

The characteristic polynomial approach to the solution of quantum chemical perturbation problems

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Abstract. An approach to the solution of finite-dimensional quantum chemical perturbation problems based on the 'characteristic polynomial' $f(\epsilon, a) = \det | \epsilon - \mathcal{H}(a) |$ is developed and discussed. Using the successive derivatives of the polynomial, an ordered perturbation sequence is constructed. From this sequence, perturbation series for individual eigenvalues are determined. Applications of this method are illustrated for cases of non-degenerate eigenvalues, two-fold energy degeneracy lifted in first order, and q -fold energy degeneracy. A re-derivation of the well-known Rayleigh-Schrödinger perturbation formulae from their corresponding characteristic polynomial expressions is presented, and an additional illustration is made of the use of the reduced characteristic polynomial by considering a benzene molecule with three adjacent carbon atoms 'perturbed' in some way.

Keywords. Characteristic polynomial ; quantum chemical perturbation ; non-degenerate eigenvalues ; Rayleigh-Schrödinger formula ; perturbation calculation ; operator formalism ; polynomial formalism.

1. Introduction

Perturbation theory in its most widely used form (see, for example, Schiff 1949; Morse and Feshbach 1953; Hirschfelder *et al* 1964; Wilcox 1966) involves starting with a system characterised by a known Hamiltonian operator, eigenvalues and eigenvectors and calculating the changes in the latter two resulting from a finite change—or perturbation—in the operator, in particular when the operator depends on a parameter analytically. However, the questions of existence, analyticity and convergence of the perturbation series have been frequently discussed problems in physical sciences. Since Rellich (1953) initiated the mathematical theory of perturbations in Hilbert space as far back as nearly three decades ago, several analytical treatments of perturbation theory have appeared (Kato 1949, 1966; Titchmarsh 1958; Davis 1963; Friedrichs 1965). Davis (1963) presents a generalised study of perturbations that bring about finite changes of eigenvalues and eigenvectors, while the monograph by Friedrichs (1965) deals with the computational aspects of perturbation theory where the interaction Hamiltonian is assumed to be a smooth function of the perturbation parameters. Later, Kato (1966) published a detailed function-theoretical treatment of 'resolvents', in particular of the expression of eigenvectors as contour integrals of the resolvent.

Other, more recent, techniques of obtaining perturbation theory solutions to degenerate energy levels include the geometric (series) or 'selective summation' approximation (Kelly 1963; Shulman and Musher 1968) and the use of time-ordered 'folded' diagrams for solving time-dependent perturbation problems (Michels and Suttorp 1978). The *ideas* and *methods* of perturbation theory have been reviewed recently in a very readable article by Killingbeck (1977).

We now develop an alternative general approach to the solution of typical time-independent, finite-dimensional quantum chemical perturbation problems, based *not* on the perturbed Hamiltonian operator itself but rather on a 'characteristic polynomial' function of this operator (for definition, *vide infra*). Indeed, the use of such polynomials had been envisaged from time to time in simple time-independent perturbation theory approaches to finding derivatives of the total energy of electrons in the π -system of conjugated molecules (Coulson 1940; Coulson and Longuet-Higgins 1947; Rutherford 1945, 1951; Fukui *et al* 1959) and in formulating paramagnetic resonance conditions for multiplet state electronic spin systems (Coope 1966). We expand and generalise the ideas of these earlier workers, and render the technique useful for application to (a) any arbitrary perturbation parameters, (b) any order of perturbation, and (c) cases of degenerate eigenvalues. We shall demonstrate that our approach has the following features of mathematical expediency: (i) an ordered perturbation sequence in terms of derivatives of the characteristic polynomial may be constructed and, from this sequence, perturbation series for individual eigenvalues established accurately, (ii) in computing the perturbed eigenvalues, we make no explicit use of wave functions, which are tedious entities to be calculated anyway.

2. Formulation of theory

We consider a generalised system of n energy levels, with an n -dimensional (Hermitian) Hamiltonian operator $\mathcal{H}(a)$. As the notation indicates, the operator is an analytic function of one or more perturbation parameters a typifying any perturbation of the system such as external fields, hyperfine interactions, field gradients, etc. We define a characteristic polynomial function for such a system as

$$f(\epsilon, a) = \epsilon^n + a_1 \epsilon^{n-1} + a_2 \epsilon^{n-2} + \dots + a_n = \det |\epsilon - \mathcal{H}(a)| \quad (1)$$

which has the factorisation

$$f(\epsilon, a) = \prod_{i=1}^n [\epsilon - E_i(a)], \quad (2)$$

where $E_i(a)$, the eigenvalues of $\mathcal{H}(a)$, are real-valued analytic functions of a . The values of ϵ for which the *characteristic equation*

$$f(\epsilon, a) = 0 \quad (3)$$

is satisfied are the eigenvalues of $\mathcal{H}(a)$.

The Taylor series for any particular eigenvalue, $E_p(a)$, expanded about the origin, $a = 0$, is

$$E_p(a) = E_p(0) + aDE_p(0) + (a^2/2!) D^2 E_p(0) + \dots \quad (4)$$

where we follow the notation of Killingbeck (1975) and set $D = d/da$, $D^2 = d^2/da^2$, etc. In (4), the zeroth derivative, namely, the unperturbed eigenvalue $E_p(0)$, is assumed to be known.

The basic idea of our approach is to regard the characteristic equation, equation (3), as implicitly defining ϵ as a function of a , for ϵ in some proximity of the unperturbed eigenvalue $E_p(0)$, and for a in some proximity of $a = 0$.

In general, then, one obtains a sequence of equations for the implicit derivatives $D^m \epsilon$. Since

$$D^m \epsilon|_{\epsilon=E_p(0), a=0} = D^m E_p(0),$$

an expression for $D^m \epsilon$ obtained from the sequence, when evaluated at $\epsilon = E_p(0)$ and $a = 0$, will yield the required derivative $D^m E_p(0)$. However, since we have defined ϵ as a function of a , the total differential with respect to a is given by

$$D = \frac{\partial}{\partial a} + D\epsilon \frac{\partial}{\partial \epsilon}.$$

Upon taking the total differential of the characteristic equation with respect to a we obtain

$$Df = f_a + f_\epsilon D\epsilon = 0, \tag{5}$$

where the subscripts now denote partial derivatives. In this notation, successive total derivatives may be written as a sequence of equations, e.g.,

$$D^2 f = f_{a^2} + 2f_{\epsilon a} D\epsilon + f_{\epsilon^2} (D\epsilon)^2 + f_\epsilon D^2 \epsilon = 0, \text{ etc.} \tag{6}$$

We shall now see that the terms occurring in each equation of the sequence such as equation (6) lend themselves to a convenient grouping which will simplify our subsequent computations. To accomplish this grouping of terms, we employ the notation

$$f_{\epsilon^p}^{(n)} = \sum_{r=0}^n \binom{n}{r} f_{\epsilon^{p+r} a^{n-r}} (D\epsilon)^r \tag{7}$$

where $\binom{n}{r}$ is the binomial coefficient $n!/(n-r)!r!$.

In this notation, $f_{\epsilon^p}^{(n)}$ is seen to have the property

$$Df_{\epsilon^p}^{(n)} = f_{\epsilon^p}^{(n+1)} + n f_{\epsilon^{p+1}}^{(n-1)} D\epsilon. \tag{8}$$

The first three equations of the sequence can be written according to the above notation as

$$\left. \begin{aligned} Df &= Df_{\epsilon^0}^{(0)} = f_{\epsilon^0}^{(1)} = 0, \\ D^2 f &= f_{\epsilon^0}^{(2)} + f_{\epsilon^1}^0 D^2 \epsilon = 0, \text{ and} \\ D^3 f &= f_{\epsilon^0}^{(3)} + \binom{3}{2} f_{\epsilon^1}^{(1)} D^2 \epsilon + \dots \\ &\quad + \binom{3}{3} f_{\epsilon^1}^{(0)} D^3 \epsilon = 0 \end{aligned} \right\} \tag{9}$$

To facilitate writing the higher equations in a systematic way, we introduce the combinatorial coefficient $\binom{n}{\sigma_1, \dots, \sigma_k}$ (Abramowitz and Stegun 1965). Given n objects, i.e., our n perturbation parameters, a_1 to a_n , this combinatorial coefficient represents the number of ways $\sigma_1 + \dots + \sigma_k \leq n$ of these parameters can be partitioned into k sets, with σ_i parameters in the i th set. It is to be noted that the order within each set, and between sets containing the same number of parameters, is immaterial. As examples of the combinatorial coefficients, we have

$$\binom{5}{2,2} = \frac{5!}{2!2!} \cdot \frac{1}{2!},$$

and
$$\binom{5}{2,3} = \frac{5!}{2!3!}.$$

It then turns out that, in the n th equation of the sequence, there are terms such as

$$\binom{n}{\sigma_1, \dots, \sigma_k} f_{\epsilon^k}^{(n-[\sigma_1+\dots+\sigma_k])} (D^{\sigma_1} \epsilon) \dots (D^{\sigma_k} \epsilon),$$

where $\sigma_i \geq 2, i = 1, \dots, k, \sigma_1 + \dots + \sigma_k \leq n$ and $\sigma_1 \leq \dots \leq \sigma_k$ (to avoid “double-counting”). If we choose the square-bracketed symbol

$$\left[\begin{matrix} n \\ \sigma_1, \dots, \sigma_k \end{matrix} \right],$$

to denote all the terms above in which the σ_i 's satisfy the restrictions stated, then the n th equation can be conveniently written as

$$f_{\epsilon^0}^{(n)} + \left[\begin{matrix} n \\ \sigma_1 \end{matrix} \right] + \left[\begin{matrix} n \\ \sigma_1, \sigma_2 \end{matrix} \right] + \dots + \left[\begin{matrix} n \\ \sigma_1, \dots, \sigma_m \end{matrix} \right] = 0, \tag{10}$$

where m is the largest integer such that $m \leq n/2$. For example, the sixth equation in the perturbation sequence is

$$\begin{aligned} f_{\epsilon^0}^{(6)} + \left[\begin{matrix} 6 \\ \sigma_1 \end{matrix} \right] + \left[\begin{matrix} 6 \\ \sigma_1, \sigma_2 \end{matrix} \right] + \left[\begin{matrix} 6 \\ \sigma_1, \sigma_2, \sigma_3 \end{matrix} \right] \\ = f_{\epsilon^0}^{(6)} + \binom{6}{2} f_{\epsilon^1}^{(4)} D^2 \epsilon + \binom{6}{2,2} f_{\epsilon^2}^{(2)} (D^2 \epsilon)^2 \\ + \binom{6}{2,2,2} f_{\epsilon^2}^{(0)} (D^2 \epsilon)^3 + \binom{6}{3} f_{\epsilon^3}^{(3)} D^3 \epsilon \\ + \binom{6}{2,3} f_{\epsilon^2}^{(1)} (D^2 \epsilon) (D^3 \epsilon) + \binom{6}{4} f_{\epsilon^2}^{(2)} D^4 \epsilon \\ + \binom{6}{2,4} f_{\epsilon^2}^{(0)} (D^2 \epsilon) (D^4 \epsilon) + \binom{6}{5} f_{\epsilon^2}^{(1)} D^5 \epsilon \\ + \binom{6}{3,3} f_{\epsilon^2}^{(0)} (D^3 \epsilon)^2 + \binom{6}{6} f_{\epsilon^2}^{(0)} D^6 \epsilon = 0. \end{aligned} \tag{11}$$

We thus have a useful and compact way of writing any particular equation in the sequence.

The essential merit of our method, then, is that terms in the Taylor series expansion, equation (4), may thus be found and the perturbed eigenvalue $E_p(\alpha)$ obtained, *correct* to any order in α ; thereby the perturbation theory becomes essentially a study of the way in which the roots of a polynomial change as its coefficients are varied a little, i.e., as α varies.

3. Applications to typical cases of perturbation calculations

We shall apply the above formalism to some typical cases, viz., non-degenerate eigenvalues, two-fold degeneracy lifted in first order, q -fold degeneracy, and the derivation of Rayleigh-Schrödinger formulae. In each case, the equations of the perturbation sequence are derived and shown to have a special form that is readily adapted for computational purposes.

3.1. Non-degenerate eigenvalues

For a non-degenerate eigenvalue, i.e., $E_p(0) \neq E_q(0)$ for $p \neq q$, $f_\epsilon(E_p(0), 0)$ is non-zero. In this case, the equations of our polynomial sequence may be simply rearranged to yield explicit expressions for all the derivatives $D^m E_p(0)$, $m = 1, \dots, n, \dots$. We thus have, for example,

$$DE_p(0) = -f_\alpha/f_\epsilon, \tag{12}$$

$$\begin{aligned} D^2 E_p(0) &= -(f_{\alpha^2} + 2f_{\epsilon\alpha}(D\epsilon) + f_{\epsilon^2}(D\epsilon)^2)/f_\epsilon \\ &= -f_{\epsilon^2}^{(2)}/f_\epsilon, \end{aligned} \tag{13}$$

$$\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$$

$$\begin{aligned} D^n E_p(0) &= -\left[f_{\epsilon^n}^{(n)} + \begin{bmatrix} n \\ \sigma_1 \end{bmatrix} - \binom{n}{n} f_{\epsilon^n}^{(n)}(D^n \epsilon) \right. \\ &\quad \left. + \begin{bmatrix} n \\ \sigma_1, \sigma_2 \end{bmatrix} - \dots \left(\begin{array}{c} n \\ \sigma_1, \dots, \sigma_m \end{array} \right) \right] f_\epsilon, \end{aligned} \tag{14}$$

all terms on the right of equations (12)–(14) being evaluated at the unperturbed eigenvalue, i.e., for $\epsilon = E_p(0)$ and $\alpha = 0$. The n th derivative, equation (14), is thus found from all the derivatives of lower order previously calculated in the sequence. Such calculations are most readily programmed on a computer.

In the case of *several* perturbation parameters $\alpha = (\alpha_1, \dots, \alpha_l)$, the perturbed eigenvalue $E_p(\alpha)$ has, of course, a multiple perturbation expansion:

$$E_p(\alpha) = E_p(0) + \sum_{i=1}^l \alpha_i \frac{\partial E_p(0)}{\partial \alpha_i} + \sum_{i, j=1}^l \frac{\alpha_i \alpha_j}{2!} \frac{\partial^2 E_p(0)}{\partial \alpha_i \partial \alpha_j} + \dots \tag{15}$$

$$\text{where } \partial E_p(0)/\partial \alpha_i = -f_{\alpha_i}/f_\epsilon, \quad (16)$$

$$\begin{aligned} & \partial^2 E_p(0)/\partial \alpha_i \partial \alpha_j \\ &= - \left[f_{\alpha_i \alpha_j} + f_{\epsilon \alpha_i} \frac{\partial \epsilon}{\partial \alpha_j} + f_{\epsilon \alpha_j} \frac{\partial \epsilon}{\partial \alpha_i} + f_{\epsilon^2} \frac{\partial \epsilon}{\partial \alpha_i} \frac{\partial \epsilon}{\partial \alpha_j} \right] / f_\epsilon, \text{ etc.} \end{aligned} \quad (17)$$

Here, again, all terms on the right side are evaluated for $\epsilon = E_p(0)$ and $\alpha = 0$. The higher mixed derivatives in (17) can be obtained by suitably modifying the expression for $D^n E_p(0)$.

3.2. Two-fold degeneracy lifted in first order

In our quantum chemical problem, if $E_p(0)$ is two-fold degenerate, i.e.,

$$E_p(0) = E_{p+1}(0) \neq E_q(0) \text{ for } q \neq p, p+1,$$

then

$f_\epsilon(E_p(0), 0) = 0$, but $f_{\epsilon^2}(E_p(0), 0)$ is nonzero. The first equation of the sequence, equation (5), will then be identically zero, but the second equation, equation (6), is a quadratic in $D\epsilon$, which will give

$$DE_i(0) = - \frac{f_{\epsilon \alpha}}{f_{\epsilon^2}} \pm \frac{\{(f_{\epsilon \alpha})^2 - f_{\epsilon^2} f_{\alpha^2}\}^{1/2}}{f_{\epsilon^2}} \Big] \epsilon = E_i(0), \alpha = 0, \quad (18)$$

$$i = p, p+1.$$

If the two roots above are distinct, the degeneracy is lifted in first order, i.e., $DE_p(0) \neq DE_{p+1}(0)$. Substitution of these two different values for $D\epsilon/\epsilon = E_p(0)$, $\alpha = 0$ into the remaining equations of the sequence then yields all the derivatives $D^m E_p(0)$ and $D^m E_{p+1}(0)$, $m > 1$.

We shall see in § 3.4 that the quadratic whose roots are given by (18) is the same that would be obtained in the Rayleigh-Schrödinger perturbation theory when diagonalising the two-fold degenerate block.

3.3. q -fold degeneracy

In the case that the eigenvalue $E_p(0)$ is q -fold degenerate, one has

$$f_{\epsilon^m}(E_p(0), 0) = 0 \neq f_{\epsilon^q}(E_p(0), 0), m = 0, 1, \dots, q-1.$$

In this case,

$$f_{\epsilon^\alpha \beta}(E_p(0), 0) = 0, \quad \alpha + \beta < q,$$

and consequently the first nonvanishing equation of the sequence is the q th. Indeed, it turns out that for the non-zero terms in the sum, $\sigma = k$, $\beta = q - k$, and the q th equation in the perturbation sequence reduces to

$$\sum_{k=0}^q \frac{q!}{(q-k)! k!} f_{\epsilon^k \alpha^{q-k}} (D\epsilon)^k = f_{\epsilon^q}^{(q)} = 0. \quad (19)$$

The roots of this equation are the q first derivatives, which may or may not be distinct. On writing out the last two terms of the summation in (19),

$$\dots q f_{\epsilon^{q-1} \alpha} (D\epsilon)^{q-1} + f_{\epsilon^q} (D\epsilon)^q = 0, \quad (20)$$

it can be seen that, if the q -fold degeneracy is not lifted in first order (i.e., if (20) has equal roots when evaluated at $\epsilon = E_p(0)$, $\alpha = 0$), then the first order shift of all q eigenvalues is merely

$$DE_i(0) = - \left. \frac{f_{\epsilon^{\alpha+1}}}{f_{\epsilon^{\alpha}}} \right]_{\epsilon = E(0), \alpha = 0, i = p, \dots, p+q-1} \quad (21)$$

since $-q [(f_{\epsilon^{\alpha+1}})/f_{\epsilon^{\alpha}}]$ is the sum of the q roots of (20). In this case a q th order equation in the second derivatives $D^2 \epsilon$ is required, and this is the $2q$ th equation of the series. The $2q$ th equation is the first to contain the required quantity $f_{\epsilon^{\alpha}}^{(0)} (D^2 \epsilon)$ which occurs in

$$\left[\begin{matrix} 2q \\ \sigma_1, \dots, \sigma_q \end{matrix} \right] = \binom{2q}{2, \dots, 2} f_{\epsilon^{\alpha}}^{(0)} (D^2 \epsilon)^{\alpha}.$$

If degeneracy is lifted in first order, then substitution of each root of (19), i.e. each of the different values of

$$D\epsilon]_{\epsilon = E_p(0), \alpha = 0}$$

into the higher order equations of the sequence yields the corresponding higher order derivatives. Once again, it is straightforward to programme these operations for a computer.

Quite often in quantum chemical calculations, energy degeneracy forces us to deal with sets of eigenvalues rather than individual ones. In such instances, we may extend our treatment for obtaining perturbation series for the coefficients of an appropriately 'reduced' characteristic polynomial (RCP). Accordingly, the term RCP denotes a polynomial $R(\epsilon, \alpha)$ of degree q in ϵ , whose zeros are a subset E_p, \dots, E_{p+q-1} , of the zeros of the original, unreduced characteristic polynomial $f(\epsilon, \alpha)$, i.e., a subset of the eigenvalues of the Hamiltonian :

$$\begin{aligned} R(\epsilon, \alpha) &= \prod_{i=p}^{p+q-1} (\epsilon - E_i) \\ &= \epsilon^q + c_1 \epsilon^{q-1} + \dots + c_q. \end{aligned}$$

The coefficients c_i depend on α , and can usually be found only after considerable effort; nevertheless, in favourable cases, numerical computations of the coefficients have been of help in assessing the convergence properties of the perturbation series (Soherr and Knight 1963; Midtdal 1965; Sprandel and Kern 1972). The idea of the RCP is closely related to the theorem (Kato 1949) that the total projection onto the subspace arising from an initially degenerate eigenvalue is analytic in α , near $|\alpha| = 0$. The factorisation theorem asserts that the coefficient c 's above are analytic functions of the perturbation parameters $\alpha = (\alpha_1, \dots, \alpha_l)$, and therefore form the series

$$c_i(\alpha) = c_i(0) + \sum_{j=1}^l \alpha_j \frac{\partial c_i(0)}{\partial \alpha_j} + \dots \quad (22)$$

which is convergent for all α in some proximity of $|\alpha| = 0$. These coefficients may be determined from eigenvalue power summations (see Appendix).

3.4. Application to the derivation of Rayleigh-Schrödinger formulae

We shall first recall the Rayleigh-Schrödinger matrix expansions. If $E_1(0)$ is a non-degenerate eigenvalue of \mathcal{H}^0 and if

$$\mathcal{H}(a) = \mathcal{H}^0 + aV,$$

then the perturbed eigenvalue $E_1(a)$ is given by

$$E_1(a) = E_1(0) + aV_{11} + a^2 \sum_{m \neq 1} \frac{V_{1m} V_{m1}}{E_1 - E_m} + a^3 \left\{ \sum_{m, n \neq 1} \frac{V_{1m} V_{mn} V_{n1}}{(E_1 - E_m)(E_1 - E_n)} - V_{11} \sum_{m \neq 1} \frac{V_{1m} V_{m1}}{(E_1 - E_m)} \right\} + \dots \quad (23)$$

[In (23), $E_i = E_i(0)$ in the energy denominators].

For q -fold degeneracy of $E_i(0)$, the above formula may still be used *provided* degeneracy is lifted in first order. The usual recipe in that case is to diagonalise the degenerate block, and re-label the zeroth order energies appearing in the denominator as

$$E_i^{\text{new}}(0) = E_i(0) + aV_{ii}, \quad i = 1, \dots, q \text{ putting } V_{ii}^{\text{new}} = 0,$$

where $E_i(0)$, $i = 1, \dots, q$ are the initially q -fold degenerate set. Up to third order, any term in a summation with m or n equal to $i \leq q$ will be multiplied by the matrix element V_{mn} , $m, n \leq q$. Since the degenerate block has been diagonalised, these elements are zero. This is equivalent to restricting the summations in (23) so as to exclude the indices $i \leq q$. However, the 'fourth order' terms in (23) are only *apparently* fourth order in this degenerate case. They do include summation indices $i \leq q$, and these give rise to terms which are actually *third* order in a . The terms in the 'traditional' perturbation series (Killingbeck 1975), (23), must hence be re-grouped to obtain the correct a -ordering.

For a two-fold degenerate level, when degeneracy is lifted in first order ($V_{11} \neq V_{22}$), this recipe leads to

$$E_1(a) = E_1(0) + aV_{11} + a^2 \sum_{m \neq 1, 2} \frac{V_{1m} V_{m1}}{E_1 - E_m} + a^3 \left\{ \sum_{m, n \neq 1, 2} \frac{V_{1m} V_{mn} V_{n1}}{(E_1 - E_m)(E_1 - E_n)} - V_{11} \sum_{m \neq 1, 2} \frac{V_{1m} V_{m1}}{(E_1 - E_m)^2} + \frac{1}{V_{11} - V_{22}} \sum_{m, n \neq 1, 2} \frac{V_{1m} V_{m2} V_{2n} V_{n1}}{(E_1 - E_m)(E_1 - E_n)} \right\} + \dots \quad (24)$$

The above formulae can be obtained from the characteristic polynomial, once an explicit expression is given to it in terms of matrix elements. For the V matrix written in a basis in which \mathcal{H}^0 is diagonal, the characteristic polynomial

$$f(\epsilon, a) = \det | \epsilon - \mathcal{H}^0 - aV |$$

has the form

$$\begin{vmatrix} \epsilon - E_1(0) - \alpha V_{11} & \alpha V_{12} & \dots & \alpha V_{1n} \\ \alpha V_{21} & \epsilon - E_2(0) - \alpha V_{22} & \dots & \dots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \alpha V_{n1} & \dots & \dots & \epsilon - E_n(0) - \alpha V_{nn} \end{vmatrix}$$

Expansion of the determinant yields

$$\begin{aligned} f(\epsilon, \alpha) = & \prod_{i=1}^n (\epsilon - E_i(0) - \alpha V_{ii}) - \alpha^2 \sum V_{mn} V_{nm} \prod_{i \neq m, n} (\epsilon - E_i(0) - \alpha V_{ii}) \\ & + \alpha^3 \sum V_{mn} V_{np} V_{pm} \prod_{i \neq m, n, p} (\epsilon - E_i(0) - \alpha V_{ii}) \\ & - \alpha^4 \sum V_{mn} V_{np} V_{ps} V_{sm} \prod_{i \neq m, n, p, s} (\epsilon - E_i(0) - \alpha V_{ii}) \\ & + \alpha^4 \sum V_{mn} V_{nm} V_{rs} V_{sr} \prod_{i \neq m, n, p, s} (\epsilon - E_i(0) - \alpha V_{ii}) + \dots \end{aligned} \quad (25)$$

One notices in the above summations that all indices are unique and double-counting does not occur : in the α^2 term for instance, $V_{12}V_{21}$ appears only *once* ; $V_{21}V_{12}$ does not get counted.

The summation terms in (25) evidently suffice to specify any mixed derivative of the characteristic polynomial, evaluated at an unperturbed eigenvalue and at $\alpha = 0$, up to fourth order in α , i.e., all derivatives $f_{\epsilon^{\sigma} \alpha^{\beta}}(E_p(0), 0)$ with $\beta \leq 4$. In particular, the first and second order derivatives are the following :

$$f_{\epsilon}(E_p(0), 0) = \prod_{i \neq p} (E_p(0) - E_i(0)), \quad (26)$$

$$f_{\alpha}(E_p(0), 0) = -V_{pp} \prod_{i \neq p} (E_p(0) - E_i(0)), \quad (27)$$

$$\begin{aligned} f_{\epsilon\alpha}(E_p(0), 0) = & -V_{pp} \sum_{i \neq p} \prod_{j \neq p, i} (E_p(0) - E_i(0)) \\ & - \sum_{i \neq p} V_{ii} \prod_{j \neq p, i} (E_p(0) - E_i(0)), \end{aligned} \quad (28)$$

$$\begin{aligned} f_{\epsilon^2}(E_p(0), 0) = & 2V_{pp} \sum_{i \neq p} V_{ii} \prod_{j \neq p, i} (E_p(0) - E_i(0)) \\ & - 2 \sum_{i \neq p} V_{pi} V_{ip} \prod_{j \neq p, i} (E_p(0) - E_i(0)). \end{aligned} \quad (29)$$

Taking the two-fold degenerate case again as an example, (18) yields the following expression for the first derivative :

$$DE_i(0) = -\frac{f_{\epsilon\alpha}}{f_{\epsilon^2}} \pm \left[\frac{(f_{\epsilon\alpha})^2 - f_{\epsilon^2} f_{\alpha^2}}{f_{\epsilon^2}^2} \right]^{1/2} \Big|_{\epsilon = E_i(0), i = 1, 2 \quad \alpha = 0}$$

Substituting (28) and (29) for the partial derivatives, this becomes

$$DE_i(0) = \frac{1}{2}(V_{11} + V_{22}) \pm \frac{1}{2}\{[(V_{11} - V_{22})^2 + 4V_{12}V_{21}]^{1/2}\}, \quad i = 1, 2. \quad (30)$$

It is readily recognised that the above is simply the solution to the quadratic obtained when diagonalising the degenerate block. If it is assumed that this block has been diagonalised, i.e., that $V_{12} = 0 = V_{21}$, then (30) simplifies to

$$DE_1(0) = V_{11}, \quad (31)$$

and $DE_2(0) = V_{22}. \quad (32)$

In the case of two-fold degeneracy lifted in first order ($V_{11} \neq V_{22}$), expressions for the second derivatives $D^2 E_1(0)$ and $D^2 E_2(0)$ are first evaluated. On substituting the partial derivatives obtained from (25), these second derivatives become

$$\frac{1}{2!} D^2 E_i(0) = \sum_{m \neq 1, 2} \frac{V_{im} V_{mi}}{E_i(0) - E_m(0)}, \quad i = 1, 2. \quad (33)$$

The right side of (33) agrees with the a^2 term of (24), but with the summation now correctly restricted, i.e., $m \neq 1, 2$.

Higher derivatives are obtained similarly. The expression evaluated for the third derivative, $(1/3!) D^3 E_i(0)$, is precisely the a^3 term of (24). The important point to note here is that, yielding as it does the Taylor series for $E_i(a)$ directly the characteristic polynomial approach automatically guarantees that the energy derivatives are correctly ordered.

3.5. A perturbation calculation on benzene

To illustrate another application of our characteristic polynomial approach, we consider a benzene molecule with three adjacent carbon atoms perturbed in some way.

The Hamiltonian $\mathcal{H}(a)$, in the Hückel approximation (Coulson 1940), is given by

$$\mathcal{H}(a) = \mathcal{H}^0 + aV$$

where \mathcal{H}^0 is of the form

$$\mathcal{H}^0 = \begin{bmatrix} A & \beta & 0 & 0 & 0 & \beta \\ \beta & A & \beta & 0 & 0 & 0 \\ 0 & \beta & A & \beta & 0 & 0 \\ 0 & 0 & \beta & A & \beta & 0 \\ 0 & 0 & 0 & \beta & A & \beta \\ \beta & 0 & 0 & 0 & \beta & A \end{bmatrix} \quad (34)$$

and
$$V = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (35)$$

Calculations will now be outlined in both the usual 'textbook-type' operator formalism and our 'characteristic polynomial' formalism, so that the amount of work involved in each may be compared.

3.5a. *Operator formalism* : The calculation may be split up into the usual steps as follows :

(i) Diagonalisation of the unperturbed operator :

The unperturbed operator \mathcal{H}^0 , as given by (34), is in an atomic orbital basis $\{\phi_i\}$. The eigenvectors of \mathcal{H}^0 are the molecular orbitals ψ_i , $i = 1, \dots, 6$. In the $\{\psi_i\}$ \mathcal{H}^0 is diagonal.

The eigenvectors of \mathcal{H}^0 are expressed as linear combinations of the atomic orbitals, ϕ_r , $r = 1, \dots, 6$,

$$\psi_i = \sum_{r=1}^6 c_{ir} \phi_r. \quad (36)$$

If the eigenvectors are normalised the matrix of the coefficients c_{ir} is the unitary matrix U , given by

$$U = \begin{bmatrix} 1/\sqrt{6} & 2/\sqrt{12} & 0 & 0 & 2/\sqrt{12} & 1/\sqrt{6} \\ 1/\sqrt{6} & 1/\sqrt{12} & \frac{1}{2} & \frac{1}{2} & -1/\sqrt{12} & -1/\sqrt{6} \\ 1/\sqrt{6} & -1/\sqrt{12} & \frac{1}{2} & -\frac{1}{2} & -1/\sqrt{12} & 1/\sqrt{6} \\ 1/\sqrt{6} & -2/\sqrt{12} & 0 & 0 & 2/\sqrt{12} & -1/\sqrt{6} \\ 1/\sqrt{6} & -1/\sqrt{12} & -\frac{1}{2} & \frac{1}{2} & -1/\sqrt{12} & 1/\sqrt{6} \\ 1/\sqrt{6} & 1/\sqrt{12} & -\frac{1}{2} & -\frac{1}{2} & -1/\sqrt{12} & -1/\sqrt{6} \end{bmatrix} \quad (37)$$

$$= \begin{bmatrix} \psi_1 & \psi_2 & \psi_3 & \psi_4 & \psi_5 & \psi_6 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

The eigenvalues $E_i(0)$, $i = 1, \dots, 6$ of \mathcal{H}^0 are

$$E_1(0) = A + 2\beta, \quad E_2(0) = A + \beta = E_3(0), \quad E_4(0) = A - \beta = E_5(0), \\ E_6(0) = A - 2\beta.$$

(ii) Basis change for the perturbing operator:

The perturbing operator V , as given by (35), is in the $\{\phi_i\}$ basis. To carry out the calculation V must be found in the basis $[\psi_i]$ in which \mathcal{H}^0 is diagonal. The necessary unitary transformation is

$$V' = U^* V U \quad (38)$$

where U is given in (37). Thus V' , the perturbing operator in the $[\psi_i]$ basis, is given by

$$V' = \begin{bmatrix} \frac{1}{2} & 1/3\sqrt{2} & 1/\sqrt{6} & 0 & 0 & \frac{1}{6} \\ 1/3\sqrt{2} & \frac{1}{2} & 0 & 1/2\sqrt{3} & \frac{1}{3} & 0 \\ 1/\sqrt{6} & 0 & \frac{1}{2} & 0 & -1/2\sqrt{3} & 0 \\ 0 & 1/2\sqrt{3} & 0 & \frac{1}{2} & 0 & -1/\sqrt{6} \\ 0 & \frac{1}{3} & -1/2\sqrt{3} & 0 & \frac{1}{2} & 1/3\sqrt{2} \\ \frac{1}{6} & 0 & 0 & -1/\sqrt{6} & 1/3\sqrt{2} & \frac{1}{2} \end{bmatrix} \quad (39)$$

(iii) Solution of the degenerate block:

We shall focus attention on the two-fold degenerate eigenvalues $E_2(0)$ and $E_3(0)$. In practice it is convenient to set

$$E_2(0) = E_3(0) = 0$$

and simply add on their actual unperturbed values at the end of the calculation.

The appropriately reduced characteristic polynomial here then is the quadratic

$$\epsilon^2 + c_1 \epsilon + c_2 \quad (40)$$

$$\text{with roots} \quad \epsilon = -\frac{c_1}{2} \pm \frac{[(c_1)^2 - 4c_2]^{1/2}}{2} \quad (41)$$

Since $V'_{22} = V'_{33}$, degeneracy is not lifted in first order, and we will have

$$\epsilon = \alpha V'_{22} + \frac{\alpha^2}{2} (Q'_{22} + Q'_{33}) \pm \alpha^2 \frac{[(Q'_{22} - Q'_{33}) - 4Q'_{23} Q'_{32}]^{1/2}}{2} + \dots \tag{42}$$

Now Q'_{22} is given by (see (24)),

$$Q'_{22} = \frac{V'_{21} V'_{12}}{E_2 - E_1} + \frac{V'_{24} V'_{42}}{E_2 - E_4} + \frac{V'_{25} V'_{52}}{E_2 - E_5} + \frac{V'_{26} V'_{62}}{E_2 - E_6}, \tag{43}$$

where $E_2 - E_1 = E_2(0) - E_1(0) = -\beta$, (44)

and similarly for the other energy denominators.

One finds that

$$Q'_{22} = -\frac{1}{24\beta},$$

$$Q'_{33} = \frac{1}{8\beta},$$

and $Q'_{23} Q'_{32} = \left(\frac{1}{4\sqrt{3}\beta}\right)^2 = \frac{1}{48\beta^2}.$

Substitution in (42) yields

$$\epsilon = \frac{\alpha}{\beta} \cdot \frac{1}{2} + \frac{\alpha^2}{\beta^2} \cdot \frac{1}{24} \pm \frac{\alpha^2}{\beta^2} \cdot \frac{1}{2} \sqrt{\frac{1}{9}} + \dots \tag{45}$$

so that finally one has

$$\begin{aligned} E_2(\alpha) &= A + \beta + \frac{\alpha}{\beta} \cdot \frac{1}{2} + \frac{\alpha^2}{\beta^2} \cdot \frac{5}{24} + \dots, \\ E_3(\alpha) &= A + \beta + \frac{\alpha}{\beta} \cdot \frac{1}{2} + \frac{\alpha^2}{\beta^2} \left(\frac{-1}{8}\right) + \dots \end{aligned} \tag{46}$$

3.5b. *Characteristic polynomial formalism* : Here the calculation has the following steps.

(i) Writing down the characteristic polynomial: The form of the polynomial $f(\epsilon', \alpha')$ = det | $\epsilon' - \mathcal{H}$ | is simplified if we set

$$\epsilon = \frac{\epsilon' - A}{\beta}, \alpha = \frac{\alpha'}{\beta}. \tag{47}$$

The determinant becomes,

$$\det | \epsilon - \mathcal{H} | = \begin{vmatrix} \epsilon - \alpha & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & \epsilon - \alpha & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & \epsilon - \alpha & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & \epsilon & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & \epsilon & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 & \epsilon & \epsilon \end{vmatrix}$$

which expands (see (25)) as

$$\begin{aligned} &= \epsilon^6 - 3\epsilon^5\alpha + \epsilon^4(-6 + 3\alpha^2) + \epsilon^2(12\alpha - \alpha^3) \\ &\quad + \epsilon^2(9 - 8\alpha^2) + \epsilon(-9\alpha + 2\alpha^3) - 4 + 2\alpha^2. \end{aligned} \tag{48}$$

(ii) Calculation of the derivatives of the characteristic polynomial :

In preparation for the construction of an appropriately reduced characteristic polynomial with $E_2(\alpha)$ and $E_3(\alpha)$ as roots, we compute derivatives of $f(\epsilon, \alpha)$ evaluated for $\epsilon = E_2(0) = E_3(0)$ and $\alpha = 0$. Because of the change of variables (47) we have

$$E_2(0) = +1 = E_3(0). \tag{49}$$

Evaluating all derivatives at $\epsilon = +1, \alpha = 0$, we find from (48) that

$$\begin{aligned} f_\epsilon &= 0, f_\alpha = 0, \\ f_{\epsilon^2} &= -24, f_{\epsilon\alpha} = +12, f_{\alpha^2} = -6, \\ f_{\epsilon^3} &= -24, f_{\epsilon^2\alpha} = +12, f_{\epsilon\alpha^2} = -8, f_{\alpha^3} = +6, \\ f_{\epsilon^4} &= +216, f_{\epsilon^3\alpha} = -108, f_{\epsilon^2\alpha^2} = +40, f_{\epsilon\alpha^3} = -6, f_{\alpha^4} = 0. \end{aligned} \tag{50}$$

Before constructing the RCP, we first note that degeneracy is not lifted in first order since

$$f_{\epsilon^2}f_{\alpha^2} - (f_{\epsilon\alpha})^2]_{\epsilon=1, \alpha=0} = 0. \tag{51}$$

Thus we have, from (21),

$$DE_2(0) = DE_3(0) = -\left. \frac{f_{\epsilon\alpha}}{f_{\epsilon^2}} \right]_{\epsilon=1, \alpha=0} = +\frac{1}{2}. \tag{52}$$

For the sake of convenience we set

$$E_2(0) = 0 = E_3(0)$$

as in the previous section. The RCP then turns out to be a quadratic with roots

$$\epsilon = -\frac{c_1}{2} \pm \frac{1}{2} \{[(c_1)^2 - 4c_2]^{1/2}\} \tag{53}$$

From equation (A6) of the Appendix and equation (50) above, we have

$$\begin{aligned} c_1 &= \alpha \left\{ \frac{2f_{\epsilon\alpha}}{f_{\epsilon^2}} \right\} + \frac{\alpha^2}{2!} \left\{ +\frac{f_{\epsilon\alpha^2}}{f_{\epsilon^2}} - \frac{1}{(f_{\epsilon^2})^2} \left[\frac{2}{3} f_{\epsilon^2}f_{\alpha^2} + 4f_{\epsilon^2\alpha}f_{\epsilon\alpha} \right] \right. \\ &\quad \left. + \frac{8}{3} \cdot \frac{f_{\epsilon^3}}{(f_{\epsilon^2})^3} (f_{\epsilon\alpha})^2 \right\} + \dots \\ &= -\alpha + \frac{\alpha^2}{2} \left\{ \frac{1}{3} - \frac{7}{6} + \frac{2}{3} \right\} + \dots \end{aligned} \tag{54}$$

and thus

$$-\frac{c_1}{2} = +\frac{\alpha}{2} + \frac{\alpha^2}{24} + \dots \tag{55}$$

Furthermore, since degeneracy is not lifted in first order, we have, firstly,

$$D\epsilon]_{\epsilon=1, \alpha=0} = DE_2(0) = DE_3(0) = \frac{1}{2}, \quad (56)$$

and, secondly, for the discriminant in (53),

$$(c_1)^2 - 4c_2 = a^4 \left\{ \left(\frac{f_{\epsilon'}^{(2)}}{f_{\epsilon'}^{(0)}} \right)^2 - \frac{1}{3} \cdot \frac{f_{\epsilon''}^{(4)}}{f_{\epsilon''}^{(2)}} \right\}, \quad (57)$$

where $f_{\epsilon'}^{(2)} = f_{\epsilon\alpha^2} + 2f_{\epsilon^2\alpha}(D\epsilon) + f_{\epsilon^3}(D\epsilon)^2$ (58)

and $f_{\epsilon''}^{(4)} = f_{\alpha^4} + 4f_{\epsilon\alpha^3}(D\epsilon) + 6f_{\epsilon^2\alpha^2}(D\epsilon)^2$
 $+ 4f_{\epsilon^3\alpha}(D\epsilon)^3 + f_{\epsilon^4}(D\epsilon)^4$. (59)

We substitute the values for the derivatives given in (50), and find that

$$f_{\epsilon'}^{(2)} = -2 \quad \text{and} \quad f_{\epsilon''}^{(4)} = 15/2.$$

Hence, from (57),

$$(c_1)^2 - 4c_2 = \left(\frac{1}{12} \right)^2 + \frac{15}{144} = \frac{1}{9} \quad (60)$$

so that, finally, we have

$$\epsilon = \frac{\alpha}{2} + \alpha^2 \cdot \frac{1}{24} \pm \frac{\alpha^2}{2} \sqrt{\frac{1}{9}} \quad (61)$$

which agrees with the result obtained from the operator formalism of the last section in (45) once α is replaced by α/β .

4. Concluding remarks

We have demonstrated that when the characteristic polynomial formalism is employed, quantum chemical perturbation theory is equivalent to a study of the way in which the roots of the polynomial change as the perturbation parameter α varies. We have explicitly shown how the total derivatives of the characteristic equation of a perturbed operator, taken with respect to α yield expressions for the perturbed eigenvalues to any order in α .

Further, starting from the characteristic polynomial expressions, we are able to arrive at the customary Rayleigh-Schrödinger perturbation formulae, with the advantage that the series obtained in this way is correctly ordered. This approach is particularly fruitful since the question of ordering in the degenerate case is usually not made clear in discussions of perturbation techniques in quantum chemistry.

There is, however, one important limitation to our computational approach*. When the number of states of the system is large, computation of the polynomials is likely to be prohibitively complicated unless one has recourse to algebraic

* The author is thankful to a referee for raising this point.

manipulation language systems such as **MATLAB** or its descendent **MACSYMA**, which are written in a symbolic list-processing language such as 'LISP' and coded at a high level for operation on a present generation computer such as **DEC** system-10.

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Appendix

The coefficients c_1, \dots, c_q of the **RCP** are symmetric functions of the eigenvalues E_p, \dots, E_{p+q-1} , namely,

$$\left. \begin{aligned}
 c_q &= (-1)^q \prod_{i=p}^{p+q-1} (E_i) \\
 c_{q-1} &= (-1)^{q-1} \sum_{i=p}^{p+q-1} \prod_{j \neq i} (E_j) \\
 &\cdot \quad \cdot \quad \cdot \quad \cdot \\
 &\cdot \quad \cdot \quad \cdot \quad \cdot \\
 &\cdot \quad \cdot \quad \cdot \quad \cdot \\
 c_1 &= -1 \sum_{i=p}^{p+q-1} E_i.
 \end{aligned} \right\} \tag{A1}$$

The above coefficients may be obtained from the eigenvalue power summations S_m , $m = 1, \dots, q$, defined by

$$S_m = \sum_{i=p}^{p+q-1} (E_i)^m \tag{A2}$$

Now to determine appropriate perturbation series for the eigenvalue power summations, we recall that our characteristic polynomial has the factorization of the form of (2) of the text, whence it follows that

$$f_\epsilon/f = \frac{\partial}{\partial \epsilon} \ln f = \sum_{i=1}^n \frac{1}{(\epsilon - E_i)}. \tag{A3}$$

The function on the right side of (A3) has a pole at each eigenvalue, with residue equal to the degeneracy. It follows, then, that

$$S_m = \frac{1}{2\pi i} \int_\gamma \epsilon^m (f_\epsilon/f) d\epsilon, \tag{A4}$$

where γ is a small circular contour which moves counterclockwise around the origin in the complex ϵ -plane enclosing the relevant eigenvalues E_p, \dots, E_{p+q-1} . For small perturbations, the integrand $\epsilon^m (f_\epsilon/f)$ is an analytic function of a . For this situation the S_m 's, and thus the c_i 's, are also analytic functions of a , and well-known contour integration procedures may then be conveniently used to determine the S_m 's (Kato 1966; Fukui *et al* 1959).

Accordingly, expansion of the integrand in (A4) about $|a| = 0$ yields

$$S_m = \frac{1}{2\pi i} \int_{\gamma} \epsilon^m \left[\frac{f_\epsilon(\epsilon, 0)}{f(\epsilon, 0)} + \sum_{i=1}^l \alpha_i \frac{\partial}{\partial \alpha_i} \frac{f_\epsilon}{f} + \dots \right] d\epsilon. \quad (\text{A5})$$

Assuming for simplicity that we have only one perturbation parameter in our problem, we may write the general term in the expansion of the integrand (A5) as

$$\frac{\alpha^n}{n!} \frac{\partial^n}{\partial \alpha^n} \frac{f_\epsilon}{f} \Big|_{|a|=0}.$$

The integrand in (A5) then simplifies to

$$\epsilon^m \left[\frac{f_\epsilon}{f} + \alpha \left\{ \frac{f_{\epsilon a}}{f} - \frac{f_\epsilon f_a}{f^2} \right\} + \frac{\alpha^2}{2!} \left\{ \frac{f_{\epsilon a^2}}{f} - \frac{2f_{\epsilon a} f_a}{f^2} - \frac{f_\epsilon f_{a^2}}{f^2} + \frac{2f_\epsilon (f_a)^2}{f^3} \right\} + \dots \right], \quad (\text{A6})$$

f and its derivatives being evaluated at $|a| = 0$ according to the techniques mentioned in § 3 of the text.

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