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Theory

Non-degenerate fourth order perturbation theory

Gilbert A. Ibitola[1*], Olanrewaju Ajanaku[1] and Abiola O. Ilori[1,2]

[1]Department of Physical Sciences, Ondo State University of Science and Technology, Okitipupa, Nigeria.
[2]School of Chemistry and Physics, University of KwaZulu-Natal, Scottsville, Pietermaritzburg Campus, South Africa.

*Corresponding author. Email: ibitolaieee@gmail.com

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ABSTRACT: There exist several forms of perturbation theory in Quantum Mechanics, namely: non-degenerate perturbation theory, degenerate perturbation theory, time-dependent perturbation theory, time-constant perturbation theory and time-harmonic perturbation theory. This paper presents an extension of the perturbation theory for non-degenerate states. It has been observed that most texts and journal papers treat only the first –order and second-order non-degenerate perturbation theory. Therefore, this paper attempts to treat and present the third order and fourth order non-degenerate perturbation theory in quantum mechanics. It can thus be asserted that the higher the order of perturbations of quantum systems that we know, the more successful will be our efforts in suppressing or eliminating them.

Keywords: Energy states, first-order, fourth-order, Hamiltonian, perturbation, perturbation-free, perturbed, second–order, third-order, unperturbed state, wave function.

INTRODUCTION

Perturbations cause shifts or changes in values of the Hamiltonian, energy states and wave functions of the particles (such as electrons) constituting atoms (Condon and Shortley, 1990; Bell, 2004). For example, there are slight perturbations in the energy levels of the hydrogen atom (Fermi, 1971), where effects of spin, electric and magnetic fields shift the energies by small amounts from the one-electron atomic model (Flugge, 1994; Nomura and Yamada, 2003). Another example is the case of a potential well that is nearly a harmonic oscillator potential but has either a weak asymmetry, or deviates from quadratic well for large excursions (Sasaki et al., 2005).

In atomic systems, perturbations can be caused by any or several of the following (Mandl, 1987; Goldman and Krivchenkov, 2003):

i. Kinetic energy:

$$T = \frac{P_n^2}{2M_n} + \sum_{i=1}^{n} \frac{P_i^2}{2M_e} \quad (1)$$

ii. Electron-nucleus electrostatic interaction:

$$V_{en} = -\sum_{i=1}^{N} \frac{Ze^2}{4\pi\varepsilon_o r_1} \quad (2)$$

iii. Electron-electron mutual electrostatic interaction (repulsion):

$$V_{ee} = \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{e^2}{4\pi\varepsilon_o r_{1j}} \quad (3)$$

iv. Spin-orbit interaction (spin angular momentum-orbital angular momentum):

$$V_{so} = -\sum_{i=1}^{N} \frac{\sigma_i l_i}{m^2 r_i c^2}\left(\frac{dV}{dr_i}\right) \quad (4)$$

v. Spin-spin interaction (electron spin-electron spin):

$$V_{ss} = \frac{\mu_0}{4\pi} \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{e^2}{m^2}\left[\frac{\sigma_i\sigma_j}{r_{ij}^3} - \frac{3(\sigma_i r_{ij})(\sigma_j r_{ij})}{r_{ij}^5}\right] \quad (5)$$

vi. Orbit-orbit interaction (electron-electron orbital angular momentum):

$$V_{oo} = \sum_{i=1}^{N} \sum_{j=1}^{i-1} C_{ij} l_i l_j \quad (6)$$

vii. Electron spin-nuclear magnetic moment:

$$V_{esnmm} = \frac{\mu_0}{4\pi} \sum_{i=1}^{N} \frac{e}{m}\left[\frac{\mu_n\sigma_i}{r_i^3} - \frac{3(\mu_n r_i)(\sigma_i r_i)}{r_i^5}\right] \quad (7)$$

viii. Nuclear spin-electron orbital angular momentum:

$$V_{esnmm} = \frac{\mu_0}{4\pi}\sum_{i=1}^{N}\frac{e}{m}\left(\frac{\mu_n l_i}{2\pi r_i^3}\right) \quad (8)$$

ix. Relativistic correction (to the kinetic energy):

$$V_{rct} = -\sum_{i=1}^{N}\frac{P_i^4}{8m^3c^2} \quad (9)$$

x. "Exchange interaction".

xi. Miscellaneous other effects, such as quadrupole interactions, finite nuclear size, etc.

The dominant terms after the first two are generally terms (x) and (iii), after which term (iv) is next and the remainder are usually negligible. For heavy atoms, sometimes term (iv) predominates over terms (x) or (iii). In order to estimate the effects of these terms that cannot be computed and treated exactly, the perturbation theory is one of the methods needed to compute accurately the Hamiltonian, energy states and wave functions for atomic systems.

NOND-EGENERATE PERTURBATION THEORY

Formally, Hamiltonian cannot solve exactly, but the dominant portion presumably can be treated analytically. Therefore, Hamiltonian is separated into a zero-order part and a first-order part (Sasaki et al., 2005):

$$\hat{H} = \hat{H}^{(o)} + \hat{H}^{(I)} \quad (10)$$

Where $\hat{H}^{(I)}$ is relatively small, and the eigenfunctions and eigenvalues of $\hat{H}^{(o)}$ are presumably known.

In the formal development of the perturbation theory, the perturbation will be "turn on" gradually, so that equation (10) can be written as:

$$\hat{H} = \hat{H}^{(o)} + \propto \hat{H}^{(I)} \quad (11)$$

Where $0 \leq \propto \leq 1$ is a parameter. Both the eigenvalues and the eigen functions in this parameter will be expanded, such that:

$$E_n = E_n^{(o)} + \propto E_n^{(1)} + \propto^2 E_n^{(2)} + \propto^3 E_n^{(3)} + ------ \quad (12)$$

$$\Psi_n = \Psi_n^{(0)} + \alpha\Psi_n^{(1)} + \alpha^2\Psi_n^{(2)} + \alpha^3\Psi_n^{(3)} + ---- \quad (13)$$

Where $E_n^{(o)}$ *and* $\Psi_n^{(0)}$ correspond to the unperturbed system ($\alpha = 0$). Then, the time-independent Schrodinger equation can be rewritten as:

$$(\hat{H} - E_n)\Psi_n = (\hat{H}^0 + \alpha\hat{H}^1 - E_n^{(o)} - \alpha E_n^{(1)} - \propto^2 E_n^{(2)} - \propto^3 E_n^{(3)} - \propto^4 E_n^{(4)} \ldots\ldots)(\Psi_n^{(0)} + \alpha\Psi_n^{(1)} + \alpha^2\Psi_n^{(2)} + \alpha^3\Psi_n^{(3)} + \alpha^4\Psi_n^{(4)} \ldots\ldots) = 0 \quad (14)$$

which becomes after collecting like terms of the same order in $\propto$,

$$(\hat{H}^0 - E_n^{(o)})\Psi_n^{(0)} + \alpha[(\hat{H}^{(1)} - E_n^{(1)})\Psi_n^{(0)} + (\hat{H}^{(0)} - E_n^{(o)})\Psi_n^{(1)}] + \alpha^2[(\hat{H}^{(0)}\Psi_n^{(3)} + \hat{H}^{(1)}\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(3)} - E_n^{(1)}\Psi_n^{(2)} - E_n^{(2)}\Psi_n^{(1)})] + \alpha^3[(\hat{H}^{(0)}\Psi_n^{(3)} + \hat{H}^{(1)}\Psi_n^{(2)} - E_n^{(0)}\Psi_n^{(3)} - E_n^{(1)}\Psi_n^{(2)} - E_n^{(2)}\Psi_n^{(1)} - E_n^{(3)}\Psi_n^{(0)})] + \alpha^4[(\hat{H}^{(0)}\Psi_n^{(4)} + \hat{H}^{(1)}\Psi_n^{(3)} - E_n^{(0)}\Psi_n^{(4)} - E_n^{(1)}\Psi_n^{(3)} - E_n^{(2)}\Psi_n^{(2)} - E_n^{(3)}\Psi_n^{(1)} - E_n^{(4)}\Psi_n^{(0)})] + \cdots = 0 \quad (15)$$

Since this equation must be valid for arbitrary values of α, the coefficients must individually vanish, so that we get:

$$(\hat{H}^{(0)} - E_n^{(o)})\Psi_n^{(0)} = 0; \quad (16)$$

$$(\hat{H}^{(1)} - E_n^{(1)})\Psi_n^{(0)} + (\hat{H}^{(0)} - E_n^{(o)})\Psi_n^{(1)} = 0; \quad (17)$$

$$\hat{H}^{(0)}\Psi_n^{(2)} + \hat{H}^{(1)}\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(2)} - E_n^{(1)}\Psi_n^{1} - E_n^{(2)}\Psi_n^{(0)} = 0; \quad (18)$$

$$\hat{H}^{(0)}\Psi_n^{(3)} + \hat{H}^{(1)}\Psi_n^{(2)} - E_n^{(0)}\Psi_n^{(3)} - E_n^{(1)}\Psi_n^{(2)} - E_n^{(2)}\Psi_n^{(1)} - E_n^{(3)}\Psi_n^{(0)} = 0; \quad (19)$$

$$\hat{H}^{(0)}\Psi_n^{(4)} + \hat{H}^{(1)}\Psi_n^{(3)} - E_n^{(0)}\Psi_n^{(4)} - E_n^{(1)}\Psi_n^{(3)} - E_n^{(2)}\Psi_n^{(2)} - E_n^{(3)}\Psi_n^{(1)} - E_n^{(4)}\Psi_n^{(0)} = 0. \quad (20)$$

Equation (16) is just the zero-order equation of the unperturbed system, and all of these zero-order quantities are known exactly.

NONDEGENERATE FIRST –ORDER PERTURBATION THEORY

In equation (17), the first-order quantities are related to the zero-order quantities. To find the first-order quantities, scalar product of equation (17) with $\Psi_n^{(0)}$ is taken to obtain (Marston and Affleck, 1998):

$$\langle\Psi_n^{(0)}|\hat{H}^{(0)}|\Psi_n^{(1)}\rangle - E_n^{(1)}\left\langle\Psi_n^{(0)}|\Psi_n^{(0)}\right\rangle + \left\langle\Psi_n^{(0)}|\hat{H}^{(0)}|\Psi_n^{(1)}\right\rangle - E_n^{(0)}\left\langle\Psi_n^{(0)}|\Psi_n^{(1)}\right\rangle = 0 \quad (21)$$

Using the Hermitian property of $\hat{H}^{(0)}$ in the third term of equation (21), we have:

$$\left\langle\Psi_n^{(0)}|\hat{H}^{(0)}|\Psi_n^{(1)}\right\rangle = \left\langle\hat{H}^{(0)}\Psi_n^{(0)}|\Psi_n^{(1)}\right\rangle = E_n^{(0)}\left\langle\Psi_n^{(0)}|\Psi_n^{(1)}\right\rangle \quad (22)$$

so that the third term cancels the fourth term of equation (21); then since $\Psi_n^{(0)}$ is normalised, we find:

$$E_n^{(1)} = \frac{\left\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_n^{(0)}\right\rangle}{\left\langle\Psi_n^{(0)}|\Psi_n^{(0)}\right\rangle} = \left\langle\Psi_n^{(0)}|\hat{H}^{(1)}|\Psi_n^{(0)}\right\rangle = \hat{H}^{(1)} \quad (23)$$

so that the first–order correction to the energy is the average value of the perturbed energy in the unperturbed state. For the first-order wave function, it can be represented in terms of the zero-order wave function since they form a complete functional set, so that:

$$\Psi_n^{(1)} = \sum_i a_{ni}\,\Psi_i^{(0)}. \quad (24)$$

Inserting equation (24) into equation (17), the first-order equation can be written as:

$$\hat{H}^{(1)}\Psi_n^{(0)} + \hat{H}^{(0)}\sum_i a_{ni}\,\Psi_i^{(0)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\sum_i a_{ni}\,\Psi_i^{(0)} \quad (25)$$

Since $i \neq n, a_{nn} = 0$ *and* $\Psi_k^{(0)} = \langle K|$, therefore equation (25) becomes:

$$\langle K|\hat{H}^{(1)}|n\rangle + \sum_i a_{ni}\,\langle K|\hat{H}^{(0)}|i\rangle = E_n^{(1)}\langle K|n\rangle + E_n^{(0)}\sum_i a_{ni}\,\langle K|i\rangle \quad (26)$$

Since the kets and bras are Eigen functions, three of the integrals reduce to Kronecker delta functions, and we get:

$$\langle K|\hat{H}^{(1)}|n\rangle + \sum_i a_{ni}\,E_i^{(0)}\delta_{ki} = E_n^{(i)}\delta_{kn} + E_o^{(n)}\sum_i a_{ni}\,\delta_{ki} \quad (27)$$

The δ_{ki} functions cancel out the summations, and we get:

$$H_{Kn}^{(1)} + a_{nk}E_K^{(0)} = E_n^{(1)}\,\delta_{Kn} + a_{nk}E_K^{(0)} \quad (28)$$

For K = n, Equation (28) becomes:

$$E_n^{(1)} = H_{nn}^{(1)}. \quad (29)$$

For K $\neq n$, Equation (28) becomes

$$H_{Kn}^{(1)} = a_{nk}(E_n^{(0)} - E_K^{(0)}) \quad (30)$$

In the non-degenerate case, $E_K^{(0)} \neq E_n^{(0)}$ such that the $a_{nk}'s$ are finite. In the degenerate case, $E_K^{(0)} = E_n^{(0)}$ such that the $a_{nk}'s$ are infinite which are not physically acceptable.

NON-DEGENERATE SECOND-ORDER PERTURBATION THEORY

Sometimes in some physical cases, $H_{nn}^{(1)} = 0$, so in order to find the lowest order of non-zero correction, we must proceed to the second order in perturbation theory (Avron et al., 1994; Abrikosov et al., 1995). In this regard, let $\Psi_n^{(2)}$ be expanded in the same basis set, so that we have:

$$\Psi_n^{(2)} = \sum_j b_{nj}\,\Psi_j^{(0)} \quad (31)$$

Thus, equation (18) becomes:

$$\hat{H}^{(0)}\sum_j b_{nj}\,\Psi_j^{(0)} + \hat{H}^{(1)}\sum_i a_{ni}\,\Psi_i^{(0)} - E_n^{(0)}\sum_j b_{nj}\,\Psi_j^{(0)} - E_n^{(1)}\sum_i a_{ni}\,\Psi_i^{(0)} - E_n^{(2)}\Psi_n^{(0)} = 0 \quad (32)$$

In equation (32), taking the scalar product with $\langle K|$, we get:

$$\sum_j b_{nj}\langle K|\hat{H}^{(o)}|j\rangle + \sum_i a_{ni}\,\langle K|\hat{H}^{(1)}|j\rangle = E_n^{(0)}\sum_j b_{nj}\,\langle K|j\rangle + E_n^{(1)}\sum_i a_{ni}\,\langle K|i\rangle + E_n^{(2)}\langle K|n\rangle. \quad (33)$$

In Equation (33), the integrals lead to Kronecker delta functions such that we get:

$$\sum_j b_{nj}\,E_j^{(0)}\delta_{Kj} + \sum_i a_{ni}\,\mathrm{H}_k^{(i)} = E_n^{(0)}\sum_j b_{nj}\,\delta_{Kj} + E_n^{(1)}\sum_i a_{ni}\delta_{Ki} + E_n^{(2)}\delta_{Kn} \quad (34)$$

In equation (34), all the summations are cancelled out by the Kronecker delta functions except one leading to:

$$b_{nk}\,E_K^{(0)} + \sum_i a_{ni}\,\mathrm{H}_{Ki}^{(1)} = E_n^{(0)}\sum_j b_{nj}\,\delta_{Kj} + E_n^{(1)}\sum_i a_{ni}\,\delta_{Ki} + E_n^{(2)}\delta_{Kn} \quad (35)$$

For k=n, equation (35) gives the second-order energy correction as:

$$E_n^{(2)} = \sum_i a_{ni}\,H_{ni}^{(1)} - a_{nn}E_n^{(1)} = \sum_i a_{ni}\,H_{ni}^{(1)} - a_{nn}H_{nn}^{(1)} = \sum_{i\neq n} a_{ni}\,H_{ni}^{(1)} \quad (36)$$

Recall from equation (30), that:

$$a_{nK} = \frac{H_{Kn}^{(1)}}{(E_n^{(0)} - E_K^{(0)})} \quad (37)$$

Hence, similarly, we have:

$$a_{ni} = \frac{H_{in}^{(1)}}{(E_n^{(0)} - E_i^{(0)})} \quad (38)$$

Using equation (38), equation (36) can be written as:

$$E_n^{(2)} = \sum_{i\neq n}\frac{H_{in}^{(1)}H_{ni}^{(1)}}{(E_n^{(0)} - E_i^{(0)})} \quad (39)$$

It should be noted here that the second-order energy correction has been obtained with only the first-order wave functions, just as the first-order energy correction was obtained with only the zero-order wave functions. To obtain the second-order wave functions, equation (35) is examined with k $\neq n$. This gives:

$$b_{nk}\left(E_K^{(0)} - E_n^{(0)}\right) = a_{nK}H_{ni}^{(1)} - \sum_i a_{ni}\,H_{Ki}^{(1)} \quad \text{or}$$

$$b_{nk} = \sum_{i\neq n}\frac{H_{in}^{(1)}H_{Ki}^{(1)}}{(E_n^{(0)} - E_K^{(0)})(E_n^{(0)} - E_i^{(0)})} - \frac{H_{Kn}^{(1)}H_{nn}^{(1)}}{(E_n^{(0)} - E_K^{(0)})^2} \quad (40)$$

The higher order wave functions are given by:

$$\Psi_n = \Psi_n^{(0)} + \sum_{k \neq n} a_{nK} \Psi_k^{(0)} + \sum_{k \neq n} b_{nK} \Psi_k^{(0)} \qquad (41)$$

Or

$$\Psi_n = \Psi_n^{(0)} + \sum_{i \neq n} a_{ni} \Psi_i^{(0)} + \sum_{j \neq n} b_{nj} \Psi_j^{(0)} \qquad (42)$$

NONDEGENERATE THIRD-ORDER PERTURBATION THEORY

In some cases, $H_{nn}^{(2)} = 0$, therefore, in order to obtain the lowest order nonzero correction, we must proceed to third-order in perturbation theory. Here again, we will expand $\Psi_n^{(3)}$ in the same basis set, such that we have:

$$\Psi_n^{(3)} = \sum_p C_{np} \Psi_p^{(0)} \qquad (43)$$

Inserting equation (43) into equation (19), we get:

$$\hat{H}^0 \sum_p C_{np} \Psi_p^{(0)} + \hat{H}^1 \sum_j b_{nj} \Psi_j^{(0)} - \mathrm{E}_n^{(0)} \sum_p C_{np} \Psi_p^{(0)} - \mathrm{E}_n^{(1)} \sum_j b_{nj} \Psi_j^{(0)} - \mathrm{E}_n^{(2)} \sum_i a_{ni} \Psi_i^{(0)} - \mathrm{E}_n^{(3)} \Psi_n^{(0)} = 0 \qquad (44)$$

Taking the scalar product of equation (44) with $\langle K|$, such that the third-order perturbation equation becomes:

$$\sum_p C_{np} \langle K|\hat{H}^{(0)}|p\rangle + \sum_j b_{nj} \langle K|\hat{H}^{(1)}|j\rangle = \mathrm{E}_n^{(0)} \sum_p C_{np} \langle K|p\rangle + \mathrm{E}_n^{(1)} \sum_j b_{nj} \langle K|j\rangle + \mathrm{E}_n^{(2)} \sum_i a_{ni} \langle K|i\rangle + \mathrm{E}_n^{(3)} \langle K|n\rangle \qquad (45)$$

The integral leads to Kronecker delta functions such that we obtain:

$$\sum_p C_{np} \mathrm{E}_p^{(0)} \delta_{Kp} + \sum_j b_{nj} \mathrm{H}_{Kj}^{(1)} = \mathrm{E}_n^{(0)} \sum_p C_{np} \delta_{Kp} + \mathrm{E}_n^{(1)} \sum_j b_{nj} \delta_{Kj} + \mathrm{E}_n^{(2)} \sum_i a_{ni} \delta_{Ki} + \mathrm{E}_n^{(3)} \delta_{Kn} \qquad (46)$$

In equation (46), all the summation signs are neutralised by the Kronecker delta functions with the exception of only one, such that we get:

$$C_{np} \mathrm{E}_p^{(0)} + b_{nj} \mathrm{H}_{Kj}^{(1)} = \mathrm{E}_n^{(0)} C_{np} + \mathrm{E}_n^{(1)} b_{nj} + \mathrm{E}_n^{(2)} a_{ni} + \mathrm{E}_n^{(3)} \delta_{Kn} \qquad (47)$$

For K = n, equation (47) yields the third-order energy correction as follows:

$$C_{np} \mathrm{E}_p^{(0)} + b_{nj} \mathrm{H}_{nj}^{(1)} = \mathrm{E}_n^{(0)} C_{np} + \mathrm{E}_n^{(1)} b_{nj} + \mathrm{E}_n^{(2)} a_{ni} + \mathrm{E}_n^{(3)} \delta_{nn}$$
$$\Longrightarrow C_{np}\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right) + \mathrm{E}_n^{(3)} = b_{nj} \mathrm{H}_{nj}^{(1)} - \mathrm{E}_n^{(1)} b_{nj} - \mathrm{E}_n^{(2)} a_{ni}$$

$$\therefore \mathrm{E}_n^{(3)} = b_{nj} \mathrm{H}_{nj}^{(1)} - C_{np}\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right) - \mathrm{E}_n^{(1)} b_{nj} - \mathrm{E}_n^{(2)} a_{ni} \qquad (48)$$

But we know that:

$$a_{ni} = \frac{\mathrm{H}_{in}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} \qquad (49)$$

$$b_{nj} = \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \frac{\mathrm{H}_{jn}^{(1)} \mathrm{H}_{nn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2} \qquad (50)$$

$$C_{np} = \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \mathrm{H}_{pi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)} - \frac{\mathrm{H}_{Kn}^{(1)} \mathrm{H}_{nn}^{(1)} \mathrm{H}_{pn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)^3} \qquad (51)$$

Substituting equations (49-51) in equation (48) we get:

$$\mathrm{E}_n^{(3)} = \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \mathrm{H}_{nj}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \frac{\mathrm{H}_{jn}^{(1)} \mathrm{H}_{nn}^{(1)} \mathrm{H}_{nj}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2} - \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \mathrm{H}_{pi}^{(1)} \left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)} + \frac{\mathrm{H}_{Kn}^{(1)} \mathrm{H}_{nn}^{(1)} \mathrm{H}_{pn}^{(1)} \left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)^3} - \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \left(\mathrm{E}_n^{(1)}\right)}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \frac{\mathrm{H}_{jn}^{(1)} \mathrm{H}_{nn}^{(1)} \left(\mathrm{E}_n^{(1)}\right)}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2} - \frac{\mathrm{H}_{in}^{(1)} \mathrm{E}_n^{(2)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} \qquad (52)$$

or, we have:

$$\mathrm{E}_n^{(3)} = \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \mathrm{H}_{nj}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \frac{\left|\mathrm{H}_{jn}^{(1)}\right|^2 \mathrm{H}_{nn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2} - \sum_{i \neq n} \frac{\mathrm{H}_{in}^{(1)} \mathrm{H}_{ji}^{(1)} \mathrm{H}_{pi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} + \frac{\mathrm{H}_{Kn}^{(1)} \mathrm{H}_{nn}^{(1)} \mathrm{H}_{pn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)^2} - \sum_{i \neq n} \frac{a_{ni} \mathrm{H}_{ni}^{(1)} \mathrm{H}_{in}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} \qquad (53)$$

We can substitute for a_{ni} in the last term of equation (53), where:

$$a_{ni} = \frac{\mathrm{H}_{in}^{(1)}}{\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}}$$

Equation (53) is the non-degenerate third-order energy correction for the atomic (quantum mechanical) system. The wave function correction for third-order perturbation is:

$$\Psi_n^{(3)} = \Psi_n^{(0)} + \sum_{i \neq n} a_{ni} \Psi_i^{(0)} + \sum_{j \neq n} b_{nj} \Psi_j^{(0)} + \sum_{p \neq n} C_{np} \Psi_p^{(0)} \qquad (54)$$

NON-DEGENERATE FOURTH-ORDER PERTURBATION THEORY

In some physical cases, $\mathrm{H}_{nn}^{(3)} = 0$, hence in order to obtain the lowest order nonzero correction, it is necessary to proceed to fourth order in perturbation theory. $\Psi_n^{(4)}$ is expanded in the similar basis set, and we get:

$$\Psi_n^{(4)} = \sum_q d_{nq} \Psi_q^{(0)}. \qquad (55)$$

Let us insert equation (55) into equation (20). Then we obtain:

$$\widehat{H}^{(0)}\sum_q d_{nq}\Psi_q^{(0)} + \widehat{H}^{(1)}\sum_q C_{nq}\Psi_q^{(0)} - \mathrm{E}_n^{(0)}\sum_q d_{nq}\Psi_q^{(0)} - \mathrm{E}_n^{(1)}\sum_q C_{nq}\Psi_q^{(0)} - \mathrm{E}_n^{(2)}\sum_j b_{nj}\Psi_j^{(0)} - \mathrm{E}_n^{(3)}\sum_i a_{ni}\Psi_i^{(0)} - \mathrm{E}_n^{(4)}\Psi_n^{(0)} = 0 \quad (56)$$

Taking the scalar product of equation (56) with $\langle K|$, such that the forth-order perturbation equation becomes:

$$\sum_q d_{nq}\left\langle K\middle|\widehat{H}^{(0)}\middle|q\right\rangle + \sum_p C_{np}\left\langle K\middle|\widehat{H}^{(1)}\middle|p\right\rangle = \mathrm{E}_n^{(0)}\sum_p d_{nq}\langle K|q\rangle + \mathrm{E}_n^{(1)}\sum_p C_{np}\langle p|K\rangle + \mathrm{E}_n^{(2)}\sum_j b_{nj}\langle K|j\rangle + \mathrm{E}_n^{(3)}\sum_i a_{ni}\langle K|i\rangle + \mathrm{E}_n^{(4)}\langle K|n\rangle \quad (57)$$

The integrals yield Kronecker delta functions so that we get:

$$\sum_q d_{nq}\,\mathrm{E}_q^{(0)}\delta_{Kq} + \sum_p C_{np}\,\mathrm{H}_{Kp}^{(1)} = \mathrm{E}_n^{(0)}\sum_q d_{nq}\,\delta_{Kq} + \mathrm{E}_n^{(1)}\sum_p C_{np}\,\delta_{Kp} + \mathrm{E}_n^{(2)}\sum_j b_{nj}\,\delta_{Kj} + \mathrm{E}_n^{(3)}\sum_i a_{ni}\,\delta_{Ki} + \mathrm{E}_n^{(4)}\delta_{Kn} \quad (58)$$

In equation (58), all the summation signs are cancelled out by the Kronecker delta functions excluding one, such that we have:

$$d_{nq}\mathrm{E}_q^{(0)} + C_{np}\mathrm{H}_{Kp}^{(1)} = \mathrm{E}_n^{(0)}d_{nq} + \mathrm{E}_n^{(1)}C_{np} + \mathrm{E}_n^{(2)}b_{nj} + \mathrm{E}_n^{(3)}a_{ni} + \mathrm{E}_n^{(4)}\delta_{Kn} \quad (59)$$

For K = n, equation (59) gives us the third-order energy correction as follows:

$$d_{nq}\mathrm{E}_q^{(0)} + C_{np}\mathrm{H}_{np}^{(1)} = \mathrm{E}_n^{(0)}d_{nq} + \mathrm{E}_n^{(1)}C_{np} + \mathrm{E}_n^{(2)}b_{nj} + \mathrm{E}_n^{(3)}a_{ni} + \mathrm{E}_n^{(4)}\delta_{nn}$$

$$\Rightarrow d_{nq}\left(\mathrm{E}_q^{(0)} - \mathrm{E}_n^{(0)}\right) + C_{np}\left(\mathrm{H}_{np}^{(1)} - \mathrm{E}_n^{(1)}\right) - \mathrm{E}_n^{(2)}b_{nj} - \mathrm{E}_n^{(3)}a_{ni} = \mathrm{E}_n^{(4)} \quad (60)$$

But we know that:

$$a_{ni} = \frac{\mathrm{H}_{in}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} \quad (61)$$

$$b_{nj} = \sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ji}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \left[\frac{\mathrm{H}_{jn}^{(1)}\mathrm{H}_{nn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2}\right] \quad (62)$$

$$C_{np} = \sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ji}^{(1)}\mathrm{H}_{pi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)} - \frac{\mathrm{H}_{Kn}^{(1)}\mathrm{H}_{nn}^{(1)}\mathrm{H}_{pn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)^3} \quad (63)$$

$$d_{nq} = \sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ij}^{(1)}\mathrm{H}_{ip}^{(1)}\mathrm{H}_{qi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_q^{(0)}\right)} - \frac{\mathrm{H}_{Kn}^{(1)}\mathrm{H}_{nn}^{(1)}\mathrm{H}_{pn}^{(1)}\mathrm{H}_{qn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_q^{(0)}\right)^4} \quad (64)$$

Substituting equations (61-64) in equation (60), we obtain the fourth-order perturbation energy correction as follows:

$$\mathrm{E}_n^{(4)} = \frac{-\mathrm{E}_n^{(3)}\mathrm{H}_{in}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \mathrm{E}_n^{(2)}\left\{\sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ji}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)} - \left[\frac{\mathrm{H}_{jn}^{(1)}\mathrm{H}_{nn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)^2}\right]\right\} + \left(\mathrm{H}_{np}^{(1)} - \mathrm{E}_n^{(1)}\right)\left\{\sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ji}^{(1)}\mathrm{H}_{pi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)} - \frac{\mathrm{H}_{Kn}^{(1)}\mathrm{H}_{nn}^{(1)}\mathrm{H}_{pn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)^3}\right\} + \left(\mathrm{E}_q^{(0)} - \mathrm{E}_n^{(0)}\right)\left\{\sum_{i\neq n}\frac{\mathrm{H}_{in}^{(1)}\mathrm{H}_{ij}^{(1)}\mathrm{H}_{ip}^{(1)}\mathrm{H}_{qi}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_i^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_j^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_p^{(0)}\right)\left(\mathrm{E}_n^{(0)} - \mathrm{E}_q^{(0)}\right)} - \frac{\mathrm{H}_{Kn}^{(1)}\mathrm{H}_{nn}^{(1)}\mathrm{H}_{pn}^{(1)}\mathrm{H}_{qn}^{(1)}}{\left(\mathrm{E}_n^{(0)} - \mathrm{E}_q^{(0)}\right)^4}\right\} \quad (65)$$

Equation (65) is the non-degenerate (i.e., energy level i$\neq$ $energy\ level\ n$) fourth –order energy correction for the quantum (atomic) system.

The wave function correction for the fourth-order perturbation is:

$$\Psi_n = \Psi_n^{(0)} + \sum_{i\neq n} a_{ni}\,\Psi_i^{(0)} + \sum_{j\neq n} b_{nj}\,\Psi_j^{(0)} + \sum_{p\neq n} C_{np}\,\Psi_p^{(0)} + \sum_{q\neq n} d_{nq}\,\Psi_q^{(0)} \quad (66)$$

RESULTS AND DISCUSSIONS

The first-order energy correction for the Hamiltonian or total energy of the electron in an atom or multi-electron quantum system is:

$$\mathrm{E}_n^{(1)} = \langle\widehat{H}^{(1)}\rangle \quad (67)$$

The second-order energy correction is given by:

$$E_n^{(2)} = \sum_{i\neq n}\frac{H_{in}^{(1)}H_{ni}^{(1)}}{(E_n^{(0)} - E_i^{(0)})} \quad . \quad (68)$$

The first-order wave function is:

$$\Psi_n^{(1)} = \Psi_n^{(0)} + \sum_i a_{ni}\,\Psi_i^{(0)}. \quad (69)$$

The second-order wave function is:

$$\Psi_n = \Psi_n^{(0)} + \sum_{i\neq n} a_{ni}\,\Psi_i^{(0)} + \sum_{j\neq n} b_{nj}\,\Psi_j^{(0)}. \quad (70)$$

The derived expressions, from basic principles, for the third-order and fourth –order energy corrections and corresponding wave functions are presented as follows here:

The third –order wave functions are given by:

$$\Psi_n^{(3)} = \Psi_n^{(0)} + \sum_{i\neq n} a_{ni}\,\Psi_i^{(0)} + \sum_{j\neq n} b_{nj}\,\Psi_j^{(0)} + \sum_{p\neq n} C_{np}\,\Psi_p^{(0)} \quad (71)$$

The fourth –order wave functions are given by:

$$\Psi_n^{(4)} = \Psi_n^{(0)} + \sum_{i\neq n} a_{ni}\,\Psi_i^{(0)} + \sum_{j\neq n} b_{nj}\,\Psi_j^{(0)} + \sum_{p\neq n} C_{np}\,\Psi_p^{(0)} + \sum_{q\neq n} d_{nq}\,\Psi_q^{(0)} \quad (72)$$

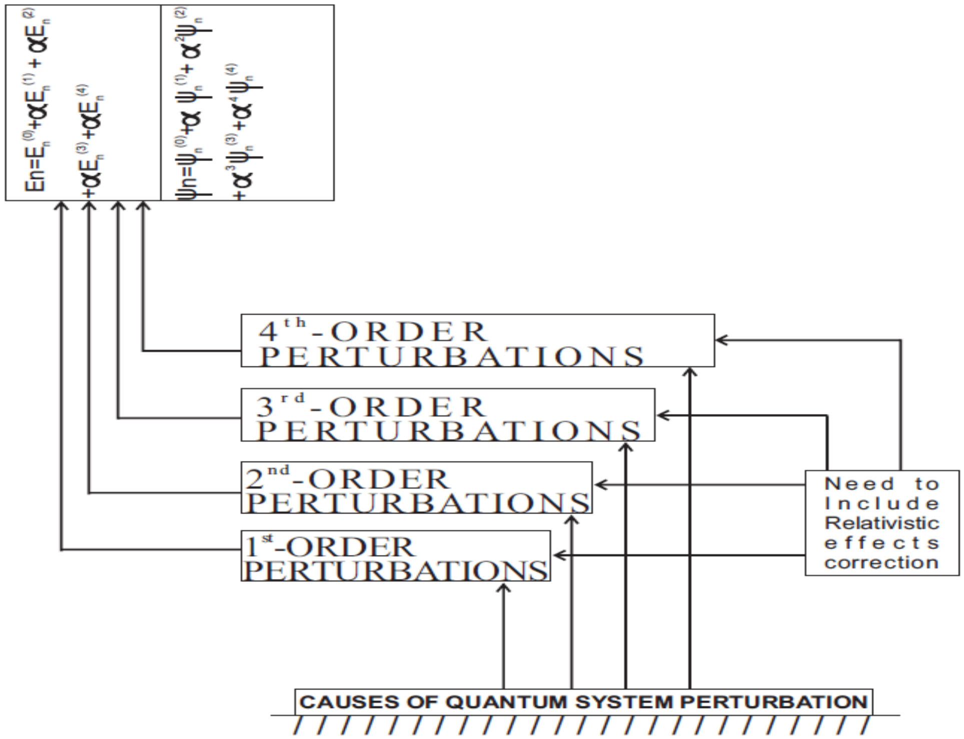

Figure 1. Organization or levels of use and accuracy of the orders of quantum system perturbations.

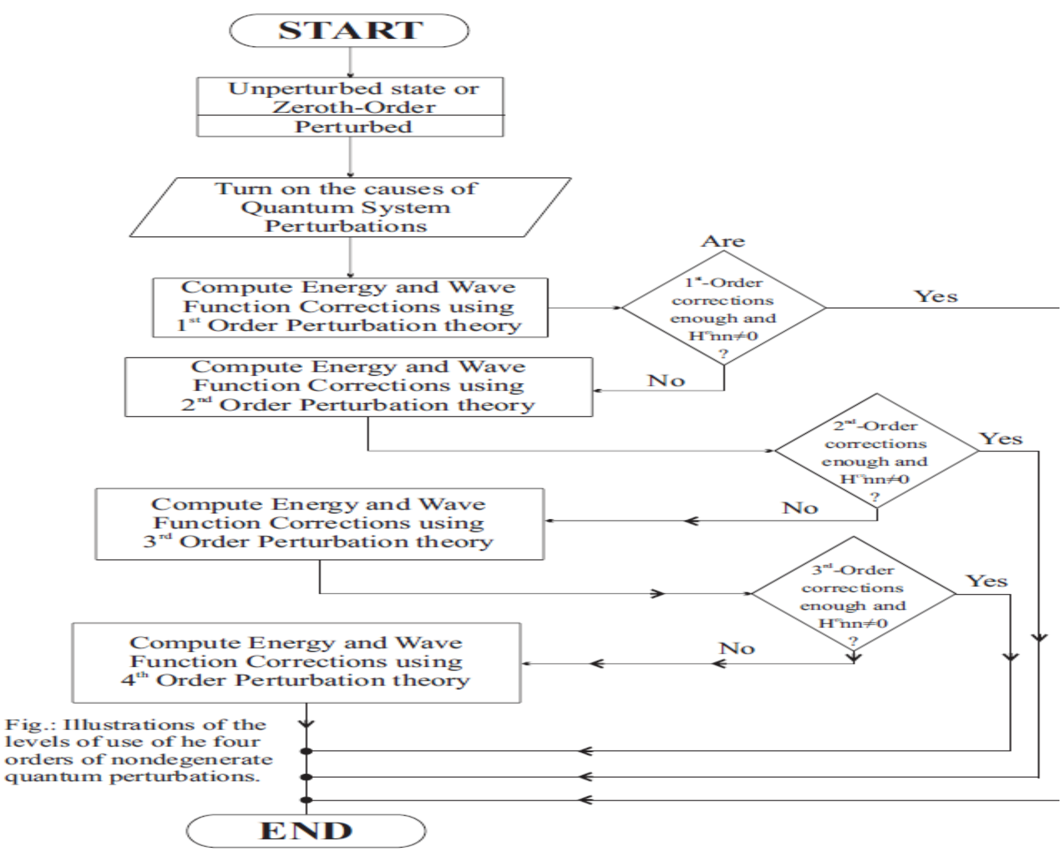

Figure 2. Illustrations of the conditional levels of use of the four orders of non-degenerate quantum system perturbations.

The third –order energy correction is found to be:

$$E_n^{(3)} = \sum_{i\neq n} \frac{H_{in}^{(1)} H_{ji}^{(1)} H_{nj}^{(1)}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_i^{(0)}\right)} - \frac{\left|H_{jn}^{(1)}\right|^2 H_{nn}^{(1)}}{\left(E_n^{(0)} - E_j^{(0)}\right)^2} - \sum_{i\neq n} \frac{H_{in}^{(1)} H_{ji}^{(1)} H_{pi}^{(1)}}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_i^{(0)}\right)} + \frac{H_{Kn}^{(1)} H_{nn}^{(1)} H_{pn}^{(1)}}{\left(E_n^{(0)} - E_p^{(0)}\right)^2} - \sum_{i\neq n} \frac{|H_{in}|^2 . H_{ni}}{\left(E_n^{(0)} - E_i^{(0)}\right)^2}$$
(73)

The fourth –order perturbation energy correction is given by equation (65).

Figure 1 depicts the hierarchical levels of selection and relationship between the perturbation orders and Figure 2 shows the Illustrations of the conditions and levels of use of the four orders of non-degenerate quantum system

perturbations.

CONCLUSIONS

In this paper, the various causes of perturbations of total energy and wave functions in atomic (quantum) systems have identified. The expressions or formulas for calculating the approximately exact values for total energies and wave functions of particles under third-order and fourth–order perturbations have been derived, that is, third-order and fourth–order energy corrections and corresponding wave functions are presented. This serves as a step forward in the dynamic field of Physics and is ahead of texts and journals that so far treat perturbations from zeroth-order, first-order, to second-order. Thus, if this research work is implemented and improved upon by scientists, we shall succeed in our drive to eliminate unwanted perturbations in quantum systems.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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