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A General Formula for Rayleigh-Schrödinger Perturbation Energy Utilizing a Power Series Expansion of the Quantum Mechanical Hamiltonian

by

John M. Herbert

MATHEMATICS AND COMPUTER SCIENCE DIVISION

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FOR THE BSc DEGREE

DEPARTMENT OF CHEMISTRY
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ABSTRACT

Perturbation theory has long been utilized by quantum chemists as a method for approximating solutions to the Schrödinger equation. Perturbation treatments represent a system's energy as a power series in which each additional term further corrects the total energy; it is therefore convenient to have an explicit formula for the *n*th-order energy correction term. If all perturbations are collected into a single Hamiltonian operator, such a closed-form expression for the *n*th-order energy correction is well known; however, use of a single perturbed Hamiltonian often leads to divergent energy series, while superior convergence behavior is obtained by expanding the perturbed Hamiltonian in a power series. This report presents a closed-form expression for the *n*th-order energy correction obtained using Rayleigh-Schrödinger perturbation theory and a power series expansion of the Hamiltonian.

I. INTRODUCTION

Since the inception of quantum mechanics, perturbation theory has been an important tool for analyzing certain molecular systems whose Schrödinger equations are too complicated to be exactly soluble [1], proving especially useful in the study of nuclear motion about or near a molecule's equilibrium geometry [2, 3]. Systems suitable for perturbation treatment can be formulated as arising via the continuous disturbance or deformation of an "ideal" system whose Schrödinger equation can be solved exactly [4].

Standard perturbation-theoretical approaches separate the full quantum mechanical Hamiltonian operator $\hat{H}$ into two parts:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}', \tag{1}$$

where $\hat{H}^{(0)}$ represents the Hamiltonian operator for an unperturbed system whose Schrödinger equation can be solved exactly and $\hat{H}'$ comprises the Hamiltonian operator for all deviations from ideality. The perturbation parameter λ is arbitrary and may take on values in the interval $0 \leq \lambda \leq 1$, with $\lambda = 0$ corresponding to the unperturbed system. For certain problems, λ has an obvious physical interpretation [1]; otherwise, it is simply set equal to unity.

Incorporating the Hamiltonian operator (1), the Schrödinger equation for the perturbed system becomes

$$(\hat{H}^{(0)} + \hat{H}')\psi_m = E_m \psi_m \ , \tag{2}$$

where E_m and ψ_m are, respectively, the system's energy and state function in non-degenerate quantum state m.[1] Since $\hat{H} = \hat{H}(\lambda)$, the eigenfunctions ψ_m and eigenvalues E_m of $\hat{H}$ both depend upon λ, and we may expand both quantities as Maclaurin series in λ:

$$\psi_m = \psi_m^{(0)} + \lambda \psi_m^{(1)} + \lambda^2 \psi_m^{(2)} + \cdots \tag{3}$$

$$E_m = E_m^{(0)} + \lambda E_m^{(1)} + \lambda^2 E_m^{(2)} + \cdots \ , \tag{4}$$

where, for convenience, the symbols $\psi_m^{(k)}$ and $E_m^{(k)}$ (the kth-order corrections to ψ_m and E_m) are introduced to represent the proper Maclaurin series coefficients of λ^k, $k = 0, 1, 2, \ldots$ [5]. When all state functions and energies refer to the same quantum state, the subscripted quantum number m is often omitted.

II. Expansion of the Hamiltonian

While the perturbation expansion (1) of the Hamiltonian is of the form most frequently encountered in perturbation theory research, this simplistic formulation quite often causes the

energy series (4) to diverge [3]. Instead of constructing the perturbed Hamiltonian as in (1), $\hat{H}$ itself can be expanded as a Maclaurin series [4,6] and written in the form

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)} + \lambda^2\hat{H}^{(2)} + \cdots \tag{5}$$

where once again $\hat{H}^{(0)}$ is the Hamiltonian operator for the unperturbed system. Rather than grouping together all perturbations into a single term $\hat{H}'$, an expansion such as (5) represents each individual perturbation with its own Hamiltonian operator.

Note that a necessary condition for convergence of the energy series (4)[2] is

$$\left|E^{(k+1)}\right| < \left|E^{(k)}\right| \tag{6}$$

for all k. Using a Hamiltonian of the form in (5), Sprandel and Kern [3] have demonstrated that the perturbation energy corrections $E^{(k)}$ for the pure vibration of H_2 decrease asymptotically to at least 50th order (the highest order examined) for each of the nine quantum states investigated. Furthermore, when the expanded Hamiltonian (5) is used, the difference between theoretical calculations and experimental values decreased smoothly with increasing order of approximation. In contrast, when a perturbed Hamiltonian such as (1) was used, the same nine energy series clearly diverged after 30 to 50 terms.

III. Perturbation Energy

Although the power series formulation (5) of the Hamiltonian has several clear advantages over the form in (1), it has not been widely adopted, presumably because the numerous terms in

---

[1] For degenerate states, the notation becomes slightly more complicated. For details see references [4] and [5].
[2] For the rigorous conditions under which (4) converges for a power series expansion of the Hamiltonian, see reference [1].

(5) lead to complicated expressions wherever $\hat{H}$ is involved. Consequently, an explicit formula for the nth-order perturbation energy, $E^{(n)}$, has not been published.[3]

A logical point of origin for an energy formula is the Schrödinger equation,

$$\hat{H}\psi = E\psi \ . \tag{7}$$

In this case, $\hat{H}$, ψ, and E are represented by the series (3-5). Substituting these series into Equation (7) and collecting powers of λ, one obtains

$$\begin{aligned}(\hat{H}^{(0)}\psi^{(0)} - E^{(0)}\psi^{(0)}) + \lambda(\hat{H}^{(0)}\psi^{(1)} + \hat{H}^{(1)}\psi^{(0)} - E^{(0)}\psi^{(1)} - E^{(1)}\psi^{(0)}) + \cdots \\ + \lambda^n(\hat{H}^{(0)}\psi^{(n)} + \hat{H}^{(1)}\psi^{(n-1)} + \cdots + \hat{H}^{(n)}\psi^{(0)} - E^{(0)}\psi^{(n)} - E^{(1)}\psi^{(n-1)} - \cdots E^{(n)}\psi^{(0)}) \\ + \cdots + \lambda^{n+n}(\hat{H}^{(0)}\psi^{(n+n)} + \cdots + \hat{H}^{(n+n)}\psi^{(0)} - E^{(0)}\psi^{(n+n)} - \cdots - E^{(n+n)}\psi^{(0)}) = 0 \ .\end{aligned} \tag{8}$$

Assuming that this series converges, Equation (8) will be true if and only if each of the coefficients of λ^k, k=0, 1, 2, ..., is separately zero [5]. Applying this condition to the first n+1 coefficients, one obtains [7] the following perturbation equations:

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \tag{9}$$

$$\sum_{i=0}^{n}(\hat{H}^{(i)} - E^{(i)})\psi^{(n-i)} = 0 \ . \tag{10}$$

Notice that the zero-order perturbation equation (9) is simply the Schrödinger equation for the unperturbed system. The remaining perturbation equations serve to relate the separate terms of $\hat{H}$, ψ, and E, and need not have any independent physical significance [8].

Multiplying the n^{th}-order perturbation equation (10) by $\psi^{(0)*}$ and integrating over all configuration space τ, one obtains

$$\langle\psi^{(0)}|\hat{H}^{(0)}|\psi^{(n)}\rangle + \cdots + \langle\psi^{(0)}|\hat{H}^{(n)}|\psi^{(0)}\rangle = E^{(0)}\langle\psi^{(0)}|\psi^{(n)}\rangle + \cdots + E^{(n)}\langle\psi^{(0)}|\psi^{(0)}\rangle \ , \tag{11}$$

where

[3] When the perturbation is written as a single term $\hat{H}'$, such a formula is known; see reference [1].

$$\left\langle \psi^{(i)} \middle| \hat{H}^{(j)} \middle| \psi^{(k)} \right\rangle \equiv \int \psi^{(i)*} \hat{H}^{(j)} \psi^{(k)} d\tau \tag{12}$$

and

$$\left\langle \psi^{(i)} \middle| \psi^{(j)} \right\rangle \equiv \int \psi^{(i)*} \psi^{(j)} d\tau \ . \tag{13}$$

Since the unperturbed Schrödinger equation (9) is soluble (by hypothesis), the complete set of wave functions $\left\{\psi_m^{(0)}\right\}$ is fully known. Moreover, each $\psi_m^{(0)}$ is an eigenfunction of the Hermitian operator $\hat{H}^{(0)}$, so $\left\{\psi_m^{(0)}\right\}$ is an orthogonal set [5]. Finally, one may assume that the unperturbed wave functions are normalized to integration, so that

$$\left\langle \psi_i^{(0)} \middle| \psi_j^{(0)} \right\rangle = \delta_{i,j} \ , \tag{14}$$

where $\delta_{i,j}$ is the Kronecker delta function. Applying Condition (14) to Equation (11), one finds that the *n*th-order energy correction is given by the recursive relation

$$\begin{aligned} E^{(n)} = &\left\langle \psi^{(0)} \middle| \hat{H}^{(0)} \middle| \psi^{(n)} \right\rangle + \cdots + \left\langle \psi^{(0)} \middle| \hat{H}^{(n)} \middle| \psi^{(0)} \right\rangle \\ &- E^{(0)} \left\langle \psi^{(0)} \middle| \psi^{(n)} \right\rangle - \cdots - E^{(n-1)} \left\langle \psi^{(0)} \middle| \psi^{(1)} \right\rangle \ . \end{aligned} \tag{15}$$

IV. Rayleigh-Schrödinger Perturbation Theory

Equation (15) can be simplified considerably by resorting to the Rayleigh-Schrödinger form of perturbation theory. If the system of interest is roughly modeled by an unperturbed system with Hamiltonian operator $\hat{H}^{(0)}$, it is reasonable to assume that the complete set $\left\{\psi_m^{(0)}\right\}$ of unperturbed wave functions forms a basis for the Hilbert space of the Hermitian operator $\hat{H}$ corresponding to the *perturbed* system [9]; this assumption is the foundation of Rayleigh-

Schrödinger perturbation theory.[4] In light of this assumption, one may express all perturbed wave functions $\psi_m^{(i)}$ as linear combinations of the basis functions belonging to $\{\psi_m^{(0)}\}$:

$$\psi_m^{(i)} = \sum_j c_j^{(i)} \psi_j^{(0)} \tag{16}$$

where are $c_0^{(i)}$, $c_1^{(i)}$, $c_2^{(i)}$, ... are constants.

The linear expansion (16) precipitates an important result that greatly simplifies perturbation theory calculations. It can be shown [5, 8] that the coefficient $c_m^{(i)}$ in (16) does not affect any of the perturbation energy corrections, so this coefficient will be assigned a value of zero. Thus,

$$\psi_m^{(i)} = \sum_{j \neq m} c_j^{(i)} \psi_j^{(0)} \tag{17}$$

and

$$\begin{aligned} \left\langle \psi_m^{(0)} \middle| \psi_m^{(n)} \right\rangle &= \sum_{j \neq m} c_j^{(n)} \left\langle \psi_m^{(0)} \middle| \psi_j^{(0)} \right\rangle \\ &= \sum_{j \neq m} c_j^{(n)} \delta_{m,j} \end{aligned} \tag{18}$$

by (17) and (14). Note that the summation in (18) precludes $j = m$, so that $\delta_{m,j} = 0$. Hence, one obtains the condition

$$\left\langle \psi_m^{(0)} \middle| \psi_m^{(n)} \right\rangle = \delta_{0,n} \tag{19}$$

for all n.

Equation (19)— which implies that each perturbed wave function is orthogonal to the unperturbed basis function corresponding to the same state— is often misquoted as the fundamental assumption of Rayleigh-Schrödinger perturbation theory. As shown in (18), this orthogonality condition is actually a consequence of the Rayleigh-Schrödinger condition (16).

[4] Note that the Rayleigh-Schrödinger assumption is most likely to be valid when the perturbation from ideality is small; thus, Rayleigh-Schrödinger perturbation theory is not suited for the study of highly excited quantum states.

V. Reduced Formulae

As a consequence of orthogonality condition (19), all overlap integrals in the energy expression (15) disappear, leaving

$$E^{(n)} = \sum_{j=0}^{n} \left\langle \psi^{(0)} \middle| \hat{H}^{(n-j)} \middle| \psi^{(j)} \right\rangle \ . \tag{20}$$

This expression for the nth-order energy correction involves n+1 different wave functions, while in general it is possible to express the (2p+1)st perturbation energy in terms of only the wave functions $\psi^{(0)}, \psi^{(1)}, \ \ldots \ , \psi^{(p)}$ [8]. Thus, the challenge is to reduce (20) to an expression involving the minimum possible number of wave functions.

To accomplish this reduction, first consider the case where n is odd; that is, $n = 2k+1$ for $k = 0, 1, 2, \ldots$. From (20),

$$E^{(2k+1)} = \left\langle \psi^{(0)} \middle| \hat{H}^{(2k+1)} \middle| \psi^{(0)} \right\rangle + \left\langle \psi^{(0)} \middle| \hat{H}^{(2k)} \middle| \psi^{(1)} \right\rangle + \ \cdots \ + \left\langle \psi^{(0)} \middle| \hat{H}^{(1)} \middle| \psi^{(2k)} \right\rangle , \tag{21}$$

since

$$\left\langle \psi^{(0)} \middle| \hat{H}^{(0)} \middle| \psi^{(2k+1)} \right\rangle = 0 \tag{22}$$

by (9) and (19). Substitution for $\hat{H}^{(k)}\psi^{(0)}, \hat{H}^{(k-1)}\psi^{(0)}, \ \ldots \ , \hat{H}^{(1)}\psi^{(0)}$ from the first k perturbation equations[5] and use of (19) provides

$$\begin{aligned} E^{(2k+1)} = {} & \left\langle \psi^{(0)} \middle| \hat{H}^{(2k+1)} \middle| \psi^{(0)} \right\rangle + \ \cdots \ + \left\langle \psi^{(0)} \middle| \hat{H}^{(k+1)} \middle| \psi^{(k)} \right\rangle + \left\langle \psi^{(1)} \middle| E^{(k-1)} - \hat{H}^{(k-1)} \middle| \psi^{(k+1)} \right\rangle \\ & + \left\langle \psi^{(2)} \middle| E^{(k-2)} - \hat{H}^{(k-2)} \middle| \psi^{(k+1)} \right\rangle + \ \cdots \left\langle \psi^{(k)} \middle| E^{(0)} - \hat{H}^{(0)} \middle| \psi^{(k+1)} \right\rangle \\ & + \ \cdots \ + \left\langle \psi^{(1)} \middle| E^{(0)} - \hat{H}^{(0)} \middle| \psi^{(2k)} \right\rangle , \end{aligned} \tag{23}$$

which still contains wave functions of order higher than k. To eliminate these, substitute for $(E^{(0)} - \hat{H}^{(0)})\psi^{(k+1)}, (E^{(0)} - \hat{H}^{(0)})\psi^{(k+2)}, \ \ldots \ , (E^{(0)} - \hat{H}^{(0)})\psi^{(2k)}$ from the next k perturbation equations. This step yields

$$
\begin{aligned}
E^{(2k+1)} = &\left\langle \psi^{(0)} \middle| \hat{H}^{(2k+1)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(0)} \middle| \hat{H}^{(k+1)} \middle| \psi^{(k)} \right\rangle \\
&+ \left\langle \psi^{(1)} \middle| E^{(k-1)} - \hat{H}^{(k-1)} \middle| \psi^{(k+1)} \right\rangle + \cdots + \left\langle \psi^{(k-1)} \middle| E^{(1)} - \hat{H}^{(1)} \middle| \psi^{(k+1)} \right\rangle \\
&+ \left\langle \psi^{(k)} \middle| \hat{H}^{(k+1)} - E^{(k+1)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(k)} \middle| \hat{H}^{(1)} - E^{(1)} \middle| \psi^{(k)} \right\rangle \\
&\vdots \\
&+ \left\langle \psi^{(1)} \middle| \hat{H}^{(2k)} - E^{(2k)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(1)} \middle| \hat{H}^{(1)} - E^{(1)} \middle| \psi^{(2k-1)} \right\rangle .
\end{aligned}
\tag{24}
$$

All matrix elements in (24) containing $\psi^{(k+1)}, \psi^{(k+2)}, \ldots, \psi^{(2k)}$ cancel out of this expression, affording

$$
\begin{aligned}
E^{(2k+1)} = &\left\langle \psi^{(0)} \middle| H^{(2k+1)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(0)} \middle| \hat{H}^{(k+1)} \middle| \psi^{(k)} \right\rangle \\
&+ \left\langle \psi^{(k)} \middle| \hat{H}^{(k+1)} - E^{(k+1)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(k)} \middle| \hat{H}^{(1)} - E^{(1)} \middle| \psi^{(k)} \right\rangle \\
&+ \left\langle \psi^{(k-1)} \middle| \hat{H}^{(k+2)} - E^{(k+2)} \middle| \psi^{(0)} \right\rangle + \cdots + \left\langle \psi^{(k-1)} \middle| \hat{H}^{(2)} - E^{(2)} \middle| \psi^{(k)} \right\rangle \\
&\vdots \\
&+ \left\langle \psi^{(1)} \middle| \hat{H}^{(2k)} - E^{(2k)} \middle| \psi^{(0)} \right\rangle
\end{aligned}
\tag{25}
$$

$$
\begin{aligned}
= &\left\langle \psi^{(0)} \middle| \hat{H}^{(2k+1)} \middle| \psi^{(0)} \right\rangle + \sum_{i=1}^{k} \left\langle \psi^{(i)} \middle| \hat{H}^{(2k+1-2i)} - E^{(2k+1-2i)} \middle| \psi^{(i)} \right\rangle \\
&+ 2 \sum_{j=1}^{k} \sum_{i=j}^{k} \left\langle \psi^{(j-1)} \middle| \hat{H}^{(2k-i-j+2)} - E^{(2k-i-j+2)} \middle| \psi^{(i)} \right\rangle .
\end{aligned}
$$

Since $n = 2k+1$, application of (19) to Equation (25) provides

$$
\begin{aligned}
E^{(n)} = &\sum_{i=0}^{\frac{1}{2}(n-1)} \left\langle \psi^{(i)} \middle| \hat{H}^{(n-2i)} \middle| \psi^{(i)} \right\rangle + 2 \sum_{j=1}^{\frac{1}{2}(n-1)} \sum_{i=j}^{\frac{1}{2}(n-1)} \left\langle \psi^{(j-1)} \middle| \hat{H}^{(n-i-j+1)} \middle| \psi^{(i)} \right\rangle \\
&- \sum_{i=1}^{\frac{1}{2}(n-1)} E^{(n-2i)} \left\langle \psi^{(i)} \middle| \psi^{(i)} \right\rangle - 2 \sum_{j=2}^{\frac{1}{2}(n-1)} \sum_{i=j}^{\frac{1}{2}(n-1)} E^{(n-i-j+1)} \left\langle \psi^{(j-1)} \middle| \psi^{(i)} \right\rangle
\end{aligned}
\tag{26}
$$

for odd n. While Equation (25) perhaps has a simpler form, Equation (26) separates the nth-order perturbation energy into its separate contributors: Hamiltonian matrix elements, overlap integrals, and lower-order perturbation energies.

A similar derivation for even n yields

---

[5] The k^{th} perturbation equation is equation (10) with $n = k$.

$$E^{(n)} = \sum_{i=0}^{\frac{1}{2}n-1} \left\langle \psi^{(i)} \middle| \hat{H}^{(n-2i)} \middle| \psi^{(i)} \right\rangle + 2 \sum_{j=1}^{\frac{1}{2}n-1} \sum_{i=j}^{\frac{1}{2}n-1} \left\langle \psi^{(j-1)} \middle| \hat{H}^{(n-i-j+1)} \middle| \psi^{(i)} \right\rangle$$
$$+ \sum_{i=0}^{\frac{1}{2}n-1} \left\langle \psi^{(i)} \middle| \hat{H}^{(\frac{1}{2}n-i)} \middle| \psi^{(\frac{1}{2}n)} \right\rangle - 2 \sum_{j=2}^{\frac{1}{2}n-1} \sum_{i=j}^{\frac{1}{2}n-1} E^{(n-i-j+1)} \left\langle \psi^{(j-1)} \middle| \psi^{(i)} \right\rangle \qquad (27)$$
$$- \sum_{i=1}^{\frac{1}{2}n-1} E^{(n-2i)} \left\langle \psi^{(i)} \middle| \psi^{(i)} \right\rangle - \sum_{i=1}^{\frac{1}{2}n-1} E^{(\frac{1}{2}n-i)} \left\langle \psi^{(i)} \middle| \psi^{(\frac{1}{2}n)} \right\rangle .$$

The sole difference between (26) and (27) is the coefficients of the overlap integrals and Hamiltonian matrix elements when $i = n$.

For some applications, it is useful to possess a formula that is valid for all n. As above, let $k = \frac{1}{2}n$ for even n and $k = \frac{1}{2}(n-1)$ for odd n. Then $\left\{\psi^{(0)}, \psi^{(1)}, \ldots, \psi^{(k)}\right\}$ is the smallest set of wave functions spanning $\left\{E^{(0)}, E^{(1)}, \ldots, E^{(n)}\right\}$. Incorporating k and the Kronecker delta function, one may combine Equations (26) and (27) into a single perturbation energy formula:

$$E^{(n)} = \sum_{j=1}^{k} \sum_{i=j}^{k} \left[\left(2 - \delta_{n,2i}\right) \left\langle \psi^{(j-1)} \middle| \hat{H}^{(n-i-j+1)} \middle| \psi^{(i)} \right\rangle \right] + \sum_{i=0}^{k-1} \left\langle \psi^{(i)} \middle| \hat{H}^{(n-2i)} \middle| \psi^{(i)} \right\rangle$$
$$- \sum_{j=2}^{k} \sum_{i=j}^{k} \left[\left(2 - \delta_{n,2i}\right) E^{(n-i-j+1)} \left\langle \psi^{(j-1)} \middle| \psi^{(i)} \right\rangle \right] - \sum_{i=1}^{k-1} E^{(n-2i)} \left\langle \psi^{(i)} \middle| \psi^{(i)} \right\rangle \qquad (28)$$
$$+ \left[\left\langle \psi^{(k)} \middle| \hat{H}^{(1)} \middle| \psi^{(k)} \right\rangle - E^{(1)} \left\langle \psi^{(k)} \middle| \psi^{(k)} \right\rangle (1 - \delta_{n,1}) \right] \delta_{n,2k+1}$$

for $n > 0$.

The generalized energy formula (28) is recursive, since the nth-order energy is a function of lower-order energies. Elimination of these lower-order energies from (28) is tedious, but in principle it is possible to express $E^{(n)}$ solely in terms of overlap integrals and Hamiltonian matrix elements. This procedure, however, results in an energy formula involving an infinite number of separate summations (only finitely many of which are non-zero for a given n). Thus, only as a recursive relation can the nth-order perturbation energy be expressed in a compact, closed form. Ultimately, the recursive nature of (28) poses no additional burden, since the entire sequence of

perturbations energies $E^{(1)}$, $E^{(2)}$, ..., $E^{(n)}$ should be calculated in order to investigate the convergence behavior of the energy series (4).

Note also that Equations (26-28) contain overlap integrals of the form $\langle \psi_m^{(i)} | \psi_m^{(i)} \rangle$. When $i = 0$, such integrals are equal to unity, since the unperturbed wave functions are assumed to be normalized. Imposing the restriction that the total wave function ψ_m be normalized and substituting for ψ_m from (3) provides

$$\langle \psi_m^{(0)} + \lambda\psi_m^{(1)} + \cdots + \lambda^n\psi_m^{(n)} | \psi_m^{(0)} + \lambda\psi_m^{(1)} + \cdots + \lambda^n\psi_m^{(n)} \rangle = 1 \ . \tag{29}$$

Expanding (29), collecting powers of λ, and applying (19), one obtains [1] the following set of equations:

$$\sum_{i=0}^{n} \langle \psi_m^{(n)} | \psi_m^{(n-i)} \rangle = 0 \ . \tag{30}$$

These equations demonstrate that in general $\langle \psi_m^{(i)} | \psi_m^{(i)} \rangle \neq 1$ for $i > 0$, so normalization of the total wave function ψ_m precludes normalization of the perturbed wave functions. Since ψ_m is the wave function of an actual physical system, its normalization condition will be retained.[6]

VI. Conclusion

The energy expression (28) is extremely general, for its derivation involved few assumptions. The first assumption— that the total wave function and the unperturbed wave functions are normalized— is trivial, and the assumption that $\hat{H}$ may be expanded as a power series is the foundation of this particular approach to perturbation theory. While the Rayleigh-Schrödinger condition (16) is certainly not trivial, it was used in this context only to derive the

[6] Recall that the perturbed wave functions, when taken individually, need not correspond to an actual physical system.

orthogonality condition (19). In the absence of Conditions (16) and (19), Equation (25)— along with an analogous expression for even n— is still valid.

Beyond these assumptions, however, the form of the expansion (3) of ψ_m requires that quantum state m of the unperturbed system be non-degenerate, since $\lim_{\lambda \to 0} \psi_m = \psi_m^{(0)}$ only for non-degenerate states m [5]. While Equation (28) is therefore valid only when the unperturbed system is non-degenerate, modifications can be made to accommodate degeneracy [4, 5].

In light of the superior convergence behavior of perturbation energies when a power series Hamiltonian is used, a general formula such as (28) is extremely important. In subsequent work, the Rayleigh-Schrödinger condition (16) will be used to express all wave functions in (28) as linear combinations of the state functions in the complete set $\left\{\psi_m^{(0)}\right\}$. Since the wave functions of this set are fully known (by hypothesis), the perturbation energy can thus be calculated (to arbitrarily high order) without knowledge of *any* perturbed wave functions. Furthermore, since empirical data [3] suggest that use of Equation (28) will lead to asymptotically decreasing perturbation energies, one simply increases n until the energy corrections fall below an appropriate tolerance. The system's total energy is then given by (4).

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