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On Degenerate Time-Independent Perturbation Theory

CARLOS E. SOLIVEREZ
Departamento de Fisica, Facultad de Ciencias Fisicomatemáticas, Universidad Nacional de La Plata, La Plata, Argentina
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A formalism is presented in which both the degenerate and nondegenerate cases can be treated in the same fashion. Nonlinear integral equations are written for the perturbed wavefunctions, which lead to the usual formulas when solved by iteration. The method provides a simple way to set—up to any desired order—secular equations for the energy shifts and zeroth-order perturbed wavefunctions.

LET H^o be the unperturbed Hamiltonian and ϕ_m, ϵ_m its eigenfunctions and energy eigenvalues

$$H^o \phi_m = \epsilon_m \phi_m, \tag{1}$$

where the ϵ_m's may have any degree of degeneracy. Upon introducing a perturbation V, the Schrödinger equation reads

$$(H^o + V)\, \psi_m = E_m \psi_m. \tag{2}$$

We now look at any of the unperturbed energy levels, e.g., ϵ_o degenerate of order f. Call ϕ_a, ϕ_b $(a, b = 1, \cdots, f)$ the eigenfunctions belonging to ϵ_o, and ϕ_α, ϕ_β the ones belonging to any other energy level. Taking them orthonormalized:

$$\int \phi_m^* \phi_n \, d\tau = (\phi_m, \phi_n) = \delta_{mn}. \tag{3}$$

Under the perturbation V, the degeneracy of ϵ_o will, in general, be only partially lifted. Let E_a $(a = 1, \cdots, f)$ be the energy levels into which ϵ_o is split (several of them may be equal), and ψ_a the corresponding f linearly independent eigenfunctions. If we let V go to zero, the E_a will coalesce into ϵ_o and the ψ_a will go into some linear combination of the ϕ_a. The calculation of the right zeroth-order perturbed wavefunctions $\psi_a^{(o)}$ is the basic problem in degenerate perturbation theory, one that does not arise in the nondegenerate case.

Putting

$$E_a = \epsilon_o + \Delta_a, \tag{4}$$

we can rewrite Eqs. (1) and (2) for the levels of our interest:

$$(H^o - \epsilon_o)\, \phi_a = 0, \tag{5a}$$

$$(H^o - \epsilon_o)\, \psi_b = (\Delta_b - V)\, \psi_b, \tag{5b}$$

where $a, b = 1, \cdots, f$. As a result of $H^o - \epsilon_o$ being a Hermitian operator, ϕ_a and the right member of Eq. (5b) are orthogonal (see Appendix):

$$(\phi_a, [\Delta_b - V]\, \psi_b) = 0. \tag{6}$$

The eigenfunctions of H^o provide a complete basis for the discrete spectrum (to which we are

restricting ourselves) so that we can write

$$\psi_a = \sum_{b=1}^{f} U_{ab}\,\phi_b + \sum_{\alpha}' U_{a\alpha}\,\phi_\alpha.$$

The first sum in the right member is the zeroth-order approximation $\psi_a^{(o)}$

$$\psi_a^{(o)} = \sum_{b=1}^{f} U_{ab}\,\phi_b, \tag{7}$$

so that

$$\psi_a = \psi_a^{(o)} + \sum_{\alpha}' U_{a\alpha}\,\phi_\alpha. \tag{8}$$

Our problem is to find the coefficients U_{ab} and $U_{a\alpha}$ in Eqs. (7) and (8).

It is always possible to choose the ψ_a in such a way that the zeroth-order wavefunctions turn out to be orthonormalized. Therefore, take

$$(\psi_a^{(o)}, \psi_b^{(o)}) = \delta_{ab}. \tag{9}$$

As can be seen from the formula immediately below, this choice implies that the ψ_a are not orthonormalized [see also Eq. (17)],

$$(\psi_a, \psi_b) = \delta_{ab} + \sum_{\alpha}' U_{a\alpha}^{*}\,U_{b\alpha}. \tag{10}$$

Of course, we have to take proper care of this before doing any actual calculations. We introduce this trivial complication because Eq. (9) will lead to great simplifications in our formulas.

Upon multiplication of Eq. (5a) with U_{ab} and addition over b, we obtain

$$(H^o - \epsilon_o)\,\psi_a^{(o)} = 0; \tag{11}$$

and, from Eqs. (11) and (5b) and the hermiticity of $H^o - \epsilon_o$,

$$(\psi_a^{(o)}, [\Delta_b - V]\,\psi_b) = 0. \tag{12}$$

These are all the equations needed for solving our problem.

Expanding Eq. (12) and taking into account the fact that

$$(\psi_a^{(o)}, \psi_b) = \delta_{ab}$$

we obtain

$$(\psi_a^{(o)}, V\psi_b) = \Delta_a\,\delta_{ab}. \tag{14}$$

For $a = b$ the latter leads to an integral equation for the energy shifts

$$\Delta_a = (\psi_a^{(o)}, V\psi_a). \tag{15}$$

We now find an expression for the perturbed wavefunctions ψ_a in terms of the $\psi_a^{(o)}$. After that we solve a secular equation for the Δ_a, from which we are able to determine the U_{ab} and from this $\psi_a^{(o)}$. This accomplished, the problem is completely solved.

If we introduce Eq. (8) into the left member of Eq. (5b), we get

$$\sum_{\alpha}' U_{a\alpha}\,(\epsilon_\alpha - \epsilon_o)\,\phi_\alpha = (\Delta_a - V)\psi_a, \tag{16}$$

where we have used Eqs. (11) and (1). Upon scalar multiplication with ϕ_β, and introducing Δ_a from equation (15),

$$U_{a\alpha} = \frac{(\phi_\alpha, V\psi_a) - (\phi_\alpha, \psi_a)\cdot(\psi_a^{(o)}, V\psi_a)}{\epsilon_o - \epsilon_\alpha}. \tag{17}$$

We thus obtain the following nonlinear integral equation for ψ_a:

$$\psi_a = \psi_a^{(o)} + \sum_{\alpha}' \frac{(\phi_\alpha, V\psi_a) - (\phi_\alpha, \psi_a)\cdot(\psi_a, V\psi_a)}{\epsilon_o - \epsilon_\alpha}\phi_\alpha, \tag{18}$$

that can be solved by iteration if $\psi_a^{(o)}$ is known.

Successive replacements of the right member of Eq. (18) into the scalar products give rise to terms of increasing degree in matrix elements of V. By degree we mean here the number of matrix elements that appear in a given term. Characterizing the degree by a superscript, the wavefunction ψ_a may be written

$$\psi_a = \psi_a^{(o)} + \psi_a^{(1)} + \cdots + \psi_a^{(k)} + \cdots, \tag{19}$$

an expression that is given in the standard textbooks as arising from a suitable Taylor's expansion over V. In our case we may think of the superscript k as characterizing in some way the "order of smallness" of the term.

It is now easy to obtain the recurrence expression

$$\psi_a^{(k)} = \sum_{\alpha}' [(\phi_\alpha, V\psi_a^{(k-1)}) - \sum_{l=1}^{k} (\phi_\alpha, \psi_a^{(l-1)})\cdot(\psi_a^{(o)}, V\psi_a^{(k-l)})]\phi_\alpha/(\epsilon_o - \epsilon_\alpha), \quad k \geqq 1. \tag{20}$$

For instance,

$$\psi_a^{(1)} = \sum_\alpha \frac{V'_{\alpha a}}{\epsilon_o - \epsilon_\alpha}\phi_\alpha, \tag{21}$$

$$\psi_a^{(2)} = \sum_{\alpha,\beta} \frac{V_{\alpha\beta}V'_{\beta a}}{(\epsilon_o - \epsilon_\alpha)(\epsilon_o - \epsilon_\beta)}\phi_\alpha - \sum_\alpha \frac{V'_{\alpha a}V'_{a a}}{(\epsilon_o - \epsilon_\alpha)^2}\phi_\alpha, \tag{22}$$

that, upon addition of a normalization term, these are analogous to the usual formulas for the nondegenerate case. We have written

$$V'_{\alpha a} = (\phi_\alpha, V\psi_a^{(o)}), \tag{23}$$

where the prime indicates that we are taking matrix elements between the linear combinations (7) instead of the simple eigenfunctions ϕ_a. When the latter is the case, drop the primes. The other matrix elements are defined in a similar way.

In the nondegenerate case, the energy shifts can be obtained easily from Eq. (15). Let ϕ_o be the zeroth-order wavefunction, which is now unique. Then, by iteration,

$$\Delta_o = \Delta_o^{(1)} + \Delta_o^{(2)} + \cdots + \Delta_o^{(k)} + \cdots, \tag{24}$$

where

$$\Delta_o^{(k)} = (\phi_o, V\psi_o^{(k-1)}), \quad k \geqq 1. \tag{25}$$

Thus,

$$\Delta_o^{(1)} = V_{oo}, \quad \Delta_o^{(2)} = \sum_\alpha \frac{V_{o\alpha}V_{\alpha o}}{\epsilon_o - \epsilon_\alpha},$$

$$\Delta_o^{(3)} = \sum_{\alpha,\beta} \frac{V_{o\alpha}V_{\alpha\beta}V_{\beta o}}{(\epsilon_o - \epsilon_\alpha)(\epsilon_o - \epsilon_\beta)} - \sum_\alpha \frac{V_{o\alpha}V_{\alpha o}V_{oo}}{(\epsilon_o - \epsilon_\alpha)^2},$$

and so on.

For the degenerate case, we cannot obtain the energy levels in such a simple way. In order to simplify the treatment, we first introduce some modifications in the formulas. If we use Eq. (14) instead of (15) when reducing (16), we obtain

$$U_{a\alpha} = \frac{(\phi_\alpha, V\psi_a) - \sum_b (\phi_\alpha, \psi_b)(\psi_b^{(o)}, V\psi_a)}{\epsilon_o - \epsilon_\alpha}, \tag{26}$$

which leads to

$$\psi_a^{(k)} = \sum_\alpha \frac{(\phi_\alpha, V\psi_a^{(k-1)}) - \sum_{l=1}^{k}\sum_b (\phi_\alpha, \psi_b^{(l-1)})(\psi_b^{(o)}, V\psi_a^{(k-l)})}{\epsilon_o - \epsilon_\alpha}\phi_\alpha, \quad k \geqq 1. \tag{27}$$

From here, we obtain (notice that we are now dropping the primes):

$$\psi_b^{(1)} = \sum_c U_{bc} \sum_\alpha \frac{V_{\alpha c}}{\epsilon_o - \epsilon_\alpha}\phi_\alpha, \tag{28}$$

$$\psi_b^{(2)} = \sum_c U_{bc}\left[\sum_{\alpha,\beta} \frac{V_{\alpha\beta}V_{\beta c}}{(\epsilon_o - \epsilon_\alpha)(\epsilon_o - \epsilon_\beta)}\phi_\alpha - \sum_{\alpha,d} \frac{V_{\alpha d}V_{dc}}{(\epsilon_o - \epsilon_\alpha)^2}\phi_\alpha\right], \tag{29}$$

where we have used Eq. (9), that is,

$$\sum_c U_{ac}^* U_{bc} = \delta_{ab}. \tag{30}$$

We now use Eq. (6). Keeping b fixed and letting a run from 1 to f, we obtain the following system of integral equations:

$$\sum_c U_{bc}(V_{ac} - \Delta_b \delta_{ac}) + \sum_{k=1}^{\infty}(\phi_a, V\psi_b^{(k)}) = 0, \quad a = 1,2,\cdots,f, \quad b = \text{const.} \tag{31}$$

Up to third-degree terms in V, we obtain the homogeneous system

$$\sum_c U_{bc}\left[V_{ac} + \sum_\alpha \frac{V_{a\alpha}V_{\alpha c}}{\epsilon_o - \epsilon_\alpha} + \sum_{\alpha,\beta} \frac{V_{a\alpha}V_{\alpha\beta}V_{\beta c}}{(\epsilon_o - \epsilon_\alpha)(\epsilon_o - \epsilon_\beta)} - \sum_{\alpha,d} \frac{V_{a\alpha}V_{\alpha d}V_{dc}}{(\epsilon_o - \epsilon_\alpha)^2} - \Delta\,\delta_{ac}\right] = 0. \tag{32}$$

The necessary and sufficient condition for the existence of nontrivial solutions for U_{bc} is that the determinant of the matrix corresponding to the square brackets in (32) be zero. We can disregard the lower index in Δ because the same secular equation is obtained, regardless of which is chosen. Solving this determinant, one obtains the f energy shifts. These, together with the orthonormality conditions (9), allow us to calculate the f sets of coefficients U_{ab} which give the third-order approximation to the zeroth-order wavefunctions. With them, we can finally determine the fourth-order approximation to the perturbed wavefunctions from Eq. (27).

In a second-order approximation with $V_{ac} = 0$, the secular determinant reduces to the well-known one for the removal or degeneracy in second order[1]:

$$\det\left[\sum_{\alpha}{}' \frac{V_{a\alpha}V_{\alpha c}}{\epsilon_o - \epsilon_\alpha} - \Delta\,\delta_{ac}\right] = 0. \quad (33)$$

The formalism allows to obtain a better insight of several hypothesis widely used in perturbation theory. Thus, it is clearly seen how to obtain "expansions" of the energy levels and perturbed wavefunctions in powers of V. Equation (20) shows that the degenerate case may be treated in the same way as the nondegenerate one provided that we use the right zeroth-order perturbed wavefunctions. The method of the inversion of $H^o - \epsilon_o{}^2$ is contained in Eq. (17). From Eq. (14) the reader can verify that the method of diagonalizing the matrix of V between the $\psi_a^{(o)}$ is correct up to first order, but that this is not necessarily so in higher orders. Finally, the formalism clearly exhibits the fact that the zeroth-order perturbed wavefunctions depend on the chosen order of approximation.

Equation (32) should prove useful in all those problems in which second- and higher-order terms are important. This is the case, for instance, in paramagnetic resonance, where a formula resembling our own has been used,[3] although it was obtained from a variational approach.[4]

The author has also found that it is possible to arrive to an identical expression by using Bloch's operational approach.[5]

APPENDIX

Let A be a Hermitian operator. If the equation

$$A\phi = 0$$

has nontrivial solutions $\phi \neq 0$ and $A\psi = f$, where f is known, then

$$(\phi, f) = (\phi, A\psi) = (A\phi, \psi) = 0,$$

where we have used the hermiticity in the third step. That is,

$$(\phi, f) = 0. \quad (A1)$$

Note that because (A1) is a result of the hermiticity of A it is a consequence of the boundary conditions imposed upon ϕ and ψ.

[1] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1949), p. 156.

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[3] R. D. Mattuck and M. P. Strandberg, Phys. Rev. **119**, 1204 (1960).

[4] P.-O.Löwdin, J. Chem. Phys. **19**, 1396 (1951).

[5] C. Bloch, Nucl. Phys. **6**, 329 (1958).