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On the Hellmann–Feynman theorem and the corrections to the energy in the Rayleigh–Schrödinger perturbation theory

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In this work we present an alternative method, based on the Hellmann–Feynman theorem, to generate energy corrections within the standard Rayleigh–Schrödinger perturbation theory. As a result, compact expressions for the corrections to the energy at different orders are obtained. We also review a method that allows us to calculate the corrections to the wave function needed in the energy calculations. Finally, our results are compared with those obtained by other authors by a different technique.

KEY WORDS: Hellmann–Feynman theorem, perturbation theory

1. Introduction

Rayleigh–Schrödinger perturbation theory (RSPT) has become an integral part of any course in quantum mechanics. Its validity depends on the premise that the eigenvalues $E_N(\lambda)$ and eigenfunctions $\psi_N(\lambda)$ are analytic functions of the perturbation parameter λ, appearing in the Hamiltonian $\widehat{H} = \widehat{H}^{(0)} + \lambda\widehat{V}$. In most of the textbooks, each of the terms of the expansion of E_N and ψ_N are obtained as function of the so-called zero order solution $\psi_N^{(0)}$ of the unperturbed problem, $\widehat{H}^{(0)}\psi_N^{(0)} = E_N^{(0)}\psi_N^{(0)}$. However, alternative methods to obtain approximations to E_N and ψ_N have been proposed [1–3], and at this time several comprehensive reviews on this topic are available [4,5]. On the other hand, the Hellmann–Feynman theorem (HFT), also discussed in many textbooks in quantum mechanics [6,7], has been widely used to calculate expectation values of some dynamical quantities [8,10]. Several extensions of this theorem have been proposed in the literature [11,13] and applications have been done covering a wide range of problems. The usefulness of the HFT in solving physical and chemical problems becomes clear from the number and diversity of applications where it has been employed. An interesting and instructive list of those applications has been presented in the book edited by Deb [14].

The relationship between perturbation theory and the HFT has been explored by several authors. Some have dealt with the accuracy of the theorem, when the wave function is approximated by the first j terms of its perturbation expansion [14], other have employed the HFT to rederive the RSPT for the nondegenerate and degenerate cases [1]

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and to obtain explicit expressions for the higher-order corrections to the energy [15]. The classical version of the HFT [16] has also been employed to generate canonical series expansions of the energy for separable classical Hamiltonians, which can be proved to correspond to series obtained from Rayleigh–Schrödinger perturbation expansions when an approximate classical limit is taken, while keeping the value of the classical action fixed.

In this work we show an alternative method for generating the energy corrections within the standard RSPT. As a result, compact expressions for the corrections to the perturbed energies at different orders are obtained. We also review a method that allows us to calculate the corrections to the wave function, needed in the energy calculations. Finally, our results are compared with those obtained by Killingbeck [4] by a different technique.

The layout of this work is as follows. In section 2 we outline the notation and present the method to obtain the perturbative energy corrections. Section 3 deals with the obtention of expressions for the perturbative corrections to the wave function, and finally, in section 4 a discussion is given about the difference between the results presented in section 2 and those reported by Killingbeck [4].

2. Recurrence relations for the perturbative energy corrections

Within the RSPT, Hamiltonians of the form

$$\widehat{H} = \widehat{H}^{(0)} + \lambda \widehat{V} \tag{1}$$

are considered. Here, $\widehat{H}^{(0)}$ and $\widehat{V}$ denote the unperturbed and perturbation operators, respectively. It is assumed that both operators are Hermitian and that $\widehat{H}^{(0)}$ possesses a complete set of orthonormal eigenfunctions $|\psi_N^{(0)}\rangle$ with distinct eigenvalues $E_N^{(0)}$,

$$\widehat{H}^{(0)}\big|\psi_N^{(0)}\big\rangle = E_N^{(0)}\big|\psi_N^{(0)}\big\rangle. \tag{2}$$

As mentioned in the introduction, standard RSPT assumes that the eigenvalues and eigenfunctions of the Schrödinger equation (SE)

$$\widehat{H}|\psi_N\rangle = E_N|\psi_N\rangle, \tag{3}$$

admit series expansions of the form

$$E_N = E_N(\lambda) = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k E_N}{\partial \lambda^k}\bigg|_{\lambda=0} \lambda^k = \sum_{k=0}^{\infty} E_N^{(k)} \lambda^k, \tag{4}$$

$$|\psi_N\rangle = \sum_{k=0}^{\infty} \frac{1}{k!} \frac{\partial^k \psi_N}{\partial \lambda^k}\bigg|_{\lambda=0} \lambda^k = \sum_{k=0}^{\infty} \big|\psi_N^{(k)}\big\rangle \lambda^k. \tag{5}$$

On the other hand, if $\widehat{H}$ is a time-independent Hermitian operator that depends explicitly on a real scalar parameter σ, the HFT states that [6,14]

$$\frac{\partial E_N}{\partial \sigma} = \langle \psi_N | \frac{\partial \widehat{H}}{\partial \sigma} | \psi_N \rangle, \tag{6}$$

where it is assumed that the normalization condition, $\langle \psi_N | \psi_N \rangle = 1$, holds.

Now, identifying σ with the perturbation parameter λ, we have that $\partial \widehat{H}/\partial \lambda = \widehat{V}$. Substitution of expansion (5) and the derivatives with respect to λ of expansion (4) into (6) renders

$$\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \langle \psi_N^{(i)} \lambda^i | \widehat{V} | \psi_N^{(j)} \lambda^j \rangle = \sum_{k=1}^{\infty} k \lambda^{k-1} E_N^{(k)}. \tag{7}$$

Next, collecting the terms with equal powers of λ and comparing coefficients we obtain

$$E_N^{(1)} = \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(0)} \rangle, \tag{8}$$

$$\begin{aligned} E_N^{(2)} &= \frac{1}{2} \left[\langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(1)} \rangle + \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(0)} \rangle \right] \\ &= \mathrm{Re} \left\{ \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(1)} \rangle \right\}, \end{aligned} \tag{9}$$

$$\begin{aligned} E_N^{(3)} &= \frac{1}{3} \left[\langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(2)} \rangle + \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(1)} \rangle + \langle \psi_N^{(2)} | \widehat{V} | \psi_N^{(0)} \rangle \right] \\ &= \frac{1}{3} \left[\langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(1)} \rangle + 2\mathrm{Re} \left\{ \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(2)} \rangle \right\} \right], \end{aligned} \tag{10}$$

$$\begin{aligned} E_N^{(4)} &= \frac{1}{4} \left[\langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(3)} \rangle + \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(2)} \rangle + \langle \psi_N^{(3)} | \widehat{V} | \psi_N^{(0)} \rangle + \langle \psi_N^{(2)} | \widehat{V} | \psi_N^{(1)} \rangle \right] \\ &= \frac{1}{4} \left[2\mathrm{Re} \left\{ \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(3)} \rangle \right\} + 2\mathrm{Re} \left\{ \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(2)} \rangle \right\} \right], \end{aligned} \tag{11}$$

$$\vdots$$

Here, $\mathrm{Re}(z)$ denotes the real part of the argument z. These relations can be generalized to obtain

$$E_N^{(2k+1)} = \frac{1}{2k+1} \left[\langle \psi_N^{(k)} | \widehat{V} | \psi_N^{(k)} \rangle + \sum_{i=0}^{k-1} 2\mathrm{Re} \left\{ \langle \psi_N^{(i)} | \widehat{V} | \psi_N^{(2k-i)} \rangle \right\} \right], \tag{12}$$

$$E_N^{(2k)} = \frac{1}{k} \sum_{i=0}^{k-1} \mathrm{Re} \left\{ \langle \psi_N^{(i)} | \widehat{V} | \psi_N^{(2k-i-1)} \rangle \right\}. \tag{13}$$

From these expressions, the corrections, to any order, to the zero-order energy can be obtained.

3. The wave function corrections

The recurrence relations obtained in the previous section confirm the well-known result that the correction of nth order to the energy depends on the corrections up to order $n-1$ in the wave function. Thus, if those relations are to be of any practical use, it is necessary to have available a way to readily generate the correction to the wave function. In order to do so, let us substitute (1), (4) and (5) into the SE (3), that is,

$$\left(H^{(0)}+\lambda\widehat{V}\right)\left(\sum_{k=0}^{\infty}|\psi_N^{(k)}\rangle\lambda^k\right)=\left(\sum_{k=0}^{\infty}E_N^{(k)}\lambda^k\right)\left(\sum_{k=0}^{\infty}|\psi_N^{(k)}\rangle\lambda^k\right). \tag{14}$$

Next, by differentiating both sides of this equation with respect to λ and comparing coefficients of equal power of the perturbation parameter, the following sequence of equations is obtained:

$$\begin{aligned}
&\left(\widehat{H}^{(0)}-E_N^{(0)}\right)\left|\psi_N^{(1)}\right\rangle=\left(E_N^{(1)}-\widehat{V}\right)\left|\psi_N^{(0)}\right\rangle,\\
&\left(\widehat{H}^{(0)}-E_N^{(0)}\right)\left|\psi_N^{(2)}\right\rangle=\left(E_N^{(1)}-\widehat{V}\right)\left|\psi_N^{(1)}\right\rangle+E_N^{(2)}\left|\psi_N^{(0)}\right\rangle,\\
&\left(\widehat{H}^{(0)}-E_N^{(0)}\right)\left|\psi_N^{(3)}\right\rangle=\left(E_N^{(1)}-\widehat{V}\right)\left|\psi_N^{(2)}\right\rangle+E_N^{(2)}\left|\psi_N^{(1)}\right\rangle+E_N^{(3)}\left|\psi_N^{(0)}\right\rangle,\\
&\left(\widehat{H}^{(0)}-E_N^{(0)}\right)\left|\psi_N^{(4)}\right\rangle=\left(E_N^{(1)}-\widehat{V}\right)\left|\psi_N^{(3)}\right\rangle+E_N^{(2)}\left|\psi_N^{(2)}\right\rangle+E_N^{(3)}\left|\psi_N^{(1)}\right\rangle+E_N^{(4)}\left|\psi_N^{(0)}\right\rangle,\\
&\qquad\vdots
\end{aligned} \tag{15}$$

For corrections in the wave function of order equal or larger than two, the previous equations can be generalized to yield

$$\left(\widehat{H}^{(0)}-E_N^{(0)}\right)\left|\psi_N^{(j)}\right\rangle=\left(E_N^{(1)}-\widehat{V}\right)\left|\psi_N^{(j-1)}\right\rangle+\sum_{k=0}^{j-2}E_N^{(j-k)}\left|\psi_N^{(k)}\right\rangle,\quad j\geqslant 2. \tag{16}$$

The method employed to solve this kind of equations is well known [4,7], nevertheless, as a manner of example, let us show the solution for the first-order correction. Thus, by invoking the closure relation for the zero-order eigenfunction and employing (15) we have

$$\begin{aligned}
\left(-\widehat{H}^{(0)}+E_N^{(0)}\right)\left|\psi_N^{(1)}\right\rangle&=\sum_J\left|\psi_J^{(0)}\right\rangle\left\langle\psi_J^{(0)}\right|\widehat{V}-E_N^{(1)}\left|\psi_N^{(0)}\right\rangle\\
&=\sum_{J\neq N}\left|\psi_J^{(0)}\right\rangle\left\langle\psi_J^{(0)}\right|\widehat{V}\left|\psi_N^{(0)}\right\rangle+E_N^{(1)}\left|\psi_N^{(0)}\right\rangle-E_N^{(1)}\left|\psi_N^{(0)}\right\rangle,
\end{aligned}$$

and by applying the operator $(E_N^{(0)}-\widehat{H}^{(0)})^{-1}$ to both sides of this equation we obtain

$$\left|\psi_N^{(1)}\right\rangle=\sum_{J\neq N}\frac{V_{JN}}{E_N^{(0)}-E_J^{(0)}}\left|\psi_J^{(0)}\right\rangle, \tag{17}$$

where the matrix element $V_{JN}=\langle\psi_J^{(0)}|\widehat{V}|\psi_N^{(0)}\rangle$ has been introduced.

4. The Killingbeck energy relations

In his work, Killingbeck [4] presented relations for the perturbation corrections to the energy, some of which at first glance look different to the ones shown in section 2. Thus, for the third and fourth order corrections he obtained

$$E_N^{(3)} = \langle \psi_N^{(1)} | \widehat{V} - E_N^{(1)} | \psi_N^{(1)} \rangle,$$
$$E_N^{(4)} = \langle \psi_N^{(2)} | E_N^{(0)} - \widehat{H}^{(0)} | \psi_N^{(2)} \rangle - E_N^{(2)} \langle \psi_N^{(1)} | \psi_N^{(1)} \rangle.$$

Before continuing, it is worth mentioning that he arrived to these equations by employing a different methodology than the one used here. As an exercise, it would be interesting to explore the reasons for this seeming difference between these two results.

In order to do so, let us start by clearly stating the conditions employed by Killingbeck in his work. There, he assumed that the $\psi_N^{(k)}$ are real functions and that the perturbed wave function ψ_N obeys the intermediate normalization condition, $\langle \psi_N | \psi_N^{(0)} \rangle = 1$. In what follows, we will relax the first condition (i.e., we will consider complex functions), but we will stick to the intermediate normalization. Now, let us notice that from this normalization condition, it follows that $\langle \psi_N^{(k)} | \psi_N^{(0)} \rangle = 0$, $k = 1, 2, \ldots$. Thus, by employing this result and (5) we obtain

$$\langle \psi_N | \psi_N \rangle = 1 + \sum_{j=1} \sum_{k=1} \lambda^{k+j} \langle \psi_N^{(k)} | \psi_N^{(j)} \rangle, \tag{18}$$

which is in general different from one. Next, we realize that under this condition, instead of (6), the HFT has to be taken as

$$\frac{\partial E}{\partial \lambda} = \frac{\langle \psi_N | \partial \widehat{H} / \partial \lambda | \psi_N \rangle}{\langle \psi_N | \psi_N \rangle}. \tag{19}$$

Thus, after substituting (4), (5) and (18) into (19), performing the algebra involved, and collecting equal powers of λ, the following equations are obtained:

$$E_N^{(1)} = \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(0)} \rangle,$$
$$E_N^{(2)} = \mathrm{Re}\{ \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(1)} \rangle \},$$
$$E_N^{(3)} = \frac{1}{3} \big[2\mathrm{Re}\{ \langle \psi_N^{(0)} | \widehat{V} | \psi_N^{(2)} \rangle \} + \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(1)} \rangle - E_N^{(1)} \langle \psi_N^{(1)} | \psi_N^{(1)} \rangle \big],$$
$$E_N^{(4)} = \frac{1}{4} \big[2\mathrm{Re}\{ \langle \psi_N^{(1)} | \widehat{V} | \psi_N^{(2)} \rangle \} - 2\big(E_N^{(2)} \langle \psi_N^{(1)} | \psi_N^{(1)} \rangle + E_N^{(1)} \mathrm{Re}\{ \langle \psi_N^{(1)} | \psi_N^{(2)} \rangle \} \big) \big],$$
$$\vdots$$

By employing equations (15) and (16), the last two equations can be transformed into

$$E_N^{(3)} = \langle \psi_N^{(1)} | \widehat{V} - E_N^{(1)} | \psi_N^{(1)} \rangle,$$
$$E_N^{(4)} = \langle \psi_N^{(2)} | E_N^{(0)} - \widehat{H}^{(0)} | \psi_N^{(2)} \rangle - E_N^{(2)} \langle \psi_N^{(1)} | \psi_N^{(1)} \rangle.$$

The energy corrections obtained in this manner are identical to the ones reported by Killingbeck. Thus, we can see that the difference between these results and the ones reported in section 2 is only due to the fact that different normalization conditions are used in each case. This example illustrates the fact that the method employed in this work proves to be versatile enough to give the right energy corrections under the proper conditions.

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