

Practical recursive solution of degenerate Rayleigh-Schrödinger perturbation theory and application to high-order calculations of the Zeeman effect in hydrogen

Harris J. Silverstone and Richard K. Moats

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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With the aim of high-order calculations, a new recursive solution for the degenerate Rayleigh-Schrödinger perturbation-theory wave function and energy has been derived. The final formulas,

$$\chi_{\sigma}^{(N)} = R^{(-\sigma)} \sum_{k=0}^{N-1} \bar{\mathcal{K}}_{\sigma+1}^{(\sigma+1+k)} \chi_{\sigma}^{(N-1-k)},$$

$$E^{(N+\sigma)} = \langle 0 | \mathcal{K}_{\sigma+1}^{(N+\sigma)} | 0 \rangle + \langle 0 | \sum_{k=0}^{N-2} \bar{\mathcal{K}}_{\sigma+1}^{(\sigma+1+k)} | \chi_{\sigma}^{(N-1-k)} \rangle,$$

which involve new Hamiltonian-related operators $\mathcal{K}_{\sigma+1}^{(\sigma+1+k)}$ and $\bar{\mathcal{K}}_{\sigma+1}^{(\sigma+1+k)}$, strongly resemble the standard nondegenerate recursive formulas. As an illustration, the perturbed energy coefficients for the $3s-3d_0$ states of hydrogen in the Zeeman effect have been calculated recursively through 87th order in the square of the magnetic field. Our treatment is compared with that of Hirschfelder and Certain [J. Chem. Phys. **60**, 1118 (1974)], and some relative advantages of each are pointed out.

I. INTRODUCTION

Despite much work,¹⁻⁵ degenerate Rayleigh-Schrödinger perturbation theory (RSPT) is still an intimidating subject. As elementary a problem as the Zeeman effect in hydrogen requires degenerate perturbation theory for excited states.⁶ It is our purpose here to give a new recursive solution of degenerate RSPT, whose formal structure is almost as simple as for nondegenerate RSPT, and then to apply it to the Zeeman effect (in a slightly nonstandard way—*vide infra*).

The general degenerate problem appears to have been treated first by Hirschfelder,² who developed recursion formulas for operators used to generate the wave function ψ and energy E from the unperturbed wave function. Earlier general treatments, particularly by Bloch⁷ and Kato,⁸ did not obtain true RSPT series for ψ and E . Silverstone³ developed explicit formulas for ψ and E of the Huby⁹-Brueckner¹⁰ type and Silverstone and Holloway⁴ developed explicit formulas using Lagrange's formula.¹¹ These treatments have resolved the special difficulties of degenerate RSPT—determination of the "correct" zeroth-order functions and determination of the components of ψ in the originally degenerate subspace. They are nicely suited for discussing the low orders of perturbation theory, but they are less suited for high-order calculations, which in turn are of great interest because of recent analytical and experimental work connected with the Stark and Zeeman effects.^{6,12-17}

A few years ago Hirschfelder and Certain⁵ developed a recursive solution for degenerate RSPT suitable for high-order calculations. The new recursive solution given here differs significantly in the organization of the calculation and in the final working equations. The main difference is

that the Hirschfelder-Certain solution obtains all information consistent with a given order of the perturbed Schrödinger equation, whereas the present solution extracts information from higher orders of the Schrödinger equation to obtain the entire wave function to a given order. The two methods are compared in Sec. III.

The standard recursive solution of nondegenerate RSPT expresses the perturbed energy and wave-function coefficients, $E^{(N)}$ and $\chi^{(N)}$, in terms of lower-order $E^{(k)}$ and $\chi^{(k)}$. In Sec. II we develop similar formulas for the degenerate case that are the natural generalization of the nondegenerate formulas. Along the way, new operators of the nature of effective Hamiltonians are introduced. In Sec. IV we apply the new formulas to the Zeeman effect in hydrogen. The application parallels that of Refs. 6 and 12 similarly uses SO(4,2) to compute matrix elements.¹⁸⁻²⁰ The treatment here is, however, interestingly different in that it has been cast as an eigenvalue problem for the perturbed principal quantum number.

II. DEGENERATE RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

A. Preliminaries

By RSPT, we mean that ψ , E , and the Hamiltonian H are all expanded in a power series in a perturbation parameter λ :

$$H = \sum_{N=0}^{\infty} \lambda^N H^{(N)}; \quad E = \sum_{N=0}^{\infty} \lambda^N E^{(N)}; \quad \psi = \sum_{N=0}^{\infty} \lambda^N \chi^{(N)}. \quad (1)$$

Following Hirschfelder,² we denote $H - E$ by $\bar{H}$:

$$\bar{H}^{(N)} = H^{(N)} - E^{(N)}. \quad (2)$$

We denote the unperturbed eigenfunctions and energies by $|i\rangle$ and $E_i^{(0)}$:

$$H^{(0)}|i\rangle = E_i^{(0)}|i\rangle. \quad (3)$$

The state being perturbed is $|0\rangle$, and we use synonymously $\chi^{(0)} = |0\rangle$, $E^{(0)} = E_0^{(0)}$.

Let the degeneracy of $E^{(0)}$ be g . We assume that $|0\rangle, |1\rangle, \dots, |g-1\rangle$ are the "correct" zeroth-order eigenfunctions, which means that they satisfy a nested sequence of diagonalization conditions^{2,3} that we discuss briefly in Sec. II C 4.

The $|i\rangle$ can be classified according to the order in which they first split off from $|0\rangle$. The states not degenerate with $|0\rangle$ form class $C_0 = \{|g\rangle, |g+1\rangle, \dots\}$. The states that split off from $|0\rangle$ in first order constitute class C_1 , and so forth, up to the class C_r , after which no degeneracy remains (unless because of symmetry). (We assume that, apart from symmetry, E is a nondegenerate level of H .) The state $|0\rangle$ is in a class by itself. The $g-1$ other "correct" zeroth-order degenerate eigenfunctions comprise the classes $C_1, C_2, \dots, C_r$ (some of which may be empty). For each class, one can form projection and resolvent operators:

$$P_\alpha = \sum_{i \in C_\alpha} |i\rangle\langle i|; \quad R^{(-\alpha)} = \sum_{i \in C_\alpha} \frac{|i\rangle\langle i|}{E_0^{(0)} - E_i^{(\alpha)}}. \quad (4)$$

Here $E^{(\alpha)}$ is the α -th-order energy coefficient for state i . Note that $1 = P_0 + P_1 + \dots + P_r + |0\rangle\langle 0|$.

Each $\chi^{(N)}$ can be decomposed into components belonging to the classes C_α :

$$\begin{aligned} \chi^{(N)} &= \chi_0^{(N)} + \chi_1^{(N)} + \dots + \chi_r^{(N)}, \\ \chi_\alpha^{(N)} &= P_\alpha \chi^{(N)} \quad (N > 0). \end{aligned} \quad (5)$$

We use "intermediate" normalization: $\langle 0|\chi^{(N)} = \delta_{N0}$.

B. Fundamental RSPT equation for $\chi^{(N)}$

The Schrödinger equation, $H\psi = 0$, yields the fundamental RSPT equation for $\chi^{(N)}$:

$$-H^{(0)}\chi^{(N)} = \sum_{k=0}^{N-1} \bar{H}^{(1+k)}\chi^{(N-1-k)}. \quad (6)$$

In the *nondegenerate* case, the fundamental RSPT equation yields the standard recursion formulas for $E^{(N)}$ and $\chi^{(N)}$:

$$E^{(N)} = \langle 0|H^{(N)}|0\rangle + \sum_{k=0}^{N-2} \langle 0|\bar{H}^{(1+k)}|\chi^{(N-1-k)}\rangle, \quad (7)$$

$$\chi^{(N)} = R^{(0)} \sum_{k=0}^{N-1} \bar{H}^{(1+k)}\chi^{(N-1-k)} \quad (\text{nondegenerate case}), \quad (8)$$

by which $E^{(N)}$ and $\chi^{(N)}$ are expressed in terms of lower-order $E^{(k)}$ and $\chi^{(k)}$ ($k \leq N-1$). In the degenerate case, Eq. (7) is still valid but Eq. (8)

is not. We seek generalizations for both Eqs. (7) and (8), valid for the degenerate case.

C. Method for solving the fundamental RSPT equation in the degenerate case

The solution for $\chi^{(N)}$ in the degenerate case is less direct. Since $\bar{H}^{(0)}P_\alpha = \delta_{\alpha 0}\bar{H}^{(0)}P_0$, the components $\chi_1^{(N)} + \chi_2^{(N)} + \dots + \chi_r^{(N)}$ drop out from the left-hand side of Eq. (6), leaving only $\chi_0^{(N)}$:

$$-\bar{H}^{(0)}\chi_0^{(N)} = \sum_{k=0}^{N-1} \bar{H}^{(1+k)}\chi^{(N-1-k)}, \quad (9)$$

$$\chi_0^{(N)} = R^{(0)} \sum_{k=0}^{N-1} \bar{H}^{(1+k)}\chi^{(N-1-k)}. \quad (10)$$

The fundamental RSPT Eq. (6) determines $\chi_0^{(N)}$ but not $\chi_1^{(N)}, \chi_2^{(N)}, \dots, \chi_r^{(N)}$.

Buried in Eq. (6), however is the determination of $\chi_1^{(N-1)}, \chi_2^{(N-2)}, \dots$. The subject of this subsection is how to extract formulas for the $\chi_\alpha^{(N-\alpha)}$ from Eq. (6). The basic procedure involves taking the P_α projection of Eq. (6), which uncovers a $\chi_\alpha^{(N-\alpha)}$, and substituting inductively obtained formulas for $\chi_0^{(N-\alpha)}, \chi_1^{(N-\alpha)}, \dots, \chi_{\alpha-1}^{(N-\alpha)}$ to get $\chi_\alpha^{(N-\alpha)}$ expressed entirely in terms of $\chi^{(k)}$ with $k \leq N-\alpha-1$. Along the way, certain Hamiltonian-related operators are introduced, some of which determine the "correct" zeroth-order eigenfunctions.

1. Determination of $\chi_1^{(N-1)}$

The determination of $\chi_1^{(N-1)}$ from Eq. (6) provides a six-step paradigm. Step 1 is to multiply Eq. (6) by $\sum_1^r P_\alpha + |0\rangle\langle 0|$ and to isolate the $\chi^{(N-1)}$ term:

$$\begin{aligned} 0 &= \left(\sum_1^r P_\alpha + |0\rangle\langle 0| \right) \bar{H}^{(1)} (\chi_0^{(N-1)} + \chi_1^{(N-1)} + \dots + \chi_r^{(N-1)}) \\ &\quad + \left(\sum_1^r P_\alpha + |0\rangle\langle 0| \right) \sum_{k=0}^{N-2} \bar{H}^{(2+k)}\chi^{(N-2-k)}. \end{aligned} \quad (11)$$

Step 2 is to use a "correct"-zeroth-order-function condition: that $\bar{H}^{(1)}$ should be diagonal within the degenerate subspace. The form taken here is that

$$\begin{aligned} \left(\sum_1^r P_\alpha + |0\rangle\langle 0| \right) \bar{H}^{(1)} \sum_0^r P_\beta \\ = \left(\sum_1^r P_\alpha + |0\rangle\langle 0| \right) \bar{H}^{(1)} P_0 + P_1 \bar{H}^{(1)} P_1; \end{aligned} \quad (12)$$

all other terms vanish. Thus Eq. (11) only involves $\chi_0^{(N-1)}, \chi_1^{(N-1)}$, and lower-order $\chi^{(k)}$ ($k \leq N-2$):

$$\begin{aligned} 0 &= P_1 \bar{H}^{(1)} \chi_1^{(N-1)} + \left(\sum_1^r P_\alpha + |0\rangle\langle 0| \right) \\ &\quad \times \left(\bar{H}^{(1)} \chi_0^{(N-1)} + \sum_{k=0}^{N-2} \bar{H}^{(2+k)}\chi^{(N-2-k)} \right). \end{aligned} \quad (13)$$

Step 3 is to use the " $N-1$ " version of Eq. (10) for $\chi_0^{(N-1)}$ in Eq. (13):

$$-P_1 \bar{H}^{(1)} \chi_1^{(N-1)} = \left(\sum_1^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \times \sum_0^{N-2} (\bar{H}^{(2+k)} + \bar{H}^{(1)} R^{(0)} \bar{H}^{(1+k)}) \chi^{(N-2-k)}. \quad (14)$$

To make Eq. (14) look more like Eq. (9), in step 4 we define the Hamiltonian-related operators $\mathcal{H}_2^{(2+k)}$ and $\mathcal{H}_2^{(2+k)}$:

$$\mathcal{H}_2^{(2+k)} = H^{(2+k)} + \bar{H}^{(1)} R^{(0)} \bar{H}^{(1+k)} \quad (k \geq 0), \quad (15)$$

$$\mathcal{H}_2^{(2+k)} = \mathcal{H}_2^{(2+k)} - E^{(2+k)}, \quad (16)$$

$$-P_1 \bar{H}^{(1)} \chi_1^{(N-1)} = \left(\sum_1^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \sum_0^{N-2} \mathcal{H}_2^{(2+k)} \chi^{(N-2-k)}. \quad (17)$$

Steps 5 and 6 are to take the P_1 and $|0\rangle$ components of Eq. (17) to get a formula for $\chi_1^{(N-1)}$ that resembles Eq. (8) and a formula for $E^{(N)}$ that is a generalization of Eq. (7):

$$\chi_1^{(N-1)} = R^{(-1)} \sum_0^{N-2} \mathcal{H}_2^{(2+k)} \chi^{(N-2-k)}, \quad (18)$$

$$E^{(N)} = \langle 0 | \mathcal{H}_2^{(2)} | 0 \rangle + \left\langle 0 \left| \sum_0^{N-2} \mathcal{H}_2^{(2+k)} \right| \chi^{(N-2-k)} \right\rangle. \quad (19)$$

2. Remarks on the determination of $\chi_2^{(N-2)}$

To determine $\chi_2^{(N-2)}$, one follows the same six steps that led to $\chi_1^{(N-1)}$ with three main adaptations: (i) Use the projection operator $(\sum_2^{\gamma} P_{\alpha} + |0\rangle\langle 0|)$ on Eq. (17) for step 1. (ii) In step 2 the second-order "correct"-zeroth-order-eigenfunction condition

takes the form

$$\left(\sum_2^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \mathcal{H}_2^{(2)} \sum_0^{\gamma} P_{\beta} = \left(\sum_2^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \mathcal{H}_2^{(2)} (P_0 + P_1) + P_2 \mathcal{H}_2^{(2)} P_2, \quad (20)$$

rather than Eq. (12). (iii) In step 3, in the analog of Eq. (13), it is necessary to substitute the " $N-2$ " version of Eq. (10) for $\chi_0^{(N-2)}$ and the $N-2$ version of Eq. (18) for $\chi_1^{(N-2)}$.

3. Inductive equations for the determination of $\chi_{\sigma}^{(N-\sigma)}$

After application of the six steps $\sigma-1$ times, one obtains formulas for $\chi_0^{(N)}$, $\chi_1^{(N-1)}$, $\chi_2^{(N-2)}$, ..., $\chi_{\sigma-1}^{(N-\sigma+1)}$, and $\sigma-1$ new formulas for $E^{(N)}$. In each case the formulas for $\chi_{\sigma}^{(N-\sigma)}$ and $E^{(N)}$ involve only (total) $\chi^{(k)}$ with $k \leq N-\sigma-1$. The next time through, one obtains for $\chi_{\sigma}^{(N-\sigma)}$ the following intermediate equations analogous to Eqs. (11)–(17) in the $\chi_1^{(N-1)}$ case: in step 1,

$$0 = \left(\sum_0^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \mathcal{H}_{\sigma}^{(\sigma)} \chi^{(N-\sigma)} + \left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \sum_0^{N-\sigma-1} \mathcal{H}_{\sigma}^{(\sigma+1+k)} \chi^{(N-\sigma-1-k)}; \quad (21)$$

in step 2,

$$\left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \mathcal{H}_{\sigma}^{(\sigma)} \sum_0^{\gamma} P_{\beta} = \left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \mathcal{H}_{\sigma}^{(\sigma)} \sum_0^{\sigma-1} P_{\beta} + P_{\sigma} \mathcal{H}_{\sigma}^{(\sigma)} P_{\sigma} \quad (22)$$

and

$$0 = P_{\sigma} \mathcal{H}_{\sigma}^{(\sigma)} \chi_{\sigma}^{(N-\sigma)} + \left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \left(\mathcal{H}_{\sigma}^{(\sigma)} \sum_0^{\sigma-1} \chi_{\beta}^{(N-\sigma)} + \sum_0^{N-\sigma-1} \mathcal{H}_{\sigma}^{(\sigma+1+k)} \chi^{(N-\sigma-1-k)} \right); \quad (23)$$

in step 3,

$$-P_{\sigma} \mathcal{H}_{\sigma}^{(\sigma)} \chi_{\sigma}^{(N-\sigma)} = \left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \sum_{k=0}^{N-\sigma-1} \left(\mathcal{H}_{\sigma}^{(\sigma+1+k)} + \mathcal{H}_{\sigma}^{(\sigma)} \sum_{\beta=0}^{\sigma-1} R^{(-\beta)} \mathcal{H}_{\beta+1}^{(\beta+1+k)} \right) \chi^{(N-\sigma-1-k)}; \quad (24)$$

in step 4 (here $\mathcal{H}_1^{(1+k)} \equiv \bar{H}^{(1+k)}$),

$$\mathcal{H}_{\sigma+1}^{(\sigma+1+k)} = \mathcal{H}_{\sigma}^{(\sigma+1+k)} + \mathcal{H}_{\sigma}^{(\sigma)} \sum_{\beta=0}^{\sigma-1} R^{(-\beta)} \mathcal{H}_{\beta+1}^{(\beta+1+k)} \quad (k \geq 0), \quad (25)$$

$$\mathcal{H}_{\sigma+1}^{(\sigma+1+k)} = \mathcal{H}_{\sigma+1}^{(\sigma+1+k)} - E^{(\sigma+1+k)}, \quad (26)$$

and

$$-P_{\sigma} \mathcal{H}_{\sigma}^{(\sigma)} \chi_{\sigma}^{(N-\sigma)} = \left(\sum_{\sigma}^{\gamma} P_{\alpha} + |0\rangle\langle 0| \right) \sum_{k=0}^{N-\sigma-1} \mathcal{H}_{\sigma+1}^{(\sigma+1+k)} \chi^{(N-\sigma-1-k)} \quad (27)$$

In steps 5 and 6, the P_{σ} and $|0\rangle$ components of Eq. (27) yield $\chi_{\sigma}^{(N-\sigma)}$ and $E^{(N)}$ in terms involving only lower-order $\chi^{(k)}$ ($k \leq N-\sigma-1$). These equations are the generalizations of Eqs. (8) and (7):

$$\chi_{\sigma}^{(N-\sigma)} = R^{(-\sigma)} \sum_{k=0}^{N-\sigma-1} \mathcal{H}_{\sigma+1}^{(\sigma+1+k)} \chi^{(N-\sigma-1-k)}, \quad (28)$$

$$E^{(N)} = \langle 0 | \mathcal{H}_{\sigma+1}^{(N)} | 0 \rangle + \left\langle 0 \left| \sum_{k=0}^{N-\sigma-2} \mathcal{H}_{\sigma+1}^{(\sigma+1+k)} \right| \chi^{(N-\sigma-1-k)} \right\rangle. \quad (29)$$

4. Comments on the determination of the "correct" zeroth-order functions and on the $\mathcal{K}_0^{(\sigma+k)}$

In a practical calculation one usually starts not with the "correct" zeroth-order functions $\{|0\rangle, |1\rangle, \dots, |g-1\rangle\}$, but with arbitrary linear combinations of them. As discussed in many elementary texts, a condition satisfied by, and used to determine the "correct" zeroth-order functions is that the $g \times g$ submatrix of $H^{(1)}$ be diagonal:

$$\langle i | H^{(1)} | j \rangle = \delta_{ij} E_i^{(1)} \quad (0 \leq i \leq g-1, 0 \leq j \leq g-1). \quad (30)$$

The states for which $E_i^{(1)} \neq E_0^{(1)}$ constitute class C_1 . [Note that if $E_i^{(1)} = E_j^{(1)} \neq E_0^{(1)}$, the condition (30) does not separate unambiguously $|i\rangle$ from $|j\rangle$, but none of the perturbation formulas for state 0 require such a distinction.] If there are states for which $E_i^{(1)} = E_0^{(1)}$, that is, the degeneracy with $E_0^{(1)}$ is not removed completely in first order, then the operator $H^{(2)} + H^{(1)} R^{(0)} H^{(1)}$ must be diagonalized over the remaining states:

$$\begin{aligned} \langle i | H^{(2)} + H^{(1)} R^{(0)} H^{(1)} | j \rangle \\ = \delta_{ij} E_i^{(2)} \quad (i \leq g-1, j \leq g-1, i \notin C_1, j \notin C_1). \end{aligned} \quad (31)$$

Those states for which $E_i^{(2)} \neq E_0^{(2)}$ constitute class C_2 .

If degeneracy with state 0 remains after second order, it is necessary to diagonalize third- or higher-order operators over the remaining states. The general situation was discussed by Hirschfelder,² Silverstone,³ and Hirschfelder and Certain.⁵

For the reader not familiar with those papers, we make the following remark: Equations (12) and (22) are consistency requirements necessary to make the equations solvable; their resolution is the system of matrix eigenvalue equations that determine the "correct" $|i\rangle$:

$$\langle i | \mathcal{K}_0^{(\sigma)} | j \rangle = \delta_{ij} E_i^{(\sigma)} \quad (0 \leq i \leq g-1, 0 \leq j \leq g-1; i, j \notin C_1, C_2, \dots, C_{\sigma-1}). \quad (32)$$

(Note that

$$\begin{aligned} \mathcal{K}_2^{(2)} = H^{(2)} + H^{(1)} R^{(0)} H^{(1)} \\ + \{E^{(1)} R^{(0)} E^{(1)} - E^{(1)} R^{(0)} H^{(1)} - H^{(1)} R^{(0)} E^{(1)}\} \\ \neq H^{(2)} + H^{(1)} R^{(0)} H^{(1)}, \end{aligned}$$

which appears in elementary texts, but that the braced terms are identically zero in the subspace spanned by $|0\rangle$ and $C_2, C_3, \dots, C_{\sigma-1}$. One detail, however, is missing: that the $\mathcal{K}_0^{(\sigma)}$ are Hermitian. It is not trivial to prove Hermiticity from the recursive definition, Eqs. (1), (2), (15), (16), (25), and (26). Indeed, the $\mathcal{K}_0^{(\sigma+k)}$ ($k > 0$) are in general

not Hermitian (e.g., $\mathcal{K}_2^{(3)}$). However, it is not too difficult to show that $\mathcal{K}_0^{(\sigma)}$ (here) $= Q_{\sigma-2}^{(\sigma)}$ of Hirschfelder,² which is closely related to $\mathcal{K}^{(\sigma)}$ of Silverstone,³ and $Q_{\sigma-2}^{(\sigma)}$ and $\mathcal{K}^{(\sigma)}$ are known to be Hermitian.^{2,3,5}

D. Summary of formulas of the recursive solution

In a practical calculation the order of formulas is important. $E^{(1)}$ must be calculated before $\chi^{(2)}$, because $E^{(1)}$ appears in the formula for $\chi^{(2)}$. In summarizing in this subsection all formulas needed in practice, we shift the indices in the $\chi^{(N-\sigma)}$ and $E^{(N)}$ formulas (18), (19), (28), and (29) to be more in line with computational sequence:

$$\mathcal{K}_1^{(1+k)} = H^{(1+k)}, \quad (33)$$

$$\mathcal{K}_{\sigma+1}^{(\sigma+k+1)} = \mathcal{K}_\sigma^{(\sigma+k+1)} + \mathcal{K}_\sigma^{(\sigma)} \sum_{\beta=0}^{\sigma-1} R^{(-\beta)} \mathcal{K}_{\beta+1}^{(\beta+k)} \quad (\sigma \geq 1, k \geq 0) \quad (34)$$

$$\mathcal{K}_{\sigma+1}^{(\sigma+k+1)} = \mathcal{K}_{\sigma+1}^{(\sigma+k+1)} - E^{(\sigma+k+1)} \quad (\sigma \geq 0, k \geq 0) \quad (35)$$

$$\begin{aligned} \langle i | \mathcal{K}_\sigma^{(\sigma)} | j \rangle = \delta_{ij} E_i^{(\sigma)} \quad (i \leq g-1, j \leq g-1, \\ \text{both } i, j \notin C_1, C_2, \dots, C_{\sigma-1}), \end{aligned} \quad (36)$$

$$R^{(-\sigma)} = \sum_{i \in C_\sigma} \frac{|i\rangle \langle i|}{E_0^{(\sigma)} - E_i^{(\sigma)}}, \quad (37)$$

$$\chi_\sigma^{(N)} = R^{(-\sigma)} \sum_{k=0}^{N-1} \mathcal{K}_{\sigma+1}^{(\sigma+1+k)} \chi^{(N-1-k)}, \quad (38)$$

$$E^{(N+\sigma)} = \langle 0 | \mathcal{K}_{\sigma+1}^{(N+\sigma)} | 0 \rangle + \left\langle 0 \left| \sum_{k=0}^{N-2} \mathcal{K}_{\sigma+1}^{(\sigma+1+k)} \right| \chi^{(N-1-k)} \right\rangle. \quad (39)$$

We emphasize again the similar structure of Eqs. (38) and (39) of the degenerate case and Eqs. (8) and (7) of the nondegenerate case.

One additional energy formula we have found to be most useful is due to Hirschfelder² and is valid both in the nondegenerate and degenerate case (with intermediate normalization):

$$\begin{aligned} E^{(J+K+1)} = \langle 0 | H^{(J+K+1)} | 0 \rangle \\ + \sum_{j=0}^J \sum_{k=0}^K \langle \chi^{(j)} | H^{(J-j+K-k+1)} | \chi^{(k)} \rangle. \end{aligned} \quad (40)$$

If $\chi^{(k)}$ has been determined up to some maximum order, say N , then Eq. (40) permits calculation of $E^{(k)}$ through order $2N+1$.

III. COMPARISON WITH HIRSCHFELDER AND CERTAIN'S RECURSIVE WAVE-FUNCTION SCHEME

In this section we characterize the differences with Hirschfelder and Certain's recursive wave-function solution.⁵ The primary focus in the recursive scheme developed by Hirschfelder and Certain is

the N th-order fundamental RSPT equation. From the N th- and lower-order equations, only part of $\chi^{(N)}$ can be determined (as discussed in Sec. IIC)—and similarly for $\chi^{(N-1)}$, $\chi^{(N-2)}$, ..., $\chi^{(N-\gamma+1)}$. The $\chi^{(N-\gamma)}$ is the highest-order wave function that is completely determined at the N th-order equation. Hirschfelder and Certain's basic recursive unit is that part of $\chi^{(M)}$ which is determined by the RSPT equations 1 through N : $\phi_{[N]q}^{(M)}$, in their notation. Explicit in the notation $[N]$ is that the "correct" zeroth-order functions are not completely determined unless $N \geq \gamma$, but we do not need to elaborate on that aspect here. When $M - N \geq \gamma$, the $\phi_{[N]q}^{(M)}$ is the exact $\chi^{(M)}$:

$$\chi^{(M)} = \phi_{[M+\gamma]q}^{(M)} = \phi_{[M+\gamma+1]q}^{(M)} = \dots \quad (41)$$

When $M - N < \gamma$, $\phi_{[N]q}^{(M)} \neq \chi^{(M)}$.

In contrast, the main focus of our recursive scheme is the N th-order wave function $\chi^{(N)}$. All additional information needed from equations $N+1$, $N+2$, ..., $N+\gamma$, to completely specify $\chi^{(N)}$ is built into the operators $\mathcal{R}_\sigma^{(\alpha+k)}$. Proliferation of intermediate, incomplete wave-function-like quantities is avoided at the expense of proliferation of Hamiltonian-like quantities. Thus the philosophy of organization is completely different.

A secondary feature of the Hirschfelder-Certain formulation concerns $R^{(0)}$: $R^{(0)}$ appears only at the extreme left of an expression, which is especially convenient if the expression is to be evaluated by solving an inhomogeneous differential equation rather than by using an explicit formula [such as Eq. (37)] for $R^{(0)}$. In contrast, $R^{(0)}$'s here are embedded in the $\mathcal{R}_\sigma^{(\alpha+k)}$. The present formalism is best suited for explicit $R^{(0)}$ as in the Zeeman-effect example of Sec. IV. The formalism could be developed into a form directly suitable for a differential-equation approach to $R^{(0)}$, but it would not look so simple as Eqs. (33)–(39), and we do not do so here.

A third, more subtle difference concerns the so-called $2N+1$ rule [Eq. (40)]. The Hirschfelder-Certain version⁵ involves $\phi_{[J+K]q}^{(j)}$ and $\phi_{[J+K]q}^{(k)}$ ($j \leq J$, $k \leq K$). If either $J+K-j < \gamma$ or $J+K-k < \gamma$, the corresponding $\phi^{(j)}$ or $\phi^{(k)}$ is less than the complete $\chi^{(j)}$ or $\chi^{(k)}$ that appears in the original Hirschfelder² version used here. But if both $J \geq \gamma$ and $K \geq \gamma$, the sparser version reduces to the original version.

At an operational level, the similarity or dissimilarity of the two methods depends on the order γ in which degeneracy is completely lifted. There is little difference if $\gamma=1$; our recursive formulas are

$$\chi^{(N)} = \sum_{\alpha=0}^{\gamma} \chi_{\alpha}^{(N)}, \quad (42)$$

$$\chi_0^{(N)} = R^{(0)} \sum_0^{N-1} \bar{H}^{(1+k)} \chi^{(N-1-k)}, \quad (43)$$

$$\chi_1^{(N)} = R^{(-1)} \sum_0^{N-1} \mathcal{R}_2^{(2+k)} \chi^{(N-1-k)}, \quad (44)$$

$$\mathcal{R}_2^{(2+k)} = \bar{H}^{(2+k)} + \bar{H}^{(1)} R^{(0)} \bar{H}^{(1+k)}. \quad (45)$$

Their recursive formulas are [see Eqs. (141)–(143) of Ref. 5], partly in our notation,

$$\chi^{(N)} = \phi_{[N+1]q}^{(N)} = \phi_{[N]q}^{(N)} + R^{(-1)} A_{[1]}^{(N+1)}, \quad (46)$$

$$\phi_{[N]q}^{(N)} = \chi_0^{(N)} \text{ [Eq. (43) above]}, \quad (47)$$

$$A_{[1]}^{(N+1)} = \bar{H}^{(1)} \chi_0^{(N)} + \sum_0^{N-1} \bar{H}^{(2+k)} \chi^{(N-1-k)}. \quad (48)$$

The great similarity in the $\gamma=1$ case is the consequence of the complete determination of $\chi_0^{(N)}$ from the N th-order equation.

The organizational difference is more marked when the degeneracy is lifted in second order: $\gamma=2$. Our scheme requires two additional equations:

$$\chi_2^{(N)} = R^{(-2)} \sum_0^{N-1} \mathcal{R}_3^{(3+k)} \chi^{(N-1-k)}, \quad (49)$$

$$\mathcal{R}_3^{(3+k)} = \mathcal{R}_2^{(3+k)} + \mathcal{R}_2^{(2)} R^{(0)} \bar{H}^{(1+k)} + \mathcal{R}_2^{(2)} R^{(-1)} \mathcal{R}_2^{(2+k)}. \quad (50)$$

Their scheme requires instead, the following equations [Eqs. (144)–(148) of Ref. 5, again, with some liberty taken with their notation]:

$$\chi^{(N)} = \phi_{[N+2]q}^{(N)} = \phi_{[N+1]q}^{(N)} + R^{(-2)} A_{[2]}^{(N+2)}; \quad (51)$$

$$\phi_{[N+1]q}^{(N)} = \phi_{[N]q}^{(N)} + R^{(-1)} A_{[1]}^{(N+1)} + \hat{\phi}_{[2]}^{(1)} R^{(-2)} A_{[2]}^{(N+1)} \quad (52)$$

$$= \chi_0^{(N)} - \chi_2^{(N)}; \quad (53)$$

$$\phi_{[N]q}^{(N)} = R^{(0)} \bar{H}^{(1)} \phi_{[N]q}^{(N-1)} + R^{(0)} \sum_1^{N-1} \bar{H}^{(1+k)} \chi^{(N-1-k)} \quad (54)$$

$$= \chi_0^{(N)} - R^{(0)} \bar{H}^{(1)} \chi_2^{(N-1)}; \quad (55)$$

$$\hat{\phi}_{[2]}^{(1)} = [R^{(0)} H^{(1)} + R^{(-1)} (H^{(2)} + H^{(1)} R^{(0)} H^{(1)})] P_2; \quad (56)$$

$$A_{[1]}^{(N+1)} = P_1 \left(\bar{H}^{(1)} \phi_{[N]q}^{(N)} + \bar{H}^{(2)} \phi_{[N]q}^{(N-1)} + \sum_0^{N-2} \bar{H}^{(3+k)} \chi^{(N-2-k)} \right), \quad (57)$$

$$A_{[2]}^{(N+1)} = P_2 \left(\bar{H}^{(2)} \phi_{[N]q}^{(N-1)} + \sum_0^{N-2} \bar{H}^{(3+k)} \chi^{(N-2-k)} \right) + P_2 \hat{\phi}_{[2]}^{(1)†} \left(\bar{H}^{(1)} \phi_{[N]q}^{(N-1)} + \sum_0^{N-2} \bar{H}^{(2+k)} \chi^{(N-2-k)} \right); \quad (58)$$

and a similar equation for $A_{[2]}^{(N+2)}$.

The question naturally arises as to which method is more suitable in which situation. As already mentioned, the Hirschfelder-Certain method requires no modification to handle $R^{(0)}$ via inhomogeneous

geneous differential equations, while ours does. When, however, $R^{(0)}$ enters explicitly, we find the present method easier to program on a computer, but such a preference is a highly subjective opinion of the programmers. Computational efficiency in a specific case might favor one or the other or even an adaptation where the base unit would be $\chi_\alpha^{(n)}$. In practice, we actually use a mixture for the $\gamma=1$ case worked in Sec. IV for the Zeeman effect. For the $\gamma=2$ case (such as for the combined Stark and Zeeman effects), our computer adaptation is much closer to the present formulation than to Hirschfelder and Certain's. In any event, both approaches lead to the same end, and it is not clear that the question of suitability is well posed.

Hirschfelder and Certain⁵ also discuss the variational calculation of the $\phi_{(N)1}^{(M)}$. Similar variational techniques could be used here. The reader is referred to their paper⁵ for the basic outline, as well as for a discussion of other aspects of degenerate perturbation theory, including Hirschfelder's original operator solution.²

IV. ZEEMAN EFFECT IN HYDROGEN

The Zeeman effect in excited states of hydrogen is a familiar, real problem that requires the use of degenerate RSPT. It is especially useful as an illustration because the $\chi^{(N)}$ can be obtained in simple closed form. Moreover, conservation of "m," conservation of parity, and the use of group theory greatly simplify the technical details. The Zeeman-effect perturbation series is not convergent but asymptotic; analysis of the dependence of the energy coefficients on N has been reported in Refs. 6 and 12.

The Zeeman-effect Hamiltonian, in atomic units is

$$\hat{H}_{\text{Zeeman}} = -\frac{1}{2}\nabla^2 - \frac{1}{r} + b\hat{l}_z + \frac{1}{2}b^2(x^2 + y^2) \quad (59)$$

$$= \epsilon_{\text{Zeeman}} \quad (59)$$

Here ϵ denotes the perturbed energy, $b = \hbar^3 B / (2m_e^2 c e^3)$, and B denotes the strength of the uniform static magnetic field that points in the z direction. The term linear in b is constant, since $\hat{l}_z$ is conserved, leading one to define an m -independent Hamiltonian, $\hat{h}$:

$$\hat{h} = \hat{H}_{\text{Zeeman}} - bm = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{1}{2}b^2(x^2 + y^2) \quad (60)$$

$$= \epsilon_{\text{Zeeman}} - bm \quad (61)$$

Equation (42) shows clearly that $\frac{1}{2}b^2$ is the natural perturbation parameter rather than b itself.

Direct solution of the RSPT for $\hat{h}$, although feasible, is complicated by the n dependence of the

exponential factors $e^{-r/n}$ in the unperturbed hydrogenic wave functions. In particular, the summation form (37) for $R^{(0)}$ does not truncate in practice and is not useful. A way around the $e^{-r/n}$ complication is developed in the next subsection.

A. Reformulation of the hydrogenic Zeeman effect as an eigenvalue problem for the perturbed principal quantum number

To remove the $1/n$ factor from the "orbital exponent" and give all the radial functions the common factor e^{-r} , we use an energy-dependent scale transformation with scale factor η ,

$$\eta \equiv (-2\epsilon)^{-1/2} = (-2\epsilon_{\text{Zeeman}} + 2bm)^{-1/2} \quad (62)$$

η is essentially the "perturbed principal quantum number" ($\eta^{(0)} = n$), and the transformed Eqs. (60) and (61) end up as an eigenvalue equation for η . Accordingly, we put $r = \eta r_{\text{new}}$ into $H = \eta r(\hat{h} - \epsilon + 1/r)$ $= \eta$ and then drop the subscript "new" to obtain

$$H = -\frac{1}{2}r\nabla^2 + \frac{1}{2}r + \frac{1}{2}\eta^4 b^2 r(x^2 + y^2) \quad (63)$$

$$= -\frac{1}{2}r\nabla^2 + \frac{1}{2}r + \lambda r(x^2 + y^2) \quad (64)$$

$$= \eta \quad (65)$$

Note the specification of the perturbation parameter λ ,

$$\lambda = \frac{1}{2}\eta^4 b^2 \quad (66)$$

After solving Eqs. (64) and (65) for $\eta(\lambda)$, it is necessary to unravel η from the implicit equation, $\eta = \eta(\frac{1}{2}\eta^4 b^2)$ (and in this respect the treatment here parallels the earlier solution of the Stark effect^{15,17}), but such unraveling is a small price (Sec. IV D) for the simplicity gained in Eq. (64): namely, that

$$H^{(0)} = -\frac{1}{2}r\nabla^2 + \frac{1}{2}r, \quad (67)$$

$$H^{(1)} = r(x^2 + y^2), \quad (68)$$

$$H^{(k)} = 0 \quad (k \geq 2) \quad (69)$$

that the spectrum of $H^{(0)}$ is purely discrete, and that only a few matrix elements of $H^{(1)}$ are non-zero. We point out that to keep H Hermitian, the usual Cartesian volume element must be divided by r : $d\tau = r \sin\theta dr d\theta d\phi$.

B. Unperturbed eigenfunctions, degeneracy and symmetry

The unperturbed eigenfunctions of $H^{(0)}$ are just the energy-scaled hydrogenic radial functions times spherical harmonics Y_l^m , and the unperturbed eigenvalues are just the principal quantum number n :

$$H^{(0)}\psi_{nlm} = \eta_{nlm}^{(0)}\psi_{nlm}, \quad (70)$$

$$\eta_{nim}^{(0)} = n, \quad (71)$$

$$\psi_{nim} = R_{ni}(r) Y_l^m(\theta, \phi), \quad (72)$$

$$R_{ni}(r) = N_{ni} r^l e^{-r} L_{n-l-1}^{(2l+1)}(2r). \quad (73)$$

We do not have to deal directly with the R_{ni} (expressed here in terms of generalized Laguerre polynomials $L_{n-l-1}^{(2l+1)}$ and normalization constants N_{ni}) because all necessary matrix elements can be found in the paper by Bednár.²⁰

The degeneracy of $\eta_{nim}^{(0)}$ is n^2 . But because m and parity are conserved, the effective degeneracy is much lower. For given n , m , and parity, there is degeneracy $[(n - |m| + 1)/2]$ for even- m -even-parity or odd- m -odd-parity, and there is degeneracy $[(n - |m|)/2]$ for the other two combinations, where $[x]$ means the largest integer $\leq x$. (Note, $n - 1$ must be $\geq |m|$).

The removal of the degeneracy is by diagonalization of $H^{(1)} = r(x^2 + y^2)$. It appears that all degeneracy (n , m , and parity being fixed) is removed in first order. (We have checked all cases with $n \leq 20$ numerically, but we do not have a general proof.) The only nonempty classes are C_0 and C_1 , and the solution is a lot simpler than if there were several C_α .

C. A few computational details

In the design of a computer program to solve the RSPT for $\eta(\lambda)$, the presence of only C_0 and C_1 and the absence of any terms in $\sum_N H^{(N)} \lambda^N$ with orders ≥ 2 [Eq. (69)], make certain important practical simplifications. Equation (10) or (38) for $\chi_0^{(N)}$ becomes (with $H^{(k)} = -E^{(k)}$ for $k \geq 2$)

$$\chi_0^{(N)} = R^{(0)} H^{(1)} \chi^{(N-1)} - \sum_{k=0}^{N-2} E^{(1+k)} R^{(0)} \chi_0^{(N-1-k)}. \quad (74)$$

For $E^{(N)}$, Eq. (7) [or Eq. (39) with $\sigma=0$] is sufficient, and only $\chi_0^{(N-1)}$ contributes:

$$E^{(N)} = \langle 0 | H^{(1)} | \chi_0^{(N-1)} \rangle. \quad (75)$$

For $\chi_1^{(N)}$, we could use Eq. (18) or (38). But to save storing the matrices of $\mathcal{H}_2^{(2+k)}$, we take a simplified form from Eq. (13) (with N increased by 1):

$$\epsilon^{(N)} = \sum_{\sigma_1 \geq 0, \sigma_2 \geq 0, \dots, \sigma_N \geq 0, (\sigma_1 + 2\sigma_2 + \dots + N\sigma_N = N)} \frac{(4N-3)! n^{4N-2+\sum \sigma_i}}{(4N-2-\sum \sigma_i)! \sigma_1! \sigma_2! \dots \sigma_N!} \eta^{(1)\sigma_1} \eta^{(2)\sigma_2} \dots \eta^{(N)\sigma_N}, \quad (81)$$

$$\epsilon^{(0)} = -\frac{1}{2} n^{-2}. \quad (82)$$

Also, as in the Stark effect,^{15,17} the explicit formula (81) becomes inefficient as N increases because of the rapid increase in the number of partitions of N . A recursion scheme can first be used to convert η to a series in $\frac{1}{2}b^2$:

$$\chi_1^{(N)} = R^{(-1)} H^{(1)} \chi_0^{(N)} - \sum_{k=0}^{N-2} E^{(2+k)} R^{(-1)} \chi_1^{(N-1-k)} \quad (76)$$

The matrix elements

$$\langle \psi_{n'l'm'} | r(x^2 + y^2) | \psi_{nim} \rangle = \langle \psi_{n'l'm'} | H^{(1)} | \psi_{nim} \rangle$$

have been worked out by Bednár²⁰ using the group SO(4,2). We note here that only a maximum of 21 $\psi_{n'l'm'}$ connect directly with ψ_{nim} . That is,

$$\langle \psi_{n'l'm'} | H^{(1)} | \psi_{nim} \rangle = 0, \text{ unless } m = m', \quad (77)$$

$$|l - l'| = 0 \text{ or } 2, \text{ and } |n - n'| \leq 3.$$

Thus in using Eq. (37) for $R^{(0)}$ and for $R^{(-1)}$, only a finite number of terms ever give a nonzero contribution. Consequently, all $\chi^{(N)}$ can be written as *finite linear combinations* of ψ_{nim} . Note also that the energy denominators in $R^{(0)}$ are the differences of integers (principal quantum numbers).

For any particular state, the eventual limitation to the order of a calculation turns out to be storage capacity for the expansion coefficients of the $\chi^{(N)}$ on the ψ_{nim} . Note that Eq. (40) can be used to get $E^{(k)}$ for $k = N_{\max} + 1$ through $2N_{\max} + 1$, where $N_{\max}$ is the highest order to which $\chi^{(N)}$ is calculated. In an example to be reported in more detail in Sec. IV E, we calculated $\chi^{(N)}$ through 43rd order for the $3s - 3d_0$ states, and then obtained $E^{(N)}$ through 87th order. (An asymptotic analysis of this calculation has been reported in Ref. 6.)

D. Unraveling $\eta = \eta(\frac{1}{2}\eta^4 b^2)$

The result of solving RSPT for $\eta(\lambda)$ is the series

$$\eta(\lambda) = \sum_{N=0}^{\infty} \eta^{(N)} \lambda^N. \quad (78)$$

To solve the Zeeman problem,

$$\epsilon_{\text{Zeeman}} = mb + \sum_{N=0}^{\infty} \epsilon^{(N)} (\frac{1}{2}b^2)^N, \quad (79)$$

we need to find the $\epsilon^{(N)}$ from the $\eta^{(N)}$ via

$$\epsilon_{\text{Zeeman}} = mb - \frac{1}{2} \eta^{-2} (\frac{1}{2} \eta^4 b^2). \quad (80)$$

As in the Stark effect,¹⁷ Lagrange's formula¹¹ yield yields the explicit relationship

$$\eta = \sum_{N=0}^{\infty} y^{(N)} (\frac{1}{2}b^2)^N. \quad (83)$$

Then the series (83) can be squared and inverted by elementary recursion.

TABLE I. Perturbed energy coefficients for the two states, $|s\rangle = 0.91562901008 |3s\rangle - 0.40202427228 |3d_0\rangle$, $|d\rangle = 0.40202427228 |3s\rangle + 0.91562901008 |3d_0\rangle$, in the Zeeman effect in hydrogen. The perturbation parameter λ is $\frac{1}{2}b^2$.

Order	Energy coefficients		Order	Energy coefficients	
	Unperturbed state = $ s\rangle$	Unperturbed state = $ d\rangle$		Unperturbed state = $ s\rangle$	Unperturbed state = $ d\rangle$
0	-5.5555555555555555 $\times 10^{-3}$	-5.5555555555555555 $\times 10^{-2}$	44	-1.7810174414368 $\times 10^{22}$	-1.1852993194506 $\times 10^{20}$
1	1.5662811813690 $\times 10^2$	4.1371881863104 $\times 10^1$	45	1.0443835372919 $\times 10^{23}$	6.9231711667937 $\times 10^{25}$
2	-5.1152374327312 $\times 10^5$	-6.5115256726876 $\times 10^4$	46	-6.3847680185714 $\times 10^{23}$	-4.2163439954028 $\times 10^{21}$
3	5.0950351187337 $\times 10^5$	3.7792144626626 $\times 10^5$	47	4.0658072962287 $\times 10^{23}$	2.6751775932580 $\times 10^{27}$
4	-8.5755669278661 $\times 10^{13}$	-3.7829694609589 $\times 10^{12}$	48	-2.6947539986809 $\times 10^{24}$	-1.7668552992566 $\times 10^{23}$
5	1.9276398815612 $\times 10^{13}$	5.4981699797638 $\times 10^{16}$	49	1.8574855273921 $\times 10^{21}$	1.2137827428650 $\times 10^{24}$
6	-5.3350543237937 $\times 10^{22}$	-1.0818128483943 $\times 10^{21}$	50	-1.3305821003923 $\times 10^{27}$	-8.6665303798366 $\times 10^{24}$
7	1.7433135557551 $\times 10^{27}$	2.7577626813608 $\times 10^{25}$	51	9.8981887171924 $\times 10^{26}$	6.4268594392229 $\times 10^{26}$
8	-6.575655609382 $\times 10^{31}$	-8.7645862491984 $\times 10^{29}$	52	-7.6412919687400 $\times 10^{26}$	-4.9464998173610 $\times 10^{26}$
9	2.8259628552238 $\times 10^{38}$	3.3552502313549 $\times 10^{34}$	53	6.1176521383892 $\times 10^{27}$	3.9486640401142 $\times 10^{27}$
10	-1.3727990509409 $\times 10^{41}$	-1.5053991057957 $\times 10^{39}$	54	-5.0760950895909 $\times 10^{28}$	-3.2671797920973 $\times 10^{27}$
11	7.4988275714702 $\times 10^{45}$	7.7640445390285 $\times 10^{43}$	55	4.3624595375129 $\times 10^{28}$	2.8002320415473 $\times 10^{28}$
12	-4.5832323693671 $\times 10^{50}$	-4.5440650270933 $\times 10^{48}$	56	-3.8808658395028 $\times 10^{29}$	-2.4845624965152 $\times 10^{29}$
13	3.134156989645 $\times 10^{55}$	2.9924208945219 $\times 10^{53}$	57	3.5716506192555 $\times 10^{29}$	2.2807956288642 $\times 10^{29}$
14	-2.3824622731824 $\times 10^{60}$	-2.2040033562912 $\times 10^{58}$	58	-3.3986643783992 $\times 10^{30}$	-2.1649974614181 $\times 10^{30}$
15	2.0087913180307 $\times 10^{65}$	1.8069876845136 $\times 10^{63}$	59	3.342029610156 $\times 10^{30}$	2.1238557461487 $\times 10^{30}$
16	-1.8722839081310 $\times 10^{70}$	-1.6422673980822 $\times 10^{68}$	60	-3.3942689864054 $\times 10^{31}$	-2.1520824040385 $\times 10^{31}$
17	1.9223411634185 $\times 10^{75}$	1.6480860469145 $\times 10^{73}$	61	3.5587262047780 $\times 10^{32}$	2.2513133541467 $\times 10^{32}$
18	-2.1667248465805 $\times 10^{80}$	-1.8139855759531 $\times 10^{78}$	62	-3.8498206545073 $\times 10^{32}$	-2.4301887624390 $\times 10^{32}$
19	2.6718449124886 $\times 10^{85}$	2.2013737797138 $\times 10^{83}$	63	4.2951248474140 $\times 10^{33}$	2.7055871633777 $\times 10^{32}$
20	-3.5926973051927 $\times 10^{90}$	-2.9091397210875 $\times 10^{88}$	64	4.9396760043490 $\times 10^{34}$	-3.1052550483848 $\times 10^{33}$
21	5.2512285099391 $\times 10^{95}$	4.1849120418275 $\times 10^{93}$	65	5.8534576863740 $\times 10^{34}$	3.6724005838530 $\times 10^{34}$
22	-8.3181954480213 $\times 10^{100}$	-6.5325926361059 $\times 10^{98}$	66	-7.1437709550098 $\times 10^{35}$	-4.4733040072832 $\times 10^{35}$
23	1.4239421138478 $\times 10^{106}$	1.1032340712093 $\times 10^{104}$	67	8.9755012703287 $\times 10^{35}$	5.6097882514996 $\times 10^{35}$
24	-2.6271622091149 $\times 10^{111}$	-2.0100887020871 $\times 10^{109}$	68	-1.1604499663120 $\times 10^{36}$	-7.2397504003297 $\times 10^{36}$
25	5.2109364185776 $\times 10^{116}$	3.9408026544694 $\times 10^{114}$	69	1.5433201317838 $\times 10^{37}$	9.6113465885158 $\times 10^{36}$
26	-1.1085242320130 $\times 10^{122}$	-8.2928140168559 $\times 10^{119}$	70	-2.1104627967467 $\times 10^{37}$	-1.3120721284425 $\times 10^{37}$
27	2.5234848602850 $\times 10^{127}$	1.8657770958315 $\times 10^{125}$	71	2.9663763944597 $\times 10^{38}$	1.8411025365640 $\times 10^{38}$
28	-6.1342760870849 $\times 10^{132}$	-4.4998906820372 $\times 10^{130}$	72	-4.2839156904414 $\times 10^{38}$	-2.6545045680966 $\times 10^{38}$
29	1.5891527760882 $\times 10^{138}$	1.1554238110138 $\times 10^{136}$	73	6.3542625821538 $\times 10^{39}$	3.9311258499782 $\times 10^{39}$
30	-4.3791343210539 $\times 10^{143}$	-3.1574231028722 $\times 10^{141}$	74	-9.6771295069265 $\times 10^{40}$	-5.9775779680597 $\times 10^{39}$
31	1.2813159943221 $\times 10^{149}$	9.1660222301274 $\times 10^{146}$	75	1.5126435593564 $\times 10^{40}$	9.3295181190448 $\times 10^{40}$
32	-3.9740744240128 $\times 10^{154}$	-2.8218500055137 $\times 10^{152}$	76	-2.4259988366859 $\times 10^{41}$	-1.4940787232583 $\times 10^{42}$
33	1.3044645446233 $\times 10^{160}$	9.1977265036266 $\times 10^{157}$	77	3.9908686379272 $\times 10^{42}$	2.4542927914586 $\times 10^{41}$
34	-4.5246553562075 $\times 10^{165}$	-3.1691782157486 $\times 10^{163}$	78	-6.7317745710355 $\times 10^{43}$	-4.1340881775698 $\times 10^{42}$
35	1.6550338626413 $\times 10^{171}$	1.1526385911790 $\times 10^{169}$	79	1.1639726787496 $\times 10^{43}$	7.1383662761346 $\times 10^{42}$
36	-6.3868656535575 $\times 10^{176}$	-4.4188865845064 $\times 10^{174}$	80	-2.0624154752528 $\times 10^{43}$	-1.2631420294892 $\times 10^{43}$
37	2.5922346219553 $\times 10^{182}$	1.7833168867249 $\times 10^{180}$	81	3.7437072278098 $\times 10^{44}$	2.2898735882874 $\times 10^{43}$
38	-1.1058307772263 $\times 10^{188}$	-7.5664247764512 $\times 10^{185}$	82	-6.9597744940678 $\times 10^{44}$	-4.2515916296909 $\times 10^{44}$

TABLE I. (Continued)

Order	Energy coefficients		Order	Energy coefficients	
	Unperturbed state = $ s\rangle$	Unperturbed state = $ s\rangle$		Unperturbed state = $ s\rangle$	Unperturbed state = $ d\rangle$
39	4.952 400 587 922 3 $\times 10^{183}$	3.371 133 131 407 6 $\times 10^{191}$	83	1.324 750 752 139 4 $\times 10^{453}$	8.082 579 496 400 1 $\times 10^{455}$
40	-2.325 754 360 918 1 $\times 10^{189}$	-1.575 377 695 697 2 $\times 10^{197}$	84	-2.581 070 478 646 8 $\times 10^{464}$	-1.572 850 213 716 4 $\times 10^{462}$
41	1.144 097 479 045 6 $\times 10^{205}$	7.713 300 704 873 4 $\times 10^{202}$	85	5.146 072 780 355 6 $\times 10^{470}$	3.132 181 807 755 7 $\times 10^{468}$
42	-5.889 303 388 342 8 $\times 10^{210}$	-3.952 636 667 243 7 $\times 10^{208}$	86	-1.049 660 073 302 7 $\times 10^{477}$	-6.381 381 413 896 1 $\times 10^{474}$
43	3.169 103 025 077 0 $\times 10^{216}$	2.117 817 974 919 4 $\times 10^{214}$	87	2.189 812 802 189 8 $\times 10^{483}$	1.329 777 789 430 0 $\times 10^{481}$

E. Specific example: $3s-3d_0$

The first case for which degenerate RSPT is a necessity consists of the $3s-3d_0$ sublevel. Diagonalization of $H^{(1)}$ yields two correct zeroth-order eigenfunctions, $|s\rangle$ and $|d\rangle$:

$$|s\rangle = 0.915\,629\,01|3s\rangle - 0.402\,024\,27|3d_0\rangle, \quad (84)$$

$$|d\rangle = 0.402\,024\,27|3s\rangle + 0.915\,629\,01|3d_0\rangle. \quad (85)$$

Either can be taken as $|0\rangle$, the other as $|1\rangle$.

We were able to calculate $\chi^{(N)}$ to 43rd order, staying in a 256 000-word core on a DEC system 10 KL computer, and we obtained $E^{(N)}$ through 87th order. The $E^{(N)}$ agreed to 13 significant figures with calculations by Adams, Avron, Cížek, and Paldus⁵ through 53rd order on an IBM computer by a significantly different procedure. Such calculations are of importance in understanding the analytic behavior of ϵ_{Zeeman} as a function of b , which is reflected in the asymptotic behavior of the $\epsilon^{(N)}$ (see especially Refs. 6 and 12). As shown in Ref. 6, the $\epsilon^{(N)}$ are given asymptotically by

$$\epsilon^{(N)} \sim C(-1)^{N+1} \frac{2^{15}}{3^4 \pi^6} \left(\frac{648}{\pi^2} \right)^N \frac{(2N+9/2)!}{(-1/2)!} \times \left(1 + \frac{A_1}{2N+9/2} + O(N^{-2}) \right), \quad (86)$$

where for $|0\rangle = |s\rangle$, the values of C and A_1 are, respectively, 1.118 869 026 7 and -43.442 76, while for $|0\rangle = |d\rangle$ the values are 0.006 130 973 271 8 and -24.650 86. The factor $(2N+9/2)!$ clearly indicates the divergent asymptotic character of the expansion.

In Table I we give $\epsilon^{(N)}$ for the two states for $0 \leq N \leq 87$.

IV. SUMMARY

A new recursive solution has been given for the energy and wave function in degenerate Rayleigh-Schrödinger perturbation theory [Eqs. (33)–(40)]. The final equations [(38) and (39)] are very similar in form to the analogous nondegenerate $\chi^{(N)}$ and $E^{(N)}$ formulas [(8) and (7)]. To achieve the similarity, new Hamiltonian-related operators were defined [Eqs. (33)–(35)].

Because of the striking similarity of the new degenerate formulas with the familiar nondegenerate formulas, to be contrasted with the greater complication of previous solutions,^{2,3,5-7} we might opine that at least translucence has displaced opacity.^{1,3} The usefulness of the recursive formulas for high-order calculations was illustrated by a calculation of the perturbed energy coefficients for the $3s-3d_0$ states of hydrogen in the Zeeman effect to 87th order in $\frac{1}{2}b^2$.

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