$ ($i>1$).

Similarly, for $R^{(-2)}$, Eq. (78) and the cancellation laws (81) and (95) imply that terms in $\sum_{i\geq 1}\mathbf{X}^{(i)}$ and $\sum_{i\geq 1}\mathcal{E}_0^{(i)}$ involving no $R^{(-j)}$ ($j\geq 3$) have orders greater than or equal to the number of $R^{(-2)}$. The longest (measured in "RV" units) terms of order N (because of the cancellation laws) are typified by

$$(R^{(-2)}VR^{(0)}VR^{(-1)}VR^{(0)}V)^N\,|\,0\rangle \tag{93}$$

and

$$\langle 0\,|\,VR^{(0)}VR^{(-1)}VR^{(0)}V(R^{(-2)}VR^{(0)}VR^{(-1)}VR^{(0)}V)^{N-3}\,|\,0\rangle. \tag{94}$$

Consequently, Nth-order terms in the wavefunction and in the energy involve at most ($4N$) and ($4N-8$) V's, respectively, if no $R^{(-i)}$ ($i\geq 3$) can appear. Thus the assertion is true for all terms involving only $R^{(0)}$, $R^{(-1)}$, and $R^{(-2)}$.

The general result for terms involving $R^{(-i)}$ ($i\leq n$), but no $R^{(-j)}$ ($j>n$), follows inductively from the observations that because of Eqs. (88), (87), (85), (82), (81), (78), (75), and (74), the order of a term is at least equal to the number of $R^{(-n)}$, and the "longest" terms of order N in the wavefunction and of order ($N+n+1$) in the energy are typified by the terms having the largest number of V's in

$$(R^{(-n)}\mathfrak{K}^{(n+1)})^N\,|\,0\rangle \tag{95}$$

and

$$\langle 0\,|\,\mathfrak{K}^{(n+1)}(R^{(-n)}\mathfrak{K}^{(n+1)})^N\,|\,0\rangle. \tag{96}$$

The Hermiticity of $\mathfrak{K}^{(n)}$ is a consequence of "left-right" symmetry. Write

$$\mathbf{X}^{(n)}+\mathbf{X}^{(n+1)}+\cdots=\mathfrak{R}\mathfrak{V}\mathfrak{G}_{n-1}\,|\,0\rangle+\mathfrak{R}\langle\mathfrak{V}\cdots\rangle\cdots\,|\,0\rangle, \tag{97}$$

where $\mathfrak{R}\mathfrak{V}\mathfrak{G}_{n-1}\,|\,0\rangle$ denotes all terms that have *no* bra to the left of the first $\mathfrak{V}$. By the structure of nondegenerate Rule 2, $\mathfrak{V}\mathfrak{G}_{n-1}$ is Hermitian,

$$(\mathfrak{V}\mathfrak{G}_{n-1})^{\dagger}=\mathfrak{V}\mathfrak{G}_{n-1}. \tag{98}$$

$\mathfrak{K}^{(n)}$ consists of all terms in $\mathfrak{V}\mathfrak{G}_{n-1}$ that are nth-order in V, that involve no $R^{(-i)}$ ($i\geq n$), and that when sandwiched between $R^{(-i)}$ ($i\geq n$) and $|\,0\rangle$, do not lead to zero because of Eqs. (43)–(45), (74), (75), (78), (81), (82), (84), and (87) and (88), with n replaced by $n-1$ in Eqs. (87) and (88). But the equations specifying which terms vanish or cancel have "left–right" symmetry, so that a given term,

$$VR^{(-a)}VR^{(-b)}\cdots VR^{(-c)}V \qquad \text{(with inserted brackets)}, \tag{99}$$

and its *Hermitian conjugate*,

$$VR^{(-c)}V\cdots R^{(-b)}VR^{(-a)}V \quad \text{(with brackets inserted in the reverse order)}, \tag{100}$$

either both appear or both do not appear in $\mathfrak{K}^{(n)}$.

QED

7. *Rules for $\mathfrak{K}^{(n)}$, "Correct" Zeroth-Order Functions, $E_0^{(n)}$, $\chi^{(n)}$*

In the preceding sections, conditions have been derived for the choice of the zeroth-order functions and $E_k^{(i)}$ that permit the perturbation series for E_0 and ψ_0 with respect to $\mathfrak{V}$ to be rearranged into series in positive powers of V. The uniqueness of power series implies that these rearranged series are the Rayleigh–Schrödinger perturbation series in V for E_0 and ψ_0. It remains only to collect the results of the preceding sections and combine them with the "nondegenerate rules" to form four "degenerate rules."

The first rule is for $\mathfrak{K}^{(n)}$ with $n\geq 3$. For $n=1$, $\mathfrak{K}^{(n)}$ is just V [Eq. (90)], and for $n=2$, $\mathfrak{K}^{(n)}$ is $VR^{(0)}V$ [Eq. (91)].

Degenerate Rule 1. To form $\mathfrak{K}^{(n)}$, first write down the basic operator of order n in V,

$$h^{(n)}=\sum_{m\geq n-3}\sum_{i_1\geq 0}\sum_{i_2\geq 0}\cdots\sum_{i_m\geq 0}{}' VR^{(0)}VR^{(-i_1)}VR^{(-i_2)}\cdots \times VR^{(-i_m)}VR^{(0)}V \qquad (m+3-i_1-i_2-\cdots-i_m=n), \tag{101}$$

where the prime (′) indicates that each term must satisfy the additional restrictions:

(i) For each pair, $R^{(-i)}$ and $R^{(-j)}$, the order of the factor enclosed between them must be at least

$$[\min(i,j)+1].$$

(ii) For each $R^{(-i)}$, the order of the factor on the left of the $R^{(-i)}$ and the order of the factor on the right must both be at least ($i+1$).

Add to this basic operator all other expansions that can be obtained from it by inserting any number of bra-ket brackets around the V factors other than the first or last in each term. The bra and ket of a pair may be separated by any number of link factors,

$$VR^{(0)}VR^{(-i)}V\cdots R^{(-j)}VR^{(0)}V, \tag{102}$$

and brackets may lie within brackets, but one bra-ket pair may not straddle another, no brackets may touch, the $R^{(-i)}$ to the left of the bra must have the same superscript as the $R^{(-i)}$ to the right of its ket partner, and within a given pair of brackets, restriction (ii) applies. The sign $(-1)^{\nu}$ is attached to each term, where ν is the number of bra-ket pairs inserted in it. Each bra-ket pair signifies the expectation value of the enclosed operator in the state $|0\rangle$. A way to construct $h^{(n)}$ that implicitly incorporates (i) and (ii) is given in Appendix B.

Degenerate Rule 2. The "correct" zeroth-order functions satisfy the nested "diagonalization" conditions,

$$\langle k|\mathcal{H}^{(n)}|l\rangle=\delta_{kl}E_k^{(n)} \qquad [0\leq(k,l)\leq g-1,\ (k,l)\notin C_i,\ i<n]. \quad (103)$$

This set of equations operationally defines the state $|0\rangle$ and the Classes $C_1, C_2,\cdots$, and it also provides for the evaluation of the $E_k^{(i)}$ needed in $R^{(-i)}$.

Degenerate Rule 3. The nth-order energy $E_0^{(n)}$ is given by

$$E_0^{(n)}=\langle 0|\mathcal{H}^{(n)}|0\rangle. \quad (104)$$

Note that the $E_0^{(n)}$ in Eqs. (104) and (105) are identical although the equations arise in different ways.

Degenerate Rule 4. To form $\chi^{(n)}$, first write down the basic function

$$\sum_{m\geq n-1}\sum_{i_1\geq 0}\sum_{i_2\geq 0}\cdots\sum_{i_m\geq 0}{}' R^{(-i_1)}VR^{(-i_2)}\cdots VR^{(-i_m)} \times VR^{(0)}V|0\rangle \quad (m+1-i_1-i_2-\cdots-i_m=n), \quad (105)$$

where the prime (′) indicates that each term must satisfy the additional restrictions:

(i) The order of the factor enclosed between each pair, $R^{(-i)}$ and $R^{(-j)}$, must be at least $[\min(i,j)+1]$.

(ii) For each $R^{(-i)}$, the order of the factor on the right (but not the factor on the left) must be at least $(i+1)$.

Add to this basic function all other expressions that can be obtained from it by inserting any number of bra-ket brackets around the V factors other than the last (rightmost) in each term. The rules for arranging and interpreting the brackets, and the sign, are the same as those in Degenerate Rule 1.

8. *Consistency of the Two Uses of $E_k^{(i)}$*

The one loose end remaining is the consistency of the use of $E_k^{(i)}$ as the ith-order energy of ψ_k and an eigenvalue of $\mathcal{H}^{(i)}$. It has already been noted just after Eq. (104) that $E_0^{(n)}$ as extracted from $\sum_i \mathcal{E}_0^{(i)}$ is the same as the corresponding eigenvalue of $\mathcal{H}^{(n)}$. That the other eigenvalues of $\mathcal{H}^{(n)}$, say $E_k^{(n)}$ with $k\in C_n$, correspond to the appropriate nth-order energy follows from interchanging the roles of k and 0 and observing that if $|k\rangle\in C_n$, with respect to ψ_0, then (1) $|0\rangle\in C_n$ with respect to ψ_k, (2) $E_0^{(i)}=E_k^{(i)}$ $(0\leq i\leq n-1)$, (3) the classification scheme with respect to ψ_k is the same as with respect to ψ_0 for Classes $C_1, C_2,\cdots, C_{n-1}$, (4) the $R^{(-i)}$ $(0\leq i\leq n-1)$ for both schemes are identical, and (5) $\mathcal{H}^{(i)}$ (with brackets corresponding to $|0\rangle$) is identical with $\mathcal{H}^{(i)}$ (with brackets corresponding to $|k\rangle$), for $(1\leq i\leq n)$. Similarly, the $|k\rangle$ with $k>0$ are the "correct" zeroth-order functions in the sense of Sec. III.B.

IV. ADDITIONAL EXAMPLES

Equations (90)–(92) and (67)–(71) already provide some examples of the use of the Degenerate Rules. As an additional illustration of the $\mathcal{H}^{(n)}$ rule, we give here $\mathcal{H}^{(4)}$. The basic operator $h^{(4)}$ [Eq. (101)], which, with inserted brackets, becomes $\mathcal{H}^{(4)}$, is

$$h^{(4)}=VR^{(0)}VR^{(0)}VR^{(0)}V+\{VR^{(0)}VR^{(-1)}VR^{(0)}VR^{(0)}V+VR^{(0)}VR^{(0)}VR^{(-1)}VR^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}VR^{(-1)}VR^{(0)}V\}$$
$$+\{(VR^{(0)}VR^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V)R^{(-2)}(VR^{(0)}VR^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V)\}. \quad (106)$$

Inserting brackets into $h^{(4)}$ as indicated in Degenerate Rule 1, we obtain $\mathcal{H}^{(4)}$,

$$\mathcal{H}^{(4)}=\{VR^{(0)}(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)R^{(0)}V-VR^{(0)}\langle VR^{(0)}V\rangle R^{(0)}V\}+\{VR^{(0)}VR^{(-1)}VR^{(0)}(V-\langle V\rangle)R^{(0)}V$$
$$+VR^{(0)}(V-\langle V\rangle)R^{(0)}VR^{(-1)}VR^{(0)}V+VR^{(0)}VR^{(-1)}(VR^{(0)}V-\langle VR^{(0)}V\rangle)R^{(-1)}VR^{(0)}V\}$$
$$+\{[VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V]R^{(-2)}[VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V]\}. \quad (107)$$

Note that Eq. (107) is much messier than it would be in the nondegenerate case (the terms in the first set of braces). Note also that $\mathcal{H}^{(4)}$ would be much simpler if there were no Class C_1, i.e., if $R^{(-1)}=0$.

Equations (67) and (68) represent the contributions to $\chi^{(1)}$ and $\chi^{(2)}$ involving no $R^{(-i)}$ with $i\geq 2$. As additional examples, we give here the contributions to $\chi^{(1)}$ involving necessarily $R^{(-2)}$ and/or $R^{(-3)}$, but not higher $R^{(-i)}$, and the contribution to $\chi^{(2)}$ involving $R^{(-2)}$, but no $R^{(-i)}$ with $i\geq 3$:

{Contribution to $\chi^{(1)}$ involving one or both of $R^{(-2)}$ and $R^{(-3)}$, but no $R^{(-i)}$ with $i\geq 4$}

$$=R^{(-2)}VR^{(0)}(V-\langle V\rangle)R^{(0)}V|0\rangle+R^{(-2)}VR^{(0)}VR^{(-1)}VR^{(0)}V|0\rangle+R^{(-3)}\mathcal{H}^{(4)}|0\rangle, \quad (108)$$

where $\mathcal{H}^{(4)}$ is given in Eq. (107):

{Contribution to $\chi^{(2)}$ involving $R^{(-2)}$, but no $R^{(-i)}$ with $i\geq 3$}

$$=R^{(-2)}\mathcal{H}^{(4)}|0\rangle-R^{(-2)}[\langle VR^{(0)}(V-\langle V\rangle)R^{(0)}V\rangle+\langle VR^{(0)}VR^{(-1)}VR^{(0)}V\rangle](R^{(-2)}[VR^{(0)}(V-\langle V\rangle)R^{(0)}V$$
$$+VR^{(0)}VR^{(-1)}VR^{(0)}V]|0\rangle+(R^{(0)}V+R^{(-1)}VR^{(0)}V)R^{(-2)}[VR^{(0)}(V-\langle V\rangle)R^{(0)}V+VR^{(0)}VR^{(-1)}VR^{(0)}V]|0\rangle. \quad (109)$$

Note that wavefunction expressions are much messier than energy (or $\mathcal{H}^{(n)}$) expressions of the same order. Moreover, the lowest-order energy to which $R^{(-n)}$ can contribute is $E_0^{(n+2)}$, but every nonvanishing $R^{(-n)}$ contributes to $\chi^{(1)}$ (at the very least, through $R^{(-n)}\mathcal{H}^{(n+1)}|0\rangle$). Considerable simplification results if all degeneracy is removed at one, and only one, order. Then all $R^{(-i)}$, $i>0$, vanish, except for one, say, $R^{(-n)}$.

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APPENDIX A: WEAKEST CONDITIONS CONCERNING "CORRECT" ZEROTH-ORDER FUNCTIONS

In nondegenerate perturbation theory, one need only know the unperturbed function $|0\rangle$ explicitly. The $\chi^{(n)}$ and $E_0^{(n)}$ can be computed with no explicit knowledge of the other unperturbed functions. In the usual presentations of degenerate perturbation theory, either one is interested in all the degenerate states individually or the impression is given that it is necessary to know explicitly *all* the "correct" zeroth-order functions to be able to compute the $\chi^{(n)}$ and $E_0^{(n)}$ for the particular state ψ_0. The purpose of this Appendix is to point out that the minimum essential explicit knowledge is the "correct" state $|0\rangle$ and *any* basis for each subspace corresponding to the Classes $C_1, C_2, \cdots$, because the formulas require only the $R^{(-i)}$ and not the explicit $|k\rangle$ $(k>0)$.

Accordingly, let the projection operator for Class C_i, denoted by P_i, be known,

$$P_i=\sum_{k\in C_i}|k\rangle\langle k|. \tag{A1}$$

Then $|k\rangle$ $(k\in C_n)$ need not be an eigenfunction of the truncated $\mathcal{H}^{(n)}$, provided that Degenerate Rule 2 is replaced by

Degenerate Rule 2′. The correct zeroth-order function, $|0\rangle$, and the projection operators P_i satisfy

$$P_i\mathcal{H}^{(n)}|0\rangle=0 \qquad (i\geq n), \tag{A2}$$

$$P_i\mathcal{H}^{(n)}P_j=0 \qquad (i\neq j,\ i\geq n, j\geq n), \tag{A3}$$

and that the definition of $R^{(-i)}$ [Eq. (41)] is replaced by

$$R^{(-i)}=P_i[P_i(\mathcal{H}^{(i)}-E_0^{(i)})P_i]^{-1}P_i, \tag{A4}$$

where the inverse is meant in the P_i subspace.

The apparent necessity for Eq. (103) to be satisfied is in part an artifact of the derivation. Had $\mathcal{H}^{(0)}$ been defined by

$$\mathcal{H}^{(0)}=H^{(0)}+\sum_{i\geq 1}P_i(\mathcal{H}^{(i)}-E_0^{(i)})P_i, \tag{A5}$$

instead of by Eq. (21), then Eqs. (A2), (A3), and (A4) would have arisen instead of Eqs. (103) and (41).

The observations of this Appendix might possibly be useful in a variation–perturbation calculation.

APPENDIX B: BASIC OPERATORS AND FUNCTIONS

Unlike the nondegenerate case, just determining the basic operators and functions [Eqs. (101) and (105)] from which $\mathcal{H}^{(n)}$ and $\chi^{(n)}$ are constructed is itself nontrivial because of the restrictions (i) and (ii) in Degenerate Rules 1 and 4. The purpose of this Appendix is to provide more explicit, auxiliary formulas that automatically incorporate the two restrictions.

Let h denote the sum of the basic operators [Eq. (101)]

$$h=V+\sum_{n=2}^{\infty}h^{(n)}. \tag{B1}$$

We redecompose h in a different way. Let $h_{(-i)}$ denote all terms in h in which there is at least one $R^{(-i)}$, but no $R^{(-j)}$ with $j>i$. Then

$$h=\sum_{i\geq 0}h_{(-i)}. \tag{B2}$$

A specific procedure for obtaining the $h_{(-i)}$ is easily obtained. One new notation is needed. Let A be any operator expressed as a series in V,

$$A=\sum_k A^{(k)}. \tag{B3}$$

Define by $A^{(\geq n)}$ the series in which all terms proportional to powers of V less than n are omitted,

$$A^{(\geq n)}=\sum_{k\geq n}A^{(k)}. \tag{B4}$$

Then one can show (the proof is omitted) that

$$h_{(0)}=V(1-R^{(0)}V)^{-1}, \tag{B5}$$

$$h_{(-1)}=h_{(0)}^{(\geq 2)}(1-R^{(-1)}h_{(0)}^{(\geq 2)})^{-1}, \tag{B6}$$

$$h_{(-2)}=(h_{(0)}+h_{(-1)})^{(\geq 3)}[1-R^{(-2)}(h_{(0)}+h_{(-1)})^{(\geq 3)}]^{-1}, \tag{B7}$$

$$\vdots$$

$$h_{(-n)}=(h_{(0)}+h_{(-1)}+\cdots+h_{(-n+1)})^{(\geq n+1)}\times[1-R^{(-n)}(h_{(0)}+h_{(-1)}+\cdots+h_{(-n+1)})^{(\geq n+1)}]^{-1}. \tag{B8}$$

The expressions for the $h_{(-i)}$ can be substituted back into Eq. (B2), and then the nth-order term is the desired $h^{(n)}$.

The basic functions for the $\chi^{(n)}$ are a bit messier. Again, we state the result, leaving the proof to the reader.

The basic function [Eq. (105)] for $\chi^{(n)}$ is the nth-order term in

$$R^{(0)}h\,|\,0\rangle+(1+R^{(0)}V)R^{(-1)}h^{(\geq 2)}\,|\,0\rangle$$
$$+(1+R^{(0)}V+R^{(0)}VR^{(0)}V+R^{(-1)}VR^{(0)}V$$
$$+R^{(0)}VR^{(-1)}VR^{(0)}V)R^{(-2)}h^{(\geq 3)}\,|\,0\rangle+\cdots$$
$$+\sum_{j_0,j_1,\cdots,j_{N-1}}{}^{\prime}(R^{(0)}h)_{j_0}(R^{(-1)}h^{(\geq 2)})_{j_1}\cdots$$
$$\times(R^{(-m)}h^{(\geq m+1)})_{j_m}\cdots(R^{(-N+1)}h^{(\geq N)})_{j_{N-1}}$$
$$\times R^{(-N)}h^{(\geq N+1)}\,|\,0\rangle+\cdots. \quad \text{(B9)}$$

In Eq. (B9), the prime (′) indicates the (somewhat involved) restrictions on the j_m,

$$j_m\geq m \quad \text{(B10)}$$

and

$$j_m\leq m', \quad \text{(B11)}$$

where m' indicates the first factor to the right of $R^{(-m)}h^{(\geq m+1)})_{j_m}$ that has $j_{m'}>m'$, i.e., m' satisfies the conditions,

$$m'>m, \quad \text{(B12)}$$

$$j_{m'}>m', \quad \text{(B13)}$$

$$j_{m''}=m'', \quad \text{for} \quad m<m''<m'. \quad \text{(B14)}$$

The meaning of the symbol $(R^{(-m)}h^{(\geq m+1)})_{j_m}$ is

$$(R^{(-m)}h^{(\geq m+1)})_m=1 \qquad (j_m=m), \quad \text{(B15)}$$

$$(R^{(-m)}h^{(\geq m+1)})_{j_m}=R^{(-m)}h^{(j_m)} \qquad (j_m>m). \quad \text{(B16)}$$

APPENDIX C: EXPLICIT EXPRESSIONS FOR HIRSCHFELDER'S $Q_i^{(n)}$ OPERATORS

We consider Hirschfelder's $Q_i^{(n)}$ operators in the context of the present formulation: V is purely first order in the perturbation parameter. (The results given here can be extended to the case treated by Hirschfelder, that V itself is a power series in the perturbation parameter, by substituting the series for V in the final expressions and recollecting terms of a given order in the perturbation parameter.) The $Q_{n-2}^{(n)}$ are closely related to the $\mathcal{H}^{(n)}$. Within the subspace in which they are diagonal, $(Q_{n-2}^{(n)}+E_0^{(n)})$ and $\mathcal{H}^{(n)}$ are identical. Outside the subspace they are different.

The easiest way to see how the $Q_i^{(n)}$ are constructed is to write down the first few in the present notation. From Eqs. (29)–(31) and (69) of Hirschfelder,[1] and noting that

$$\bar{H}^{(n)}(\text{Hirschfelder notation})=-E_0^{(n)} \qquad (n\geq 2), \quad \text{(C1)}$$

we find that

$$Q_0^{(1)}=V-\langle V\rangle, \quad \text{(C2)}$$

$$Q_0^{(2)}=(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)-\langle VR^{(0)}V\rangle, \quad \text{(C3)}$$

$$Q_0^{(3)}=(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)R^{(0)}(V-\langle V\rangle)$$
$$-(V-\langle V\rangle)R^{(0)}\langle VR^{(0)}V\rangle-\langle VR^{(0)}V\rangle R^{(0)}(V-\langle V\rangle)$$
$$-\langle VR^{(0)}(V-\langle V\rangle)R^{(0)}V\rangle, \quad \text{(C4)}$$

$$Q_1^{(3)}=Q_0^{(3)}+[(V-\langle V\rangle)R^{(0)}V-\langle VR^{(0)}V\rangle]R^{(-1)}$$
$$\times[VR^{(0)}(V-\langle V\rangle)-\langle VR^{(0)}V\rangle]. \quad \text{(C5)}$$

Comparing Eqs. (C2)–(C5) with Eqs. (90)–(92) for $\mathcal{H}^{(1)}$, $\mathcal{H}^{(2)}$, and $\mathcal{H}^{(3)}$, we see that $Q_i^{(n)}$ is essentially given by the rule for $\mathcal{H}^{(n)}$, with brackets permitted to enclose the first and last V of each term, and with terms involving any $R^{(-j)}$ $(j>i)$ omitted. Thus we infer the fifth Rule.

Degenerate Rule 5. To form $Q_j^{(n)}$, apply Degenerate Rule 1 with two modifications:

(1) The i_1, $i_2,\cdots$, of Eq. (101) each must be $\leq j$.
(2) The qualification, "other than the first or last in each term," should be stricken from the clause immediately preceding Eq. (102).

The proof of the Rule is straightforward and is similar to the proof of the Nondegenerate Rule given in Sec. III.C. It follows inductively from the recursive definitions of the $Q_i^{(n)}$ [Eqs. (26) and (68)–(70) of Hirschfelder[1]] and the method developed in this paper.

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[11] The awkwardness here is precipitated by the observation that $R^{(-1)}V\,|\,0\rangle$ would not enter ψ_0 if it were canceled out by a contribution from some $X^{(n)}$ with $n>1$. Since this possibility cannot *easily* be ruled out rigorously (at the beginning), it seems prudent to obtain Eq. (9) by appealing to simplicity. The rigorous justification is that Eq. (9) leads to power series in V for ψ_0 and E_0, and power series are unique.