

A Note on the QuantumMechanical Perturbation Theory

PerOlov Löwdin

Citation: *J. Chem. Phys.* **19**, 1396 (1951); doi: 10.1063/1.1748067

View online: <http://dx.doi.org/10.1063/1.1748067>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v19/i11>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



HAVE YOU HEARD?

Employers hiring scientists
and engineers trust
physicstodayJOBS



<http://careers.physicstoday.org/post.cfm>

A Note on the Quantum-Mechanical Perturbation Theory*

PER-OLOV LÖWDIN

Department of Physics, Duke University, Durham, North Carolina†

(Received July 23, 1951)

The solution of the quantum-mechanical eigenvalue problem is discussed for cases when a series of approximate eigenfunctions is known. If these "unperturbed" states are divided into two classes, a perturbation formula is derived giving the influence of one class of states on the other in the final solution. The formula contains as special cases: (i) the Schrödinger-Brillouin formula for the eigenvalue of a nondegenerate state, (ii) a new simple formula for treating a class of degenerate states, and (iii) the splitting of the secular equation in cases where the system naturally consists of two independent parts in mutual interaction.

1. INTRODUCTION

ONE of the most important tools for treating the fundamental quantum-mechanical eigenvalue problem

$$H\psi = \mathcal{E}\psi \quad (1)$$

is the perturbation method due to Schrödinger.¹ In its conventional form, the operator H has the form $H = H_0 + V$, and, for the derivation of the perturbation formulas, it is usually assumed² that V can be expressed as a power series in a perturbation parameter λ . Another type of derivation of these formulas has been given by Lennard-Jones³ and by Brillouin,⁴ who used the secular equation and the theory of bordered determinants. Here we will show that a still simpler treatment of the perturbation theory can be given by using the system of linear equations⁵ corresponding to the secular equation. Dividing the given "unperturbed" states into two classes, we will derive a formula which explicitly gives the influence of one class of states on the other in the final solution of (1). As special cases we will obtain the Schrödinger-Brillouin formula⁴ for the eigenvalue of a nondegenerate state, a new formula for the treatment of a class of degenerate states, and finally a formula for the splitting of the secular equation for a system which naturally consists of two independent parts in mutual interaction. Even if these formulas are here derived mainly for the application in the theory of molecules, they may be useful in other parts of quantum mechanics.

2. THE VARIATIONAL PRINCIPLE

Here we will not restrict the Hermitian operator H to having any special form, and we will only assume that we know a system of orthonormalized functions $\psi_n^{(0)}$ ($n=1, 2, \dots, N$), which are *approximate* eigenfunctions of H . This system may be finite or infinite, but it must not necessarily be complete.⁶ We will then investigate the *best* eigenfunctions of H which can be formed by linear combinations of the given functions:

$$\psi = \sum_{n=1}^N \psi_n^{(0)} c_n \quad (2)$$

For this purpose we introduce the matrix elements of the total operator H with respect to the given set:

$$H_{mn} = \int \psi_n^{*(0)} H \psi_n^{(0)} d\tau \quad (3)$$

The coefficients c_n can now be determined by the variational principle, which says that the integral

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\sum_{mn} c_m^* H_{mn} c_n}{\sum_{mn} c_m^* \delta_{mn} c_n} \quad (4)$$

gives an approximate value of \mathcal{E} , and that the best approximation is obtained when $\delta E = 0$. If $E = A/B$, we have $\delta E = (\delta A - E \delta B)/B$, which, for the coefficients c_n , gives the system of linear equations:

$$\sum_{n=1}^N (H_{mn} - E \delta_{mn}) c_n = 0, \quad m = 1, 2, \dots, N. \quad (5)$$

The condition for the existence of a non-trivial solution of (5) is $\text{Det}(H_{mn} - E \delta_{mn}) = 0$, an equation previously used by Lennard-Jones³ and by Brillouin.⁴ Here we will instead base our treatment directly on the linear system (5).

⁶ This is of special importance in the theory of molecules, where, for instance in the MO-LCAO-method, we usually know only a few approximate wave functions.

* Work supported by the ONR, under Contract N6ori-107, Task Order I, with Duke University.

† Permanent address: Institute of Mechanics and Mathematical Physics, University of Uppsala, Uppsala, Sweden.

¹ E. Schrödinger, *Ann. Physik* (4) **80**, 437 (1926).

² See, for instance, Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935); Kemble, *Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937); Mott and Sneddon, *Wave Mechanics and its Applications* (Oxford University Press, Oxford, 1948).

³ J. E. Lennard-Jones, *Proc. Roy. Soc. (London)* **129**, 604 (1930).

⁴ L. Brillouin, *J. Phys. Radium* (7) **3**, 373 (1932). See also E. Wigner, *Math. naturw. Anz. ungar. Akad. Wiss.* **53**, 477 (1935).

⁵ This idea has previously been used for special purposes by E. Gora, *Z. Physik* **120**, 121 (1942-43) and by H. Feshbach, *Phys. Rev.* **74**, 1548 (L), (1948).

3. A PERTURBATION FORMULA FOR THE MUTUAL INFLUENCE OF TWO CLASSES OF STATES

Let us assume that, in some definite way, we have divided the series of indices n of $\psi_n^{(0)}$ into two classes, (A) and (B). Let us for a moment be mainly interested in the class (A), and let us try to derive a formula by means of which we can treat the influence of the states in (B) as a perturbation. The system (5) can be written

$$(E - H_{mm})c_m = \sum_n^A H_{mn}'c_n + \sum_n^B H_{mn}'c_n, \quad (6)$$

if the sign ' on a matrix means that we omit all diagonal elements, so that $H_{mn}' = H_{mn}(1 - \delta_{mn})$. Using the notation

$$h_{mn} = H_{mn}/(E - H_{mm}), \quad (7)$$

we get then

$$c_m = \sum_n^A h_{mn}'c_n + \sum_n^B h_{mn}'c_n. \quad (8)$$

We will now eliminate the states in the class (B) by a process of iteration, expressing the coefficients c in all sums exclusively over B by the formula (8) itself. In this way we obtain the formal expansion

$$c_m = \sum_n^A (h_{mn}' + \sum_\alpha^B h_{m\alpha}'h_{\alpha n}' + \sum_{\alpha\beta}^B h_{m\alpha}'h_{\alpha\beta}'h_{\beta n}' + \dots)c_n. \quad (9)$$

Introducing the new notation

$$U_{mn}^A = H_{mn} + \sum_\alpha^B \frac{H_{m\alpha}'H_{\alpha n}'}{E - H_{\alpha\alpha}} + \sum_{\alpha\beta}^B \frac{H_{m\alpha}'H_{\alpha\beta}'H_{\beta n}'}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \dots \quad (10)$$

we get

$$c_m = \sum_n^A \frac{U_{mn}^A - H_{mn}\delta_{mn}}{E - H_{mm}}c_n. \quad (11)$$

For the two cases of m in (A) or (B), we have, therefore, the two basic formulas

$$\begin{cases} \sum_n^A (U_{mn}^A - E\delta_{mn})c_n = 0, & m \text{ in (A).} \\ c_m = \sum_n^A \frac{U_{mn}^A}{E - H_{mm}}c_n, & m \text{ in (B).} \end{cases} \quad (12) \quad (13)$$

The first formula is formally identical to (5), but it is limited only to the class (A). This gives the theorem:

An eigenvalue problem (5) with respect to a system of states belonging to two classes, (A) and (B), can be reduced only to the class (A), if the matrix elements H_{mn} are replaced by the elements U_{mn}^A , where the influence of the class (B) is taken into account by expansion (10).

When the coefficients c_n belonging to (A) have been determined, we get the coefficients c_n belonging to (B) according to (13).

We note that series (10) is here only formally derived and that, when the series is interrupted after a finite number of terms, there is a remainder containing sums exclusively over (B). A necessary condition for the validity of (10) is therefore that, for the value of E under consideration and for m and n in (B), the matrix elements h_{mn}' are small in comparison to the unity:

$$|H_{mn}'/(E - H_{mm})| \ll 1. \quad (14)$$

The problem of the convergency of (10) remains still to be investigated.

Matrix elements of the type (10), where the summation is carried out only over a restricted number of states, have previously been considered by Feenberg⁷ in his perturbation formulas without repetitive elements. It may be noted that even his formulas can simply be derived by using (5), as has been shown by Feshbach.⁸ Here we will now consider some special cases of (10), (12), and (13) in greater detail.

(i) (A) = Single Nondegenerate State k

In the case the whole class (A) consists of a single nondegenerate state, the whole system (5) is reduced to a single term, and the secular equation takes the form

$$U_{kk}^k - E = 0. \quad (15)$$

According to (10) this gives for our approximate eigenvalue $E = E_k$

$$E = U_{kk}^k = H_{kk} + \sum_{\alpha \neq k} \frac{H_{k\alpha}'H_{\alpha k}'}{E - H_{\alpha\alpha}} + \sum_{\alpha, \beta \neq k} \frac{H_{k\alpha}'H_{\alpha\beta}'H_{\beta k}'}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \dots \quad (16)$$

This formula was first derived in another way by Brillouin,⁴ and we note that E can be computed by iteration. If we introduce the conventional form $H = H_0 + V$, we have

$$H_{mn} = \begin{cases} H_{mm}^{(0)} + V_{mm} & \text{for } m = n \\ V_{mn} & \text{for } m \neq n. \end{cases} \quad (17)$$

Putting these expressions into (16), using iteration, and developing the right-hand member in a power-series in V_{mn} , we obtain the well-known perturbation formulas first given by Schrödinger.¹ In this way not only the first- and second-order terms but even the third- and fourth-order terms⁸ can be easily derived. However, we note that in general it has been recommended

⁷ E. Feenberg, Phys. Rev. 74, 206, 664 (1948).

⁸ The explicit form of the third- and fourth-order terms in Schrödinger's theory may be found, e.g., in K. F. Niessen, Phys. Rev. 34, 253 (1929).

to use formula (16) instead of the original Schrödinger formula, since (16) is simpler and seems to have better convergence properties. Equation (13) gives directly the best form of the corresponding eigenfunction.

(ii) (A) = Class of Degenerate States

Let us now consider the case that the eigenvalue problem (1) shows a degeneracy. This means here that a class of diagonal elements H_{kk} are exactly or almost the same, i.e.,

$$H_{kk} \approx E_A \quad (18)$$

but for quantities of the first or higher orders. In the conventional theory it is recommended to treat the degeneracy by performing linear transformations of the approximate wave functions $\psi_n^{(0)}$ in such a way that the matrix H becomes *diagonal* with respect to the class of degenerate states, whereafter the ordinary perturbation formulas can be applied. This means that

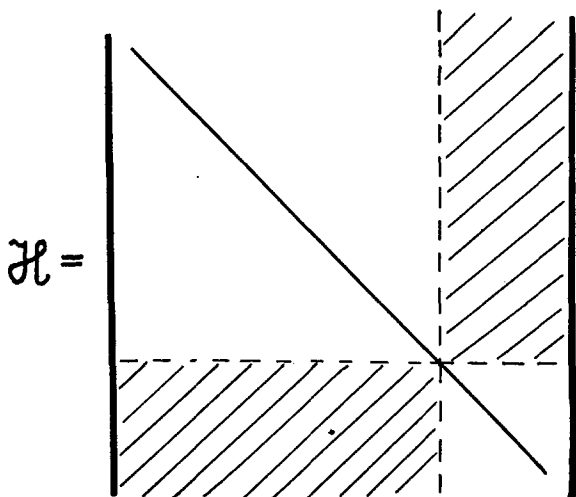


FIG. 1. Form of the matrix.

one first removes the degeneracy and then treats the perturbation problem. This theoretically simple procedure can often be rather complicated in the applications,⁹ and considerable simplifications have therefore been worked out by Van Vleck.¹⁰

The general process described in this paper gives another method of treating the degeneracy in a very simple and natural way. It takes things in the reverse order: first the perturbation problem, i.e., the influence of the states not belonging to the degenerate class under consideration, is treated according to formula (10), and then the degeneracy is removed by solving the secular equation corresponding to the system (12). For the latter step only algebraic methods are, in general, available. The coefficients c_n for the states in (A) are

⁹ For a detailed description see, for instance, Kemble, *Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937).

¹⁰ J. H. Van Vleck, *Phys. Rev.* **33**, 467 (1929); O. M. Jordahl, *Phys. Rev.* **45**, 87_a (1934).

determined from the linear system (12), and, finally, the remaining coefficients are found by using (13).

The second-order approximation takes a particularly simple form in the method given here. According to (18) we have $E \approx E_A$, but for quantities of the first and higher orders, and in the second-order approximation, (10) gives therefore

$$U_{mn}^A = H_{mn} + \sum_{\alpha}^B \frac{H_{m\alpha}' H_{\alpha n}'}{E_A - H_{\alpha\alpha}} \quad (19)$$

Since all these matrix elements are numerically given, the secular equation corresponding to (12) can be directly solved without any iterations. We have applied this method to the treatment of the one-electron wave functions in the MO-LCAO-theory of conjugated organic compounds; the results will be published elsewhere.

(iii) (A) = Class of Arbitrary States

Let us for a moment assume that the system has naturally or arbitrarily been divided into two classes, (A) and (B), and that k is a nondegenerate state in (A). According to (10) we can first eliminate the system (B), and using (16) we can then solve the perturbation problem (12). For the approximate eigenvalue $E = E_k$ we get in this way

$$E = U_{kk}^A + \sum_{\alpha \neq k}^A \frac{U_{k\alpha}^A U_{\alpha k}^A}{E - U_{\alpha\alpha}^A} + \sum_{\alpha \neq k}^B \frac{U_{k\alpha}^A U_{\alpha\beta}^A U_{\beta k}^A}{(E - U_{\alpha\alpha}^A)(E - U_{\beta\beta}^A)} + \dots \quad (20)$$

Since the result must be the same as in (16), formula (20) gives one of the possible ways of *regrouping* the terms in (16); compare reference 7.

Finally we will treat the case that our system naturally consists of two independent parts (A) and (B) in mutual interaction. We will assume that the wave functions $\psi_n^{(0)}$ have been chosen in such a way that the matrix H is diagonal with respect to (A) and (B), respectively (see Fig. 1). Since the elements $H_{\alpha\beta}'$, for α and β both in (B), are then vanishing, the expansion (10) reduces exactly to its first two terms:

$$U_{mn}^A = H_{mn} + \sum_{\alpha}^B \frac{H_{m\alpha}' H_{\alpha n}'}{E - H_{\alpha\alpha}} \quad (21)$$

It is also easily checked that the remainder in (9) vanishes.

As an application we will consider a problem in the MO-LCAO-theory of conjugated compounds, let us say a mono-substituted benzene. Let H be the one-electron Hamiltonian for the π -electrons and let ψ be the MO formed by LCAO from the six benzene π -orbitals

$\psi_1^{(0)}, \psi_2^{(0)}, \dots, \psi_6^{(0)}$, and the π -orbital $\psi_7^{(0)}$ of the substituent. The matrix H has then the form:

$$H = \begin{array}{cccc|c} H_{11} & 0 & \cdot & & H_{17} \\ 0 & H_{22} & \cdot & & H_{27} \\ \cdot & \cdot & H_{33} & & H_{37} \\ & & & \cdot & \cdot \\ & & & & H_{66} \\ \hline H_{71} & H_{72} & H_{73} \cdots H_{76} & & H_{77} \end{array}$$

The secular equation has been treated in the first approximation in the wave functions by Sklar¹¹ and by Herzfeld,¹² and recently Matsen,¹³ using conventional perturbation theory, has shown that, for instance, E_7 is given by:

$$E_7 = H_{77} + \sum_{i=1}^6 \frac{|H_{7i}|^2}{H_{77} - H_{ii}} \quad (22)$$

This perturbation theory breaks down when H_{77} is close in value to any of the H_{ii} .¹⁴

However, if we here apply formula (10) to a class (A) consisting of the only state 7, we get directly with-

$$\begin{array}{c} \left| \begin{array}{ccc|ccc} H_{11}-E & & & H_{1, n+1} \cdots & H_{1, n+p} & \\ & H_{22}-E & & H_{2, n+1} \cdots & H_{2, n+p} & \\ & & \cdot & \cdot & \cdot & \cdot \\ & & & H_{nn}-E & H_{n, n+1} \cdots & H_{n, n+p} \\ \hline H_{n+1, 1} & H_{n+1, 2} \cdots & H_{n+1, n} & H_{n+1, n+1}-E & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \\ H_{n+p, 1} & H_{n+p, 2} \cdots & H_{n+p, n} & & H_{n+p, n+p}-E & \end{array} \right| = \prod_i^{A+B} (H_{ii} - E) \end{array}$$

$$\cdot \left\{ 1 - \sum_r^A \sum_s^B \frac{|H_{rs}|^2}{(E - H_{rr})(E - H_{ss})} + \sum_{r_1 r_2}^A \sum_{s_1 s_2}^B \frac{\| \begin{array}{c} H_{r_1 s_1} H_{r_1 s_2} \\ H_{r_2 s_1} H_{r_2 s_2} \end{array} \|^2}{(E - H_{r_1 r_1})(E - H_{r_2 r_2})(E - H_{s_1 s_1})(E - H_{s_2 s_2})} + \dots \right.$$

$$\left. + (-1)^p \sum_{r_1 r_2 \cdots r_p}^A \sum_{s_1 s_2 \cdots s_p}^B \frac{\| \begin{array}{ccc} H_{r_1 s_1} & H_{r_1 s_2} \cdots & H_{r_1 s_p} \\ H_{r_2 s_1} & H_{r_2 s_2} \cdots & H_{r_2 s_p} \\ \cdot & \cdot & \cdot \\ H_{r_p s_1} & H_{r_p s_2} \cdots & H_{r_p s_p} \end{array} \|^2}{(E - H_{r_1 r_1})(E - H_{r_2 r_2}) \cdots (E - H_{r_p r_p})} \right\} \quad (24)$$

out any approximation:

$$E = H_{77} + \sum_{i=1}^6 \frac{H_{7i} H_{i7}}{E - H_{ii}} \quad (23)$$

a formula which holds even when (22) breaks down. The energy E can be found by iteration, and we note that even the derivatives of E , which are of importance, e.g., in calculating the charge distribution, can be found by implicit derivation. This example shows that the methods developed here may be useful in the theory of molecules.

Since Eq. (23) must be exactly contained in the secular equation $\text{Det}(H_{mn} - E\delta_{mn}) = 0$, there must exist a more elementary way of finding this relation from the determinant itself. This problem will be treated in the next section.

4. THE CONNECTION WITH THE THEORY OF BORDERED DETERMINANTS

In the previous section we have treated problems which are closely connected with the theory of bordered determinants. Recently Dewar¹⁵ has given some useful transformations of determinants $\text{Det}(H - E \cdot 1)$ when H has the same form as in Fig. 1. However, the general formula for the expansion of a bordered determinant was given already 1896 by Arnaldi.¹⁶ According to this formula,¹⁷ we obtain directly

¹¹ A. L. Sklar, J. Chem. Phys. 7, 984 (1939).
¹² K. F. Herzfeld, Chem. Rev. 41, 233 (1947).
¹³ F. A. Matsen, J. Am. Chem. Soc. 72, 5243 (1950).
¹⁴ See reference 13, footnote 9.
¹⁵ M. J. S. Dewar, Proc. Cambridge Phil. Soc. 45, 638 (1949).
¹⁶ M. Arnaldi, Giornale di Mat. Battaglini 34, 209 (1896).
¹⁷ See, for instance, G. Kowalewski, *Determinantentheorie* (Leipzig, 1909), pp. 89-99, or T. Muir, *Theory of Determinants* (London, 1923), IV, p. 432.

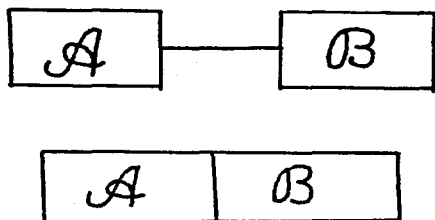


FIG. 2. Schematic diagram of singly or tightly linked molecule parts.

with $r_1 < r_2 < \dots < r_p$ and $s_1 < s_2 < \dots < s_p$. Formula (24) is given for $p \leq n$, and the sign $||$ means that we take the absolute value of a determinant. This relation can also be easily derived by using Laplace's expansion theorem with respect to the first n rows of the given determinant. We note that our formula (23) is contained as a special case for $p=1$; compare also Dewar.¹⁵ Putting the second factor in (24) equal to zero and multiplying the relation with the factor $(E - H_{kk})$, we get again a formula analogous to (16) and (20) but this time containing only a finite number of terms.

If our system is a molecule, the linkage between its two parts is of special interest. Let us as an example consider the one-electron wave functions. The MO ψ , according to Dewar's terminology, formed by LCMO (=linear combination of molecular orbitals) from the given MO $\psi_m^{(0)}$, which again are formed by LCAO from

the given atomic orbitals φ_μ :

$$\psi_m^{(0)} = \sum_\mu \varphi_\mu a_{\mu m}. \quad (25)$$

Introducing the matrix elements of H with respect to this AO,

$$\mathfrak{H}_{\mu\nu} = \int \varphi_\mu^* H \varphi_\nu d\tau \quad (26)$$

we get directly

$$H_{mn} = \sum_{\mu\nu} a_{m\mu} \dagger \mathfrak{H}_{\mu\nu} a_{\nu n} \quad (27)$$

or

$$H = a \dagger \mathfrak{H} a. \quad (28)$$

The last relation gives the MO-matrix H expressed in the AO-matrix \mathfrak{H} .

With respect to the atoms, the molecule may now consist of two natural parts (\mathfrak{A}) and (\mathfrak{B}), which may be separated or which may have atoms in common (see Fig. 2). From the AO in (\mathfrak{A}) we will build up the MO in class (A) in such a way that the operator H will be diagonalized; from the AO in (\mathfrak{B}) we will then form the MO in class (B) in the same way.[†] We will further introduce linkage classes $L_{\mathfrak{A}}$ and $L_{\mathfrak{B}}$ by the definition that an AO φ_μ in (\mathfrak{A}) belongs to $L_{\mathfrak{A}}$ if, for at least one AO φ_ν in (\mathfrak{B}), the matrix element $\mathfrak{H}_{\mu\nu}$ in (26) is essentially different from zero; the class $L_{\mathfrak{B}}$ is defined analogously.

Using a well-known theorem, we can now expand the determinants in (24) in sums of products of determinants of the three factors in (27):

$$\begin{vmatrix} H_{r_1 s_1} & H_{r_1 s_2} \cdots & H_{r_1 s_k} \\ H_{r_2 s_1} & H_{r_2 s_2} \cdots & H_{r_2 s_k} \\ \dots & \dots & \dots \\ H_{r_k s_1} & H_{r_k s_2} \cdots & H_{r_k s_k} \end{vmatrix} = \sum_{\mu_1 \mu_2 \cdots \mu_k}^{L_{\mathfrak{A}}} \sum_{\nu_1 \nu_2 \cdots \nu_k}^{L_{\mathfrak{B}}} \begin{vmatrix} a_{r_1 \mu_1} \dagger & a_{r_1 \mu_2} \dagger \cdots & a_{r_1 \mu_k} \dagger \\ a_{r_2 \mu_1} \dagger & a_{r_2 \mu_2} \dagger \cdots & a_{r_2 \mu_k} \dagger \\ \dots & \dots & \dots \\ a_{r_k \mu_1} \dagger & a_{r_k \mu_2} \dagger \cdots & a_{r_k \mu_k} \dagger \end{vmatrix} \begin{vmatrix} \mathfrak{H}_{\mu_1 \nu_1} & \mathfrak{H}_{\mu_1 \nu_2} \cdots & \mathfrak{H}_{\mu_1 \nu_k} \\ \mathfrak{H}_{\mu_2 \nu_1} & \mathfrak{H}_{\mu_2 \nu_2} \cdots & \mathfrak{H}_{\mu_2 \nu_k} \\ \dots & \dots & \dots \\ \mathfrak{H}_{\mu_k \nu_1} & \mathfrak{H}_{\mu_k \nu_2} \cdots & \mathfrak{H}_{\mu_k \nu_k} \end{vmatrix} \begin{vmatrix} a_{\nu_1 s_1} & a_{\nu_1 s_2} \cdots & a_{\nu_1 s_k} \\ a_{\nu_2 s_1} & a_{\nu_2 s_2} \cdots & a_{\nu_2 s_k} \\ \dots & \dots & \dots \\ a_{\nu_k s_1} & a_{\nu_k s_2} \cdots & a_{\nu_k s_k} \end{vmatrix}, \quad (29)$$

where $\mu_1 < \mu_2 < \dots < \mu_k$ and $\nu_1 < \nu_2 < \dots < \nu_k$. The terms in (24) can now be factorized, and, introducing the notations

$$\begin{aligned} Q_{\mu_1' \mu_2' \cdots \mu_k'}^A &= \sum_{r_1 r_2 \cdots r_k}^A \frac{\begin{vmatrix} a_{\mu_1' r_1} & a_{\mu_1' r_2} \cdots & a_{\mu_1' r_k} \\ \dots & \dots & \dots \\ a_{\mu_k' r_1} & a_{\mu_k' r_2} \cdots & a_{\mu_k' r_k} \end{vmatrix} \begin{vmatrix} a_{r_1 \mu_1} \dagger & a_{r_1 \mu_2} \dagger \cdots & a_{r_1 \mu_k} \dagger \\ \dots & \dots & \dots \\ a_{r_k \mu_1} \dagger & a_{r_k \mu_2} \dagger \cdots & a_{r_k \mu_k} \dagger \end{vmatrix}}{(E - H_{r_1 r_1})(E - H_{r_2 r_2}) \cdots (E - H_{r_k r_k})}, \\ Q_{\nu_1' \nu_2' \cdots \nu_k'}^B &= \sum_{s_1 s_2 \cdots s_k}^B \frac{\begin{vmatrix} a_{\nu_1 s_1} & a_{\nu_1 s_2} \cdots & a_{\nu_1 s_k} \\ \dots & \dots & \dots \\ a_{\nu_k s_1} & a_{\nu_k s_2} \cdots & a_{\nu_k s_k} \end{vmatrix} \begin{vmatrix} a_{s_1 \nu_1} \dagger & a_{s_1 \nu_2} \dagger \cdots & a_{s_1 \nu_k} \dagger \\ \dots & \dots & \dots \\ a_{s_k \nu_1} \dagger & a_{s_k \nu_2} \dagger \cdots & a_{s_k \nu_k} \dagger \end{vmatrix}}{(E - H_{s_1 s_1})(E - H_{s_2 s_2}) \cdots (E - H_{s_k s_k})}, \end{aligned} \quad (30)$$

we can write the determinant D in the left-hand side of (24) in the form

[†] We note that the MO in the total system ($A+B$) must be chosen in such a way that they are linearly independent.

$$\begin{aligned}
 D = \prod_i^{A+B} (H_{ii} - E) \cdot \left\{ 1 - \sum_{\mu}^{L\mathfrak{A}} \sum_{\mu'}^{L\mathfrak{B}} Q_{\mu}^A \mathfrak{S}_{\mu\nu} Q_{\nu'}^B \mathfrak{S}_{\nu'\mu'} \right. \\
 + \sum_{\mu_1\mu_2}^{L\mathfrak{A}} \sum_{\nu_1\nu_2}^{L\mathfrak{B}} Q_{\mu_1\mu_2}^A \begin{vmatrix} \mathfrak{S}_{\mu_1\nu_1} & \mathfrak{S}_{\mu_1\nu_2} \\ \mathfrak{S}_{\mu_2\nu_1} & \mathfrak{S}_{\mu_2\nu_2} \end{vmatrix} Q_{\nu_1\nu_2}^B \begin{vmatrix} \mathfrak{S}_{\nu_1'\mu_1'} & \mathfrak{S}_{\nu_1'\mu_2'} \\ \mathfrak{S}_{\nu_2'\mu_1'} & \mathfrak{S}_{\nu_2'\mu_2'} \end{vmatrix} - + \dots \\
 \left. + (-1)^p \sum_{\mu_1\mu_2 \dots \mu_p}^{L\mathfrak{A}} \sum_{\nu_1\nu_2 \dots \nu_p}^{L\mathfrak{B}} Q_{\mu_1\mu_2 \dots \mu_p}^A \begin{vmatrix} \mathfrak{S}_{\mu_1\nu_1} & \mathfrak{S}_{\mu_1\nu_2} \dots \mathfrak{S}_{\mu_1\nu_p} \\ \dots & \dots & \dots \\ \mathfrak{S}_{\mu_p\nu_1} & \mathfrak{S}_{\mu_p\nu_2} \dots \mathfrak{S}_{\mu_p\nu_p} \end{vmatrix} \dots \begin{vmatrix} \mathfrak{S}_{\nu_1'\mu_1'} & \mathfrak{S}_{\nu_1'\mu_2'} \dots \mathfrak{S}_{\nu_1'\mu_p'} \\ \dots & \dots & \dots \\ \mathfrak{S}_{\nu_p'\mu_1'} & \mathfrak{S}_{\nu_p'\mu_2'} \dots \mathfrak{S}_{\nu_p'\mu_p'} \end{vmatrix} \right\}. \quad (31)
 \end{aligned}$$

If the linkage between (A) and (B) is of a simple type, this expansion will reduce to a few terms. Formula (31) may be considered as a generalization of the formulas given by Dewar.¹⁵ We note that if the coefficients c_n for the class (A) have been determined, we get directly the coefficients for the class (B) according to (13) and (21):

$$c_m = \sum_n^A \frac{H_{mn}}{E - H_{mm}} c_n. \quad (32)$$

The example treated here is concerned with the one-electron wave functions, but we wish to emphasize that the general perturbation theory, contained in the formulas (10), (12), and (13), even can be applied to the molecular wave functions.

In conclusion, we wish to remark that, even if the methods described here were partly known previously in connection with special problems, for instance in the radiation theory given by Gora,⁵ a general treatment has not yet been published. We have given not only a simple derivation of the conventional perturbation theory, but also a new treatment of the problem of degeneracy and of the general problem of splitting the secular equation.

ACKNOWLEDGMENTS

The author should like to express his sincere gratitude to Professor Hertha Sponer, Department of Physics, Duke University, for many valuable discussions and for the great hospitality he has enjoyed during his stay in Durham, North Carolina.

APPENDIX. SYMBOLIC DERIVATION OF THE BASIC FORMULAS

The right-hand member of (9) is simply a geometrical series in the matrix h' belonging to the class (B), and it is therefore easy

to give a sufficient condition for its convergency.¹⁸ The form of the series also indicates that there might exist another simple derivation, and here we will therefore try to give a more direct derivation of (9) by using operator calculus and symbolic expansions.¹⁹

In order to separate the secular equation $Hc = Ec$ into two parts, we write the quadratic matrix H and the column matrix c in the form

$$H = \begin{bmatrix} A & \beta \\ \beta^* & B \end{bmatrix}, \quad c = \begin{bmatrix} a \\ b \end{bmatrix}, \quad (33)$$

and then we obtain

$$\begin{cases} Aa + \beta b = Ea, \\ \beta^* a + Bb = Eb. \end{cases} \quad (34)$$

Solving b from the latter equation, we get

$$b = \frac{1}{E - B} \beta^* a, \quad (35)$$

and

$$\left(A + \beta \frac{1}{E - B} \beta^* \right) a = Ea. \quad (36)$$

If we confine the indices of U^A to the class (A), we have therefore

$$U^A a = Ea, \quad (37)$$

$$U^A = A + \beta \frac{1}{E - B} \beta^*. \quad (38)$$

It is now immediately seen how the geometrical series in (9) arises. Dividing B in its diagonal and nondiagonal parts, B_d and B' , and expanding $(E - B_d - B')^{-1}$ in a power series in B' , we obtain

$$U^A = A + \beta \frac{1}{E - B_d} \beta^* + \beta \frac{1}{E - B_d} B' \frac{1}{E - B_d} \beta^* + \dots, \quad (39)$$

which is nothing but (9). Equation (37) gives then (12), and Eq. (35) gives (13). In this way all our basic formulas are derived.

¹⁸ See, for instance, Courant-Hilbert, *Methoden der Mathematischen Physik*, I (Verlag. Julius Springer, Berlin, 1931), p. 16, footnote 1.

¹⁹ Compare Gora, reference 5. For the symbolic treatment given here, the author is indebted to a discussion with Dr. G. Goertzel, Columbia University.