Generalized Perturbational Molecular Orbital (PMO) Theory*

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ABSTRACT: The useful perturbation expressions for wave functions and energies that are needed in perturbational molecular orbital (PMO) theory are rederived and generalized in two aspects: First, degenerate systems now can be treated in a systematic manner, as in the case of nondegenerate systems. Second, the new expressions can cope with complex wave functions. Two examples of applications to degenerate systems are given to show the qualitative and quantitative utility of the new expressions.   © 2000 John Wiley & Sons, Inc. Int J Quant Chem 77: 408–420, 2000

Introduction

The most successful theoretical approach to the electronic structure of molecules has been through the molecular orbital (MO) approximation and its implementation in computational programs at many different levels of sophistication. Propelled by rapidly developing computer technology, MO calculations have become easier, and the systems dealt with accurately have increased in their size.

Qualitative MO theory also has played an essential role in the field [1–3]. Mere agreement between numerical calculations and experimental results often does not satisfy chemists, unless an apprehendable rationalization—an explanation couched in words and accessing trends—is given. Qualitative MO theory often shows why the numerical results turn out as they do. It also provides a means for guided speculation about molecular properties that could lead to new experiments and to further detailed quantum mechanical calculations.

Over the years, the perturbational molecular orbital (PMO) method has been an important part of the apparatus of qualitative MO theory [2]. To understand the electronic structure of a complicated molecule, it is fruitful to relate it to a simpler one. A difference (between the electronic structure of the complex molecule and its simpler model) may then be thought of as a consequence of a certain perturbation, a distinction in their geometries or constituents. Three different types of perturbation are commonly encountered in electronic structure problems—intermolecular, geometry, and electronegativity perturbations [2]. Combined

with a fragment orbital formalism, the PMO method has been very useful in analyzing these problems systematically.

In ordinary perturbation theory, a perturbation is expressed mathematically by a perturbed Hamiltonian in the Schrödinger equation describing the whole system [4,5]. With atomic orbitals as a basis set, these perturbations manifest themselves as changes in Hamiltonian and overlap matrix elements. Therefore, it is natural to employ those matrix elements in deriving the expressions of energies and wave functions of the perturbed system. Such expressions were derived in the work of Imamura [6], Libit and Hoffmann [7], and Whangbo et al. [8].

Imamura first developed a general PMO method that is particularly useful within the extended Hückel method, a simple approximate MO procedure. Here, atomic orbital coefficients were used to express all the perturbation terms for both nondegenerate and degenerate systems. Imamura's formulas for nondegenerate systems were reformulated by Libit and Hoffmann within a fragment orbital formalism. Whangbo showed that the PMO method can be useful even within the Hartree–Fock approximation. The fragment orbital formalism was employed to derive the energies and orbital coefficients for both nondegenerate and degenerate systems. It was shown how the coefficient expressions in terms of fragment and atomic orbitals can be directly related. Whangbo et al.'s work does not contain the expressions for the higher-order perturbation terms of energies and orbital coefficients for the degenerate systems. These are sometimes useful and will be provided here. We also found a few misprints in the published expressions for the nondegenerate systems.

A second contribution of this article is that we generalize the PMO method for complex wave functions, something that has not been done generally earlier. This derivation is vital for the perturbational crystal orbital (PCO) method recently developed in our group [9]. This PCO method allows one to treat and analyze electronic-band structures of extended systems by using crystal orbitals.

Notation and Definitions

In this section, we describe the notation that we are going to use throughout the article. The notation is built upon earlier work of Imamura [6], Libit and Hoffmann [7], and Whangbo et al. [8]. At the end of this section, we set up the master equations for various orders of the perturbation theory, which we use later for the derivation of corresponding perturbative expressions for nondegenerate and degenerate cases.

In quantum chemistry, one is concerned with finding the solution for the time-independent Schrödinger equation for a given molecule or a solid:

$$\hat{H}|\Psi^0\rangle = e^0|\Psi^0\rangle. \tag{1}$$

The PMO theory that we deal with in this article is based on a one-electron approximation to the Schrödinger equation. In this model, the exact Hamiltonian $\hat{H}$ is replaced by $\hat{H}^{eff}$, where an electron interacts only with the average field created by other electrons and nuclei. Consequently, the exact Schrödinger equation (which includes all electrons interacting with each other) is replaced by a series of one-electron equations for electrons $i = 1, \ldots, N$:

$$\hat{H}^{eff}|\Psi_i^0\rangle = e_i^0|\Psi_i^0\rangle. \tag{2}$$

The perturbation theory that we develop is independent of the particular form of the effective one-electron Hamiltonian [Eq. (2)]. On the other hand, one has to choose a certain one-electron formalism when the perturbation theory results are applied to a specific molecule or a solid. When illustrating applications of the molecular perturbation theory, we use the extended Hückel [10–12] approximation for the effective Hamiltonian. For the sake of notational simplicity, we substitute $\hat{H}^{eff}$ by $\hat{H}$ throughout the remainder of the article.

MOs are usually built up as linear combinations of atomic orbitals (LCAO). The MO $|\Psi_i^0\rangle$ can be expended linearly in the atomic orbital basis as

$$|\Psi_i^0\rangle = \sum_\nu c_{\nu i}^0 |\chi_\nu\rangle, \tag{3}$$

where $|\chi_\nu\rangle$ is atomic orbital ν, weighted in sum 3 by the atomic orbital coefficient $c_{\nu i}^0$. We now substitute $|\Psi_i^0\rangle$ in Eq. (2) by its expansion from Eq. (3) and premultiply that new equation [Eq. (4)] by $\langle \chi_\mu |$:

$$\hat{H}\left(\sum_\nu c_{\nu i}^0 |\chi_\nu\rangle \right) = e_i^0 \left(\sum_\nu c_{\nu i}^0 |\chi_\nu\rangle \right), \tag{4}$$

$$\sum_\nu \langle \chi_\mu|\hat{H}|\chi_\nu\rangle c_{\nu i}^0 = e_i^0 \left(\sum_\nu c_{\nu i}^0 \langle \chi_\mu|\chi_\nu\rangle \right), \tag{5}$$

$$\sum_\nu \left(H_{\mu\nu}^0 - e_i^0 S_{\mu\nu}^0 \right) c_{\nu i}^0 = 0, \tag{6}$$

where $H_{\mu\nu}^0 = \langle \chi_\mu | \hat{H}^0 | \chi_\nu \rangle$ and $S_{\mu\nu}^0 = \langle \chi_\mu | \chi_\nu \rangle$. Secular Eq. (6) permits one to calculate energies e_i^0 and atomic orbital coefficients $c_{\nu i}^0$, if the effective Hamiltonian matrix elements $H_{\mu\nu}^0$ and the atomic orbital overlap matrix elements $S_{\mu\nu}^0$ are known.

In perturbation theory, one assumes that the solution for the original Eq. (6) is explicitly known. Next, Hamiltonian and overlap matrix elements are altered in some well-defined way, which specifies the perturbation. Typical examples include (1) an interaction of two previously noninteracting molecular fragments (an intermolecular perturbation), (2) a geometry change within a molecule (a geometry perturbation), and (3) a substitution of one atom by another (which may be viewed as an electronegativity perturbation). A new secular equation has to be written with altered matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$:

$$\sum_\nu (H_{\mu\nu} - e_i S_{\mu\nu}) c_{\nu i} = 0. \quad (7)$$

Note that we have dropped the superscript 0 from all terms in Eq. (7).

Now, we make a connection between the new and old Hamiltonian and overlap matrix elements in the atomic basis. If those changes are relatively small, then

$$H_{\mu\nu} = H_{\mu\nu}^0 + \delta H_{\mu\nu}, \quad (8)$$

$$S_{\mu\nu} = S_{\mu\nu}^0 + \delta S_{\mu\nu}. \quad (9)$$

In any sort of quantitative description, one has to calculate, first, $\delta H_{\mu\nu}$ and $\delta S_{\mu\nu}$ in Eqs. (8) and (9). However, it is often more convenient to express these changes in the MO basis:

$$H_{ij} = H_{ij}^0 + \tilde{\Delta}_{ij}, \quad (10)$$

$$S_{ij} = \delta_{ij} + \tilde{S}_{ij}. \quad (11)$$

In the last equation, it is assumed that the MO basis set, unlike the atomic orbital basis set, is orthonormal, that is, $S_{ij}^0 = \delta_{ij}$. To evaluate Eqs. (10) and (11), an explicit relationship is needed between the matrix elements in the MO basis and those in the atomic orbital basis. This connection may be established in the following way:

$$e_i^0 \delta_{ij} = \langle \Psi_i^0 | H^0 | \Psi_j^0 \rangle$$
$$= \sum_{\mu,\nu} c_{\mu i}^0 \langle \chi_\mu | H^0 | \chi_\nu \rangle c_{\nu j}^0 = \sum_{\mu,\nu} c_{\mu i}^0 H_{\mu\nu}^0 c_{\nu j}^0, \quad (12)$$

$$\delta_{ij} = \langle \Psi_i^0 | \Psi_j^0 \rangle = \sum_{\mu,\nu} c_{\mu i}^0 \langle \chi_\mu | \chi_\nu \rangle c_{\nu j}^0 = \sum_{\mu,\nu} c_{\mu i}^0 S_{\mu\nu}^0 c_{\nu j}^0, \quad (13)$$

$$\tilde{\Delta}_{ij} = \langle \Psi_i^0 | \delta H | \Psi_j^0 \rangle$$
$$= \sum_{\mu,\nu} c_{\mu i}^0 \langle \chi_\mu | \delta H | \chi_\nu \rangle c_{\nu j}^0 = \sum_{\mu,\nu} c_{\mu i}^0 \, \delta H_{\mu\nu} \, c_{\nu j}^0, \quad (14)$$

$$\tilde{S}_{ij} = \langle \Psi_i^0 | \Psi_j^0 \rangle$$
$$= \sum_{\mu,\nu} c_{\mu i}^0 \langle \chi_\mu | \chi_\nu \rangle c_{\nu j}^0 = \sum_{\mu,\nu} c_{\mu i}^0 \, \delta S_{\mu\nu} \, c_{\nu j}^0. \quad (15)$$

In the following derivations, we use mostly the left-hand equalities in Eqs. (12)–(15), keeping in mind that the right-hand double summations are necessary for obtaining numerical answers in any real perturbational calculation (see the Applications section).

If the perturbations [Eqs. (10) and (11)] are relatively small, then new energies e_i and new wave functions may be expressed as a series expansion, where the superscript n is the order of the perturbation:

$$e_i = e_i^0 + e_i^1 + e_i^2 + \cdots, \quad (16)$$

$$|\Psi_i\rangle = |\Psi_i^0\rangle + |\Psi_i^1\rangle + |\Psi_i^2\rangle + \cdots, \quad (17)$$

$$|\Psi_i^n\rangle = \sum_j t_{ji}^n |\Psi_j^0\rangle, \quad (18)$$

$$|\Psi_i\rangle = \sum_j \left(t_{ji}^0 |\Psi_j^0\rangle + t_{ji}^1 |\Psi_j^0\rangle + t_{ji}^2 |\Psi_j^0\rangle + \cdots \right). \quad (19)$$

The n-th order corrections to the original wave function are obtained as a linear combination of the zeroth-order MOs with the expansion coefficients t^n [Eq. (18)]. If we are able to calculate the elements of the t matrix and the energy corrections to any order n, and given the convergence of series (16) and (17), then by carrying out the summation of these series we should be able to obtain the exact solution of Eq. (7). However, the first few terms in expansions (16) and (17) are often sufficient for the qualitative (and often quantitative) description of chemical interactions. In this article, we derive the perturbation expansion up to second order both in energies and wave functions.

By substituting the atomic orbital expansion for $|\Psi_i\rangle$ [Eq. (18)] into the left and right sides of Eq. (17), the relationship between the transformation matrix t's and atomic orbital coefficients c's can

be established as follows:

$$\sum_{\nu} c_{\nu i}^n |\chi_\nu\rangle = |\Psi_i^n\rangle = \sum_j t_{ji}^n |\Psi_j^0\rangle = \sum_{j,\nu} t_{ji}^n c_{\nu j}^0 |\chi_\nu\rangle,$$

$$(20)$$

$$c_{\nu i}^n = \sum_j c_{\nu j}^0 t_{ji}^n. \qquad (21)$$

We infer from Eq. (21) that the n-th order corrections to the atomic orbital coefficients c^n can be obtained by multiplying from the right the zeroth-order coefficient matrix c^0 by the n-th order transform matrix t^0. This equation enables us to move in perturbative expansions from atomic bases to the molecular bases and vice versa.

At this point, all the tools are at hand for the deducing a master equation which will serve as a starting point for the derivations of both nondegenerate and degenerate corrections to the energies and wave functions. This master equation may be obtained in the following way: First, Eq. (22) for the new (perturbed) system is premultiplied by old wave function $\langle \Psi_j^0 |$, which leads to Eq. (23). This equation can be rewritten in the atomic basis by the substitution of molecular wave functions by their corresponding atomic expansion Eq. (3) [Eq. (24)]. The new atomic orbital expansion coefficients $c_{\nu i}$ may be replaced by the perturbative expansion Eq. (17) and Eq. (21):

$$\hat{H}|\Psi_i\rangle = e_i|\Psi_i\rangle, \qquad (22)$$

$$\langle \Psi_j^0|\hat{H}|\Psi_i\rangle = c_i\langle \Psi_j^0|\Psi_i\rangle, \qquad (23)$$

$$\sum_{\mu,\nu} c_{\mu j}^0 H_{\mu\nu} c_{\nu i} = e_i \sum_{\mu,\nu} c_{\mu j}^0 S_{\mu\nu} c_{\nu i}, \qquad (24)$$

$$\sum_k \sum_{\mu,\nu} \left[\left(c_{\mu j}^0 H_{\mu\nu} c_{\nu k}^0\right) t_{ki} - e_i \left(c_{\mu j}^0 S_{\mu\nu} c_{\nu k}^0\right) t_{ki} \right] = 0.$$

$$(25)$$

Equation (25) contains new Hamiltonian and overlap matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ which may be evaluated with the help of Eqs. (8) and (9). Then, the summations over μ and ν can be carried out explicitly, with the help of Eqs. (12)–(14):

$$\sum_{\mu,\nu} \left(c_{\mu j}^0 H_{\mu\nu} c_{\nu k}^0\right) = \sum_{\mu,\nu} c_{\mu j}^0 \left(H_{\mu\nu}^0 + \delta H_{\mu\nu}\right) c_{\nu k}^0$$

$$= e_j^0 \delta_{jk} + \tilde{\Delta}_{jk}, \qquad (26)$$

$$\sum_{\mu,\nu} \left(c_{\mu j}^0 S_{\mu\nu} c_{\nu k}^0\right) = \sum_{\mu,\nu} c_{\mu j}^0 \left(S_{\mu\nu}^0 + \delta S_{\mu\nu}\right) c_{\nu k}^0$$

$$= \delta_{jk} + \tilde{S}_{jk}. \qquad (27)$$

Equation (25) now may be rewritten with only one summation over index k:

$$\sum_k \left[e_j^0 \delta_{jk} + \tilde{\Delta}_{jk} - e_i \tilde{S}_{jk} - e_i \delta_{jk} \right] t_{ki} = 0. \quad (28)$$

Only energies e_i and wave-function mixing coefficients t_{ki} remain unknown in the last equation. By explicitly performing double summations in the atomic basis [Eqs. (26) and (27)], we have set up the perturbational problem in the MO basis. By expressing energies e_i and wave-function mixing coefficients t_{ki} through corresponding perturbative expressions Eqs. (16) and (17), the desired master equation of PMO theory is found:

$$\sum_k \left[\left(e_j^0 - e_i^0\right)\delta_{jk} + \left(\tilde{\Delta}_{jk} - e_i^0 \tilde{S}_{jk} - e_i^1 \delta_{jk}\right) \right.$$

$$\left. + \left(-e_i^2 \delta_{jk} - e_i^1 \tilde{S}_{jk}\right) + \cdots \right](t_{ki}^0 + t_{ki}^1 + t_{ki}^2 + \cdots)$$

$$= 0. \qquad (29)$$

Here, we assume that H^0 and S^0 in Eqs. (8) and (9) are zeroth-order quantities and, correspondingly, δH and δS are first-order quantities. Then, various terms on the left-hand side of Eq. (29) may be regrouped according to their orders of magnitude. Each of these terms is, in turn, set to zero, which ensures that Eq. (29) is always satisfied:

$$\sum_k \left[\left(e_j^0 - e_i^0\right)\delta_{jk} t_{ki}^0 \right] = 0, \qquad (30)$$

$$\sum_k \left[\left(e_j^0 - e_i^0\right)\delta_{jk} t_{ki}^1 + \left(\tilde{\Delta}_{jk} - e_i^0 \tilde{S}_{jk} - e_i^1 \delta_{jk}\right) t_{ki}^0 \right] = 0,$$

$$(31)$$

$$\sum_k \left[\left(e_j^0 - e_i^0\right)\delta_{jk} t_{ki}^2 + \left(\tilde{\Delta}_{jk} - e_i^0 \tilde{S}_{jk} - e_i^1 \delta_{jk}\right) t_{ki}^1 \right.$$

$$\left. - \left(-e_i^2 \delta_{jk} - e_i^1 \tilde{S}_{jk}\right) t_{ki}^0 \right] = 0. \quad (32)$$

The MOs which are obtained from Eqs. (30)–(32) are not properly normalized. Normalization conditions have to be applied directly in each order in the perturbation series, which, in turn, determines the diagonal corrections to the wave functions (t_{ii}^n):

$$\langle \Psi_i|\Psi_i\rangle = 1, \qquad (33)$$

$$\sum_k t_{ki}^{0*} t_{ki}^0 = 1, \qquad (34)$$

$$t_{ii}^{1*} + t_{ii}^1 + \tilde{S}_{ii} = 0, \qquad (35)$$

$$t_{ii}^{2*} + t_{ii}^2 + \sum_k \left(t_{ki}^{1*} t_{ki}^1 + t_{ki}^{1*} \tilde{S}_{ki} + t_{ki}^1 \tilde{S}_{ik} \right) = 0. \quad (36)$$

The wave function Ψ_i expressed in the way above can have an arbitrary phase. A convenient way to fix its phase is just to make t_{ii} real. It follows that t_{ii}^n for any n is a real number as well. As we will see later, when working with complex wave functions, the phases of all other t_{ji}^n's are uniquely determined by these conditions.

For the nondegenerate perturbation theory, Eq. (30) is satisfied with a t^0 which is a unit matrix, that is, the initial wave functions do not have to be mixed in the zeroth-order. The first-order energy corrections are found from Eq. (31), followed by the first-order corrections to wave functions. This procedure is iteratively applied to higher-order terms. In the next section, we derive energy and wave-function correction for a perturbation in a nondegenerate system.

For two degenerate MOs i and j ($e_i = e_j$), the zeroth-order Eq. (30) does not determine the zeroth-order mixing coefficients for the wave functions. It turns out that, unlike the nondegenerate case, the initial wave functions must be properly mixed in zeroth-order (''prepared for the perturbation'') before proceeding to higher-order corrections. The following derivation of higher-order corrections is also conceptually different from the corresponding nondegenerate derivations. Following the treatment of the nondegenerate case, we give the corrections to the energies and wave functions up to second-order for a perturbation in a degenerate system.

Nondegenerate Case

When all unperturbed wave functions, Ψ_i^0's, have different energies (i.e., $e_i^0 \neq e_j^0$, if $i \neq j$), Eq. (30) gives $t_{ji}^0 = 0$ whenever $i \neq j$. To satisfy Eq. (34), therefore, t_{ii}^0 should be 1, because this value should be a real number as defined in the previous section. To summarize,

$$t_{ji}^0 = \delta_{ji}. \tag{37}$$

Upon using Eq. (37), Eq. (31) may be simplified to

$$\left(e_j^0 - e_i^0\right)t_{ji}^1 + \left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji} - e_i^1\delta_{ji}\right) = 0. \tag{38}$$

When $i = j$, the first term in Eq. (38) disappears and, hence, gives rise to the expression for e_i^1:

$$e_i^1 = \tilde{\Delta}_{ii} - e_i^0\tilde{S}_{ii}. \tag{39}$$

When $i \neq j$, Eq. (38) may be rewritten to obtain t_{ji}^1:

$$t_{ji}^1 = \frac{\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}}{e_i^0 - e_j^0}. \tag{40}$$

Note that in Eq. (40) t_{ji}^1 has a fixed phase. This follows from using t_{ji}^0 expressed in Eq. (37), previously defined as a real number.

To obtain t_{ii}^1, we have to go back to one of the normalization condition formulas, which is, in this case, the expression of first order, Eq. (35). Since t_{ii}^1 is a real number, Eq. (35) leads to

$$t_{ii}^1 = -\frac{1}{2}\tilde{S}_{ii}. \tag{41}$$

Proceeding in a similar manner, we obtain the second-order solutions summarized below:

$$e_i^2 = -e_i^1\tilde{S}_{ii} + \sum_{k \neq i}\left(\tilde{\Delta}_{ik} - e_i^0\tilde{S}_{ik}\right)t_{ki}^1 \tag{42}$$

$$t_{ji}^2 = -\frac{1}{2}\tilde{S}_{ii}t_{ji}^1 - e_i^1\frac{\tilde{S}_{ji} + t_{ji}^1}{e_i^0 - e_j^0} + \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{jk} - e_i^0\tilde{S}_{jk}\right)t_{ki}^1}{e_i^0 - e_j^0} \tag{43}$$

$$t_{ii}^2 = -\frac{1}{2}\sum_k\left(t_{ki}^{1*}\tilde{S}_{ki} + t_{ki}^1\tilde{S}_{ik} + t_{ki}^{1*}t_{ki}^1\right). \tag{44}$$

Once again, the t_{ji}^2 values have unique phases. In Eq. (44), t_{ii}^2 has to be real, since the overlap matrix is Hermitian (i.e., $\tilde{S}_{ki} = \tilde{S}_{ik}^*$). In other words, Eq. (44) can be reformulated as

$$t_{ii}^2 = -\frac{1}{2}\sum_k\left(t_{ki}^{1*}\tilde{S}_{ik}^* + t_{ki}^1\tilde{S}_{ik} + t_{ki}^{1*}t_{ki}^1\right)$$
$$= -\frac{1}{2}\sum_k\left(2\,Re\left(t_{ki}^1\tilde{S}_{ik}\right) + t_{ki}^{1*}t_{ki}^1\right). \tag{45}$$

By substituting t_{ki} using 40, Eqs. (42) and (43) can be rewritten

$$e_i^2 = -e_i^1\tilde{S}_{ii} + \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{ik} - e_i^0\tilde{S}_{ik}\right)\left(\tilde{\Delta}_{ki} - e_i^0\tilde{S}_{ki}\right)}{\left(e_i^0 - e_k^0\right)} \tag{46}$$

$$t_{ji}^2 = -\frac{\tilde{S}_{ii}\left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}\right) + 2e_i^1\tilde{S}_{ji}}{2\left(e_i^0 - e_j^0\right)} - e_i^1\frac{\left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}\right)}{\left(e_i^0 - e_j^0\right)^2}$$
$$+ \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{jk} - e_i^0\tilde{S}_{jk}\right)\left(\tilde{\Delta}_{ki} - e_i^0\tilde{S}_{ki}\right)}{\left(e_i^0 - e_j^0\right)\left(e_i^0 - e_k^0\right)}. \tag{47}$$

These expressions have not been given before in their full and correct form.

Degenerate Case

The development of the degenerate perturbation theory is significantly different from the nondegenerate case. It is clear that expressions of the form of Eq. (40) and thereafter have to be somehow modified for degenerate orbitals; otherwise, the denominator would become zero for many terms in the perturbative series. To the best of our knowledge, only expressions for calculating zeroth-order wave functions and first-order corrections to energies for a perturbation in a system with degenerate MOs have been published. We present in this section a consistent and unambiguous procedure for developing degenerate perturbation theory to any perturbative order.

First, a little notational development is in order: We divide the set of original MOs orbitals into two subsets, of degenerate (D) and nondegenerate (N) molecular MOs. We assume for the sake of simplicity that there is only one set of degenerate orbitals, although the extension to multiple sets is straightforward. We denote the subscripts for degenerate MOs by adding a letter D to that subscript and, similarly, for nondegenerate MOs by augmenting the index with N.

ZEROTH-ORDER CORRECTIONS TO WAVE FUNCTIONS AND FIRST-ORDER CORRECTIONS TO ENERGIES

To calculate the zeroth-order correction to wave functions, we start from Eq. (30). If one of the MOs i or j belongs to the nondegenerate set, then $e_j^0 - e_i^0 \neq 0$; therefore, $t_{ji}^0 = 0$. On the other hand, if both MOs belong to the degenerate set, then $t_{j_D i_D}^0$ remains undefined by this procedure. To calculate zeroth-order correction to degenerate wave functions, we have to use first-order Eq. (31). In this case, since $e_{j_D}^0 - e_{i_D}^0 = 0$, the following secular equation is set up for the zeroth-order corrections to degenerate wave functions:

$$\sum_k \left(\tilde{\Delta}_{j_D k_D} - e_{i_D}^0 \tilde{S}_{j_D k_D} - e_{i_D}^1 \delta_{j_D k_D} \right) t_{k_D i_D}^0 = 0, \quad (48)$$

$$\begin{vmatrix} \left(\tilde{\Delta}_{11} - e_i^0 \tilde{S}_{11} \right) - e_{i_D}^1 & \left(\tilde{\Delta}_{i2} - e_i^0 \tilde{S}_{12} \right) & \cdots \\ \left(\tilde{\Delta}_{21} - e_i^0 \tilde{S}_{21} \right) & \left(\tilde{\Delta}_{22} - e_i^0 \tilde{S}_{22} \right) - e_{i_D}^1 & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}$$
$$= 0. \quad (49)$$

First, solution of secular Eq. (49) leads to the first-order energy corrections for the degenerate orbitals. We are making an assumption here that all eigenvalues of secular Eq. (49) are nondegenerate. In this case, a zeroth-order mixing of degenerate MO k_D into MO i_D, $t_{k_D i_D}^0$, can be calculated from Eqs. (48) and (49):

$$|\Psi_{i_D'}^0\rangle = \sum_k t_{k_D i_D}^0 |\Psi_{k_D}^0\rangle. \quad (50)$$

Instead of the old zeroth-order MOs i_D, we have obtained an equivalent set of new zeroth-order primed MOs i_D'. From the point of view of the original unperturbed problem, the old and new sets of degenerate MOs are completely equivalent. The difference between them arises when a perturbation is introduced—the new zeroth-order wave functions diagonalize not only the original Hamiltonian matrix, but also the first-order perturbation matrix $(\tilde{\Delta}_{j_D k_D} - e_{i_D}^1 \delta_{j_D k_D})$. Consequently, possible infinities disappear from Eq. (40).

Here, a notational change has to be introduced for simplifying further analysis. As the new degenerate wave functions $|\Psi_{i_D'}^0\rangle$ are calculated, we drop the prime from their subscripts and use them as if they were the original set of zeroth-order degenerate wave functions. In this new basis set, $t_{k_D i_D}^0$ becomes a unit matrix $\delta_{k_D i_D}^0$, and, therefore, from Eq. (48) it follows that

$$e_{i_D}^1 = \tilde{\Delta}_{i_D i_D} - e_{i_D}^0 \tilde{S}_{i_D i_D}. \quad (51)$$

Notice that Eq. (51) looks similar to the analogous Eq. (39) for the nondegenerate perturbation theory. An equivalent expression is found for the first-order corrections to the energy of orbitals belonging to the nondegenerate set in a composite degenerate–nondegenerate system.

FIRST-ORDER CORRECTIONS TO WAVE FUNCTIONS

At this point, we have the correct zeroth-order wave functions and first-order corrections to energies of MOs. Next, the first-order corrections to wave functions have to be computed. If the MO for which this correction is sought belongs to the nondegenerate set of the composite system, then the expression for $t_{ji_N}^1$ is similar to the one from

Eq. (40):

$$t^1_{ji_N} = \frac{\tilde{\Delta}_{ji_N} - e^0_{i_N} \tilde{S}_{ji_N}}{e^0_{i_N} - e^0_j}, \qquad (52)$$

where subscript j indicates both nondegenerate and degenerate MOs.

If MO i belongs to the degenerate set, then the procedure for finding $t^1_{ji_D}$ has to be modified. If j is a nondegenerate MO, then an expression for $t^1_{j_N i_D}$ is found, which is completely equivalent to Eqs. (10) and (52). The derivation is analogous to one for the nondegenerate case (see the previous section) and is omitted here. If j is also a degenerate MO, then the above-mentioned derivation does not work, because $e^0_{j_D} - e^0_{i_D} = 0$ in Eq. (38). The second-order Eq. (32) has to be used in order to find the first-order corrections to degenerate MOs $t^1_{j_D i_D}$:

$$\sum_k \left[\left(e^0_{j_D} - e^0_{i_D} \right) \delta_{j_D k} t^2_{ki_D} \right.$$

$$+ \left(\tilde{\Delta}_{j_D k} - e^0_{i_D} \tilde{S}_{j_D k} - e^1_{i_D} \delta_{j_D k} \right) t^1_{ki_D}$$

$$\left. + \left(-e^2_{i_D} \delta_{j_D k} - e^1_i \tilde{S}_{j_D k} \right) t^0_{ki_D} \right] = 0. \qquad (53)$$

The first term in Eq. (53) is identically zero. The second term can be manipulated in the following way:

$$\sum_k \left(\tilde{\Delta}_{j_D k} - e^0_{i_D} \tilde{S}_{j_D k} - e^1_{i_D} \delta_{j_D k} \right) t^1_{ki_D}$$

$$= \sum_{k \in D} \left(\tilde{\Delta}_{j_D k_D} - e^0_{i_D} \tilde{S}_{j_D k_D} - e^1_{i_D} \delta_{j_D k_D} \right) t^1_{k_D i_D}$$

$$+ \sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - ^0_{i_D} \tilde{S}_{j_D k_N} - e^1_{i_D} \delta_{j_D k_N} \right) t^1_{k_N i_D}$$

$$= \sum_{k \in D} \left(e^1_{j_D} \delta_{j_D k_D} - e^1_{i_D} \delta_{j_D k_D} \right) t^1_{k_D i_D}$$

$$+ \sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^1_{k_N i_D}$$

$$= \left(e^1_{j_D} - e^1_{i_D} \right) t^1_{j_D i_D}$$

$$+ \sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^1_{k_N i_D}. \qquad (54)$$

When deriving line 3 from line 2 in Eq. (54), we have made use of the fact the the new zeroth-order degenerate wave functions diagonalize the perturbation matrix $\left(\tilde{\Delta}_{j_D k_D} - e^1_{i_D} \delta_{j_D k_D} \right)$.

Finally, we have to calculate the third term in Eq. (53):

$$\sum_k \left(-e^2_{i_D} \delta_{j_D k} - e^1_{i_D} \tilde{S}_{j_D k} \right) t^0_{ki_D}$$

$$= \sum_k \left(-e^2_{i_D} \delta_{j_D k} - e^1_{i_D} \tilde{S}_{j_D k} \right) \delta^0_{ki_D}$$

$$= -e^2_{i_D} \delta_{j_D i_D} - e^1_{i_D} \tilde{S}_{j_D i_D} = -e^1_{i_D} \tilde{S}_{j_D i_D}. \qquad (55)$$

Now, we combine together the three terms in Eq. (53) into a single equation:

$$\left(e^1_{j_D} - e^1_{i_D} \right) t^1_{j_D i_D} + \sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^1_{k_N i_D}$$

$$- e^1_{i_D} \tilde{S}_{j_D i_D} = 0. \qquad (56)$$

The only unknown remaining in Eq. (56) is $t^1_{j_D i_D}$; therefore, it may be expressed in terms of other known quantities as

$$t^1_{j_D i_D} = \frac{1}{\left(e^1_{i_D} - e^1_{j_D} \right)}$$

$$\times \left[\sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^1_{k_N i_D} - e^1_{i_D} \tilde{S}_{j_D i_D} \right]. \qquad (57)$$

Equation (57) can be cast into more explicit form by substituting $t^1_{k_N i_D}$ by its value from Eq. (52):

$$t^1_{j_D i_D} = \frac{1}{\left(e^1_{i_D} - e^1_{j_D} \right)}$$

$$\times \left[\sum_{k \in N} \frac{\left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) \left(\tilde{\Delta}_{k_N i_D} - e^0_{i_D} \tilde{S}_{k_N i_D} \right)}{e^0_{i_D} - e^0_{k_N}} \right.$$

$$\left. - e^1_{i_D} \tilde{S}_{j_D i_D} \right]. \qquad (58)$$

As seen from Eq. (58), degenerate wave function j_D mixes into another degenerate wave function i_D through two mechanisms: First, it mixes via interaction with a nondegenerate wave function k_N and the subsequent interaction of the latter with i_D. This kind of mixing is reminiscent of the second-order mixing mechanism in the nondegenerate perturbation theory [see Eq. (43)], although here it is a formally first-order process. The small denominator $1/(e^1_{j_D} - e^1_{i_D})$ in Eq. (58) makes the expression for $t^1_{j_D i_D}$ first order in magnitude.

Two degenerate wave functions can also mix into each other through the second term in Eq. (58), if there exists a nonzero perturbation ($\tilde{S}_{j_D i_D}$) to the overlap matrix element between those MOs. The renormalization for the degenerate orbitals is done in the same way as for the nondegenerate one. The value of the first-order self-correction to degenerate MO i_D, $t^1_{i_D i_D}$, is calculated according to Eq. (41). In summary, degenerate MOs interact with each other in first order in a way similar to the second-order interactions between nondegenerate MOs.

SECOND-ORDER CORRECTIONS TO WAVE FUNCTIONS AND ENERGIES

Second-order corrections to energies of nondegenerate wave functions of the composite system are computed as prescribed by Eq. (43). To calculate the second-order corrections to energies of degenerate wave functions, we start from Eq. (32), where we set j to i. The first term disappears in Eq. (32) and we are left with the following equation:

$$\sum_k \left[\left(\tilde{\Delta}_{i_D k} - e^0_{i_D} \tilde{S}_{i_D k} - e^1_{i_D} \delta_{i_D k} \right) t^1_{k i_D} \right.$$
$$\left. + \left(-e^2_{i_D} \delta_{i_D k} - e^1_{i_D} \tilde{S}_{i_D k} \right) t^0_{k i_D} \right] = 0. \quad (59)$$

The first and second terms in term in Eq. (59) can be considerably simplified in the same manner as Eqs. (54) and (55):

$$\sum_k \left(\tilde{\Delta}_{i_D k} - e^0_{i_D} \tilde{S}_{i_D k} - e^1_{i_D} \delta_{i_D k} \right) t^1_{k i_D}$$
$$= \sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^1_{k_N i_D}, \quad (60)$$

$$\sum_k \left(-e^2_{i_D} \delta_{i_D k} - e^1_{i_D} \tilde{S}_{i_D k} \right) t^0_{k i_D} = -e^2_{i_D} - e^1_{i_D} \tilde{S}_{i_D i_D}. \quad (61)$$

The second-order correction to energies of degenerate wave functions is calculated by substituting Eqs. (60) and (61) into Eq. (59):

$$e^2_{i_D} = \sum_{k \in N} \left(\tilde{\Delta}_{i_D k_N} - e^0_{i_D} \tilde{S}_{i_D k_N} \right) t^1_{k_N i_D} - e^1_{i_D} \tilde{S}_{i_D i_D}. \quad (62)$$

Notice that Eq. (62) is similar to Eq. (42) for the nondegenerate case, except in the former case the summation over k is not carried out for the set of degenerate orbitals. Equation (62) may be rewrit-

ten in more detail by expanding the $t^1_{k_N i_D}$ term:

$$e^2_{i_D} = \sum_{k \in N} \frac{\left(\tilde{\Delta}_{i_D k_N} - e^0_{i_D} \tilde{S}_{i_D k_N} \right) \left(\tilde{\Delta}_{k_N i_D} - e^0_{i_D} \tilde{S}_{k_N i_D} \right)}{e^0_{i_D} - e^0_{k_N}}$$
$$- e^1_{i_D} \tilde{S}_{i_D i_D}. \quad (63)$$

The second-order correction to *nondegenerate* MOs in a composite system have the same form as that of Eq. (43). If one wants to derive second-order corrections to *degenerate* MOs, then a modified procedure has to be used, similar to one applied in the previous subsection. A third-order analog of Eqs. (30)–(32) becomes a starting point for subsequent computation. Without going into further detail, we provide here only the final expression for calculating the second-order mixing coefficients of nondegenerate MO j_N into degenerate MO i_D and of degenerate MO j_D into degenerate MO i_D. To use these expressions in practical calculations, the previously calculated zeroth-, first-, and second-order corrections to energies and wave functions have to be substituted into Eqs. (64) and (65):

$$t^2_{j_N i_D} = \frac{1}{\left(e^0_{i_D} - e^0_{j_N} \right)} \sum_{k \in N, D} \left(\tilde{\Delta}_{j_N k} - e^0_{i_D} \tilde{S}_{j_N k} \right) t^1_{k i_D}$$
$$- e^1_{i_D} t^1_{j_N i_D} - e^1_{i_D} \tilde{S}_{j_N i_D}, \quad (64)$$

$$t^2_{j_D i_D} = \frac{1}{\left(e^1_{i_D} - e^1_{j_D} \right)} \left[\sum_{k \in N} \left(\tilde{\Delta}_{j_D k_N} - e^0_{i_D} \tilde{S}_{j_D k_N} \right) t^2_{k_N i_D} \right.$$
$$\left. - e^1_{i_D} \sum_{k \in N, D} \tilde{S}_{j_D k} t^1_{k i_D} - e^2_{i_D} t^1_{j_D i_D} - e^2_{i_D} \tilde{S}_{j_D i_D} \right]. \quad (65)$$

Up to second-order renormalization of a degenerate wave function leads to second-order self-correction coefficient $t^2_{i_D i_D}$. $t^2_{i_D i_D}$ is calculated as in the nondegenerate theory, that is, using Eq. (44).

Higher-order corrections to wave functions and energies for a system containing degenerate orbitals can be developed in a similar manner: To obtain the n-th-order expression in perturbation theory, first, the corrections to energies are computed, using corrections to wave functions up to the $(n-1)$-th order. Next, the corrections to nondegenerate wave functions are calculated from the n-th-order master equation [see Eqs. (30)–(32)]. The peculiarity of the degenerate theory is in deriving the n-th-order coefficient of mixing of one degenerate orbital into another from the $(n+1)$-th-order master equation. Diagonal self-correction terms are calculated at the very end, in a similar manner or both nondegenerate and degenerate orbitals.

Intermolecular Perturbation: Homonuclear Diatomic Molecules

Perhaps one of the simplest examples showing the utility of the degenerate perturbation method is that of homonuclear diatomic molecules, for example, N_2. Within a PMO approach, the MOs of a diatomic molecule can be constructed from atomic orbitals of each atom, the (large) perturbation is the interatomic interaction. Defining the z-axis as the internuclear axis, the basis orbitals naturally separate into $\sigma(s, p_z)$ and $\pi(p_x, p_y)$ types [2]. Here, let us consider just the more interesting σ-type interaction, in which both s and p orbitals participate in MO formation, and, thus, $s-p$ mixing occurs. To proceed, we first obtain the correct zeroth-order wave functions in each degenerate set of s and p orbitals and next consider higher-order perturbation terms for wave-function correction. The higher-order perturbational terms will describe interactions between the zeroth-order wave functions of different types of orbitals (i.e., $s-p$) as well as of the same types of orbitals (i.e., $s-s$ and $p-p$). Since the essential qualitative aspects of these interactions are contained in first-order terms, we limit our discussion in this section to those.

Let us imagine two interacting atoms, 1 and 2, each having two orbitals, χ_s and χ_p (Fig. 1). The same types of orbitals ($s-s$ or $p-p$) are degenerate in energy. When the atoms interact, changes will occur only in off-diagonal (Hamiltonian and overlap)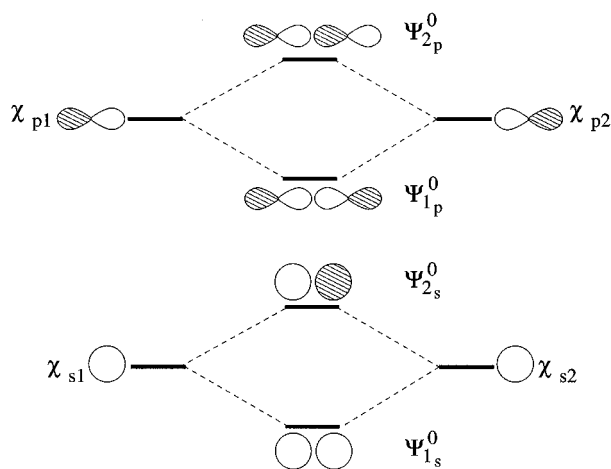 matrix elements describing the interactions between the atoms. We express those changes by δH_{ss} and δS_{ss}, δH_{pp} and δS_{pp}, and δH_{sp} and δS_{sp} for interactions between two s's, two p's, and one s and one p orbital, respectively. In Figure 1, we arrange the atomic orbitals so that all overlap terms are positive, and, thus, Hamiltonian terms should be all negative. To consider the zeroth-order corrections to the s orbitals, we set up the following secular equation using Eq. (49):

$$\begin{vmatrix} -e_{i_s}^1 & (\delta H_{ss} - e_s^0 \, \delta S_{ss}) \\ (\delta H_{ss} - e_s^0 \, \delta S_{ss}) & -e_{i_s}^1 \end{vmatrix} = 0. \quad (66)$$

From Eq. (66), we obtain the first-order energy corrections:

$$e_{1_s}^1 = \delta H_{ss} - e_s^0 \, \delta S_{ss} < 0, \quad (67)$$

$$e_{2_s}^1 = -(\delta H_{ss} - e_s^0 \, \delta S_{ss}) > 0. \quad (68)$$

The correct zeroth-order wave functions corresponding to $e_{1_s}^1$ and $e_{2_s}^1$ result from substituting those terms in Eq. (66). After normalization using Eq. (34), we get

$$\Psi_{1_s}^0 = \frac{1}{\sqrt{2}} (\chi_{s1} + \chi_{s2}), \quad (69)$$

$$\Psi_{2_s}^0 = \frac{1}{\sqrt{2}} (\chi_{s1} - \chi_{s2}). \quad (70)$$

The correct zeroth-order wave functions are drawn schematically in Figure 1. It can be seen that $\Psi_{1_s}^0$ and $\Psi_{2_s}^0$ are orthogonal to each other, the former being symmetric (bonding) and the latter being antisymmetric (antibonding) with respect to a mirror plane at the center perpendicular to the interatomic axis.

Exactly the same procedure is followed to obtain the correct zeroth-order wave functions for p orbitals and their corresponding first-order energy-correction terms. To summarize:

$$e_{1_p}^1 = \delta H_{pp} - e_p^0 \, \delta S_{pp} < 0, \quad (71)$$

$$e_{2_p}^1 = -\left(\delta H_{pp} - e_p^0 \, \delta S_{pp}\right) > 0, \quad (72)$$

$$\Psi_{1_p}^0 = \frac{1}{\sqrt{2}} (\chi_{p1} + \chi_{p2}), \quad (73)$$

$$\Psi_{2_p}^0 = \frac{1}{\sqrt{2}} (\chi_{p1} - \chi_{p2}). \quad (74)$$

FIGURE 1. Correct zeroth-order σ MOs in N_2.

The symmetry properties of the correct zeroth-order wave functions from p orbitals, $\Psi_{1_p}^0$ and $\Psi_{2_p}^0$, are exactly the same as those from s orbitals (Fig. 1). All this is pretty much as one would expect in a qualitative treatment of diatomic formation.

Now, we consider the first-order contribution to each zeroth-order wave function and the corresponding (second-order) energy correction. For this purpose, all matrix elements are calculated by putting Eqs. (69), (70), (73), and (74) into Eq. (15):

$$\tilde{S}_{1_s 1_s} = -\tilde{S}_{2_s 2_s} = \delta S_{ss}, \tag{75}$$

$$\tilde{\Delta}_{1_s 1_s} = -\tilde{\Delta}_{2_s 2_s} = \delta H_{ss}, \tag{76}$$

$$\tilde{S}_{1_p 1_p} = -\tilde{S}_{2_p 2_p} = \delta S_{pp}, \tag{77}$$

$$\tilde{\Delta}_{1_p 1_p} = -\tilde{\Delta}_{2_p 2_p} = \delta H_{pp}, \tag{78}$$

$$\tilde{S}_{1_s 1_p} = -\tilde{S}_{2_s 2_p} = \delta S_{sp}, \tag{79}$$

$$\tilde{\Delta}_{1_s 1_p} = -\tilde{\Delta}_{2_s 2_p} = \delta H_{sp}. \tag{80}$$

Due to the symmetry properties of the zeroth-order wave functions, all the other terms are zero. One immediate consequence of this will be that there is no contribution to each wave function from its paired zeroth-order wave function. This can be seen by examining Eq. (58), where all matrix elements are zero in this particular case.

The self-contribution terms are obtained from Eqs. (75), (77), and (41):

$$t_{1_s 1_s}^1 = -\frac{1}{2}\,\delta S_{ss}, \tag{81}$$

$$t_{2_s 2_s}^1 = \frac{1}{2}\,\delta S_{ss}, \tag{82}$$

$$t_{1_p 1_p}^1 = -\frac{1}{2}\,\delta S_{pp}, \tag{83}$$

$$t_{2_p 2_p}^1 = \frac{1}{2}\,\delta S_{pp}. \tag{84}$$

The negative signs in Eqs. (81) and (83) means that the self-contribution terms actually reduce the size of the coefficients of the orbitals in $\Psi_{1_s}^0$ and $\Psi_{1_p}^0$. The opposite holds for $\Psi_{2_s}^0$ and $\Psi_{2_p}^0$.

Now, we consider the first-order contributions to the wave functions. These come from the interaction between $(\Psi_{1_s}^0, \Psi_{2_s}^0)$ and $(\Psi_{1_p}^0, \Psi_{2_p}^0)$, that is, between two sets of the degenerate pairs. By substituting Eqs. (79) and (80) into Eq. (52), the first-

order coefficients are calculated as

$$t_{1_p 1_s}^1 = -t_{2_p 2_s}^1 = \frac{\delta H_{sp} - e_s^0\,\delta S_{sp}}{e_s^0 - e_p^0}, \tag{85}$$

$$t_{1_s 1_p}^1 = -t_{2_s 2_p}^1 = \frac{\delta H_{sp} - e_p^0\,\delta S_{sp}}{e_p^0 - e_s^0}. \tag{86}$$

Since $e_s^0 < e_p^0$, $t_{1_p 1_s}^1$ and $t_{2_p 2_s}^1$ are positive, while the opposite sign follows for $t_{1_s 1_p}^1$ and $t_{2_p 2_s}^1$.

Figure 2 shows the perturbed wave functions, whose shapes were drastically changed due to $s-p$ mixing through the first-order orbital corrections. The bonding and antibonding characters of Ψ_{1_s} and Ψ_{2_p}, respectively, are enhanced by $s-p$ mixing. However, the two MOs in the middle, Ψ_{2_s} and Ψ_{1_p}, became approximately nonbonding. It should be noted that these are schematic drawings, not contour diagrams, of the MOs.

As mentioned earlier, the first-order corrections to wave functions are reflected in the second-order corrections in energies. Substitution of all perturbation terms obtained above into Eq. (62) yields the following:

$$e_{1s}^2 = e_{2s}^2$$

$$= \frac{\left(\delta H_{sp} - e_s^0\,\delta S_{sp}\right)^2}{e_s^0 - e_p^0} - \left(\delta H_{ss} - e_s^0\,\delta S_{ss}\right)\delta S_{ss}, \tag{87}$$

$$e_{1p}^2 = e_{2p}^2$$

$$= -\frac{\left(\delta H_{sp} - e_s^0\,\delta S_{sp}\right)^2}{e_s^0 - e_p^0}$$

$$- \left(\delta H_{pp} - e_p^0\,\delta S_{pp}\right)\delta S_{pp}. \tag{88}$$

In all the second-order energy expressions above, the second terms are from the self-contributions and they are all positive. Therefore, the first-order self-contributions in wave functions destabilize the original zeroth-order wave functions. This is consistent with the fact that the explicit inclusion of overlap actually raises the energies of bonding and antibonding MOs [10–12]. Meanwhile, the first terms in Eqs. (87) and (88) are negative and positive, respectively. This means that $s-p$ mixing through first-order perturbation in wave functions stabilizes the low-lying s orbitals and destabilizes the high-lying p orbitals (Fig. 2).
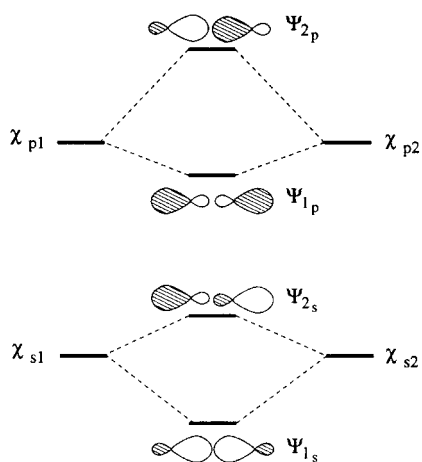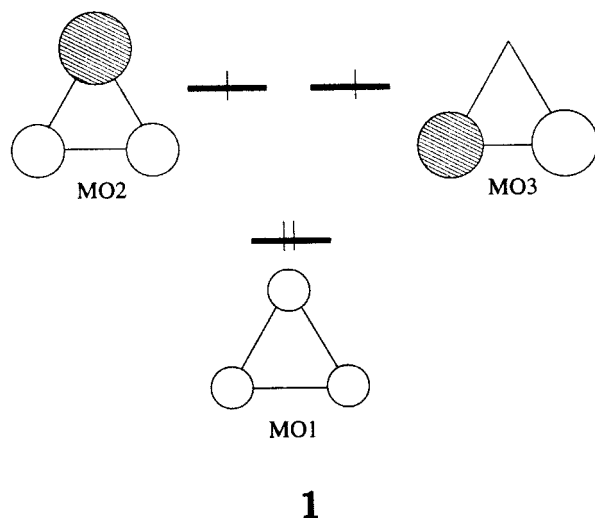
FIGURE 2. The σ MOs in N_2, with mixing through first order included.

1

Geometry Perturbation: A Sliding Distortion of an H_3 Triangle

In this section, we demonstrate that PMO theory is not only a tool for qualitative analysis but may provide quantitative results if needed. Of course, we do not expect perturbation theory to perform better than the underlying theory which it attempts to model (in this case the extended Hückel model).

The MOs of a hypothetical H_3^- molecule are depicted below (see **1**). In this molecule, there are two degenerate orbitals, MO2 and MO3, filled with two unpaired electrons. One would expect a Jahn–Teller-type distortion to occur. The distortion that we chose to consider (see **2**) is not a normal mode of the H_3 molecule but a simple horizontal sliding motion of the H3 atom. Other distortions of the H_3^- molecule may be analyzed in a similar manner.

The sliding motion of the H3 atom produces two perturbations in the atomic basis set. As a result of H3—H1 bond elongation, its corresponding overlap integral diminishes, along with the corresponding Hamiltonian matrix. The H3—H2 bond gets shorter, which induces opposite changes in the overlap and Hamiltnoian matrix elements.

After calculating the changes in the overlap and Hamiltonian matrix elements in the atomic basis, a transformation is carried out to the molecular basis according to Eqs. (14) and (15). It turns out that the original degenerate orbitals MO2 and MO3 are not

the correct zeroth-order wave functions for this perturbation. To find those, a two-by-two secular equation is set up, as suggested by Eq. (49). Calculated correct zeroth-order degenerate MOs are indicated in Table I. Since MO1 is nondegenerate, it has the correct zeroth-order form from the beginning.

As may be inferred from Table I, just getting the correct zeroth-order degenerate orbitals MO2 and MO3 captures the largest part of the wave-function change during the sliding distortion. Quantitative agreement with the exact solution is obtained when first- and second-order corrections are computed using the formalism developed in this article. For instance, there is a *first-order* mixing of degenerate MO3 into degenerate MO2 through nondegenerate MO1. When corrections up to second-order are considered, the atomic orbital coefficients of the MOs computed from perturbation theory agree to two significant figures with the full
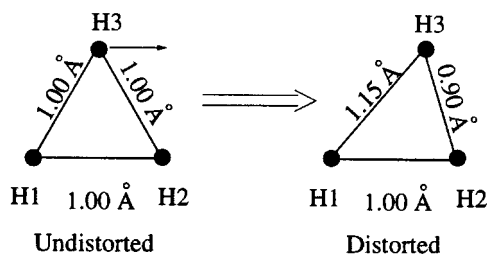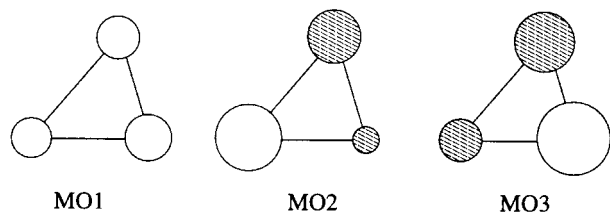

2

TABLE I _____
A sliding distortion of an H_3 perfect triangle as described in the text; the entries give the indicated AO coefficients in the perturbative expansions for (a) MO1, (b) MO2, and (c) MO3.

	AO1	AO2	AO3
(a) MO1			
$\lvert\Psi_1^0\rangle$ (initial)	0.4148	0.4148	0.4148
$\lvert\Psi_1^0\rangle$ (new)	0.4148	0.4148	0.4148
$\lvert\Psi_1^0\rangle + \lvert\Psi_1^1\rangle$	0.3963	0.4384	0.4143
$\lvert\Psi_1^0\rangle + \lvert\Psi_1^1\rangle + \lvert\Psi_1^2\rangle$	0.3960	0.4361	0.4150
$\lvert\Psi_1\rangle$ computed	0.3948	0.4372	0.4150
(b) MO2			
$\lvert\Psi_2^0\rangle$ (initial)	0.5601	0.5601	-1.1203
$\lvert\Psi_2^0\rangle$ (new)	1.0688	-0.2439	-0.8250
$\lvert\Psi_2^0\rangle + \lvert\Psi_2^1\rangle$	0.9963	-0.1954	-0.7406
$\lvert\Psi_2^0\rangle + \lvert\Psi_2^1\rangle + \lvert\Psi_2^2\rangle$	1.0080	-0.1987	-0.7501
$\lvert\Psi_2\rangle$ computed	1.0065	-0.1979	-0.7489
(c) MO3			
$\lvert\Psi_3^0\rangle$ (initial)	-0.9702	0.9702	0.0000
$\lvert\Psi_3^0\rangle$ (new)	-0.3356	1.0934	-0.7579
$\lvert\Psi_3^0\rangle + \lvert\Psi_3^1\rangle$	-0.3932	1.1469	-0.8320
$\lvert\Psi_3^0\rangle + \lvert\Psi_3^1\rangle + \lvert\Psi_3^2\rangle$	-0.3972	1.1554	-0.8391
$\lvert\Psi_3\rangle$ computed	-0.3977	1.1567	-0.8403

TABLE II _____
Distortion of a H_3 perfect triangle as described in the text; perturbative expansion for energies.

Energies (eV)	MO1	MO2	MO3
e^0	-18.5357	-4.5988	-4.5988
$e^0 + e^1$	-18.4980	-7.8411	-1.8629
$e^0 + e^1 + e^2$	-18.5044	-7.2605	-1.4189
e computed	-18.5040	-7.3469	-1.3366

producing reasonable agreement with this MO exact energy (see Table II).

Finally, we note that the zeroth-order mixing of the degenerate orbitals MO2 and MO3 predetermines the shapes of these MOs. Consider MO2, for example. The H3 orbital in the undistorted molecule has equal antibonding interactions with orbitals H1 and H2 (see **1**). In the correct zeroth-order MO2, however, the H3—H1 bond remains antibonding while the H3—H2 bond becomes bonding (see **3**). When the distortion occurs, the elongation of the H3—H1 bond leads to a weakening of the H3—H1 antibonding interactions. Conversely, the shortening of the H3—H2 bond leads to strengthening of H3—H2 bonding interactions. Therefore, the correct zeroth-order MO2 is set up for the maximum stabilization during the distortion, as is indeed observed. On the contrary, the nodal properties of correct zeroth-order MO3 (**3**) anticipate maximum destabilization during the distortion: H3—H1 bonding interactions are diminished and H3—H2 antibonding interactions enhanced.

exact extended Hückel calculations. MOs for the distorted molecule are drawn in **3**. It is remarkable that even for such large changes in the shapes of MOs perturbation theory provides quantitative results.

The energies of the MOs were calculate according to Eqs. (39), (42), (51), (62), and (63). The total energy of the H_3^- molecule is lowered by -5.43 eV during the sliding distortion, that is, the distortion is stabilizing. The largest part of this energy is contributed by the first-order energy correction to MO2, which actually overestimates the stabilization by 1.0 eV (for two electrons). The second-order correction to the energy of MO2 is essential for

MO1   MO2   MO3

3

Conclusions

Prior to this work, the apparatus of PMO theory for degenerate systems was not fully developed. In particular, we were not able to find in the literature expressions for evaluating the first- and higher-order corrections to wave functions as well as the second- and higher-order corrections to energies of degenerate MOs. It was also not clear how to incorporate degenerate perturbation theory into the more general framework of nondegenerate perturbation theory.

In the first part of this article, we set up the master equations for deriving perturbative expressions up to the second order. If complex wave

functions are used, as, for instance, one must do for crystal orbitals in the solid state, we suggested that all diagonal corrections to MOs be kept real. In that case, no ambiguity remains in determining the phases of corrections to wave functions.

We rederived the familiar perturbation theory for nondegenerate systems and corrected a small number of misprints found in the literature expressions. For the degenerate systems, we developed a systematic way of determining higher-order corrections to energies and wave functions. By the way that we constructed the theory, the degenerate system is naturally incorporated into a larger nondegenerate–degenerate composite system. One of the peculiarities of degenerate perturbation theory is that the first-order corrections to wave functions look similar to second-order corrections in the nondegenerate case.

Finally, we tested the perturbation theory formalism developed on two cases: N_2 molecule formation out of two N atoms (an intermolecular perturbation) and a sliding distortion of an H_3^- triangle (a geometry perturbation). We demonstrated that degenerate perturbation theory may be applied both qualitatively as well as in quantitative calculations.

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