Handling Overlap as a Perturbation

István Mayer

*Central Research Institute for Chemistry of the Hungarian Academy
of Sciences, H–1525 Budapest, P.O.Box 17, Hungary*

and

Péter R. Surján[1]

*Laboratory for Theoretical Chemistry, Eötvös University,
H–1518 Budapest 112, P.O. Box 32, Hungary*

The off-diagonal part of the overlap matrix (appearing in the right hand
side of a secular equation written down in a non-orthogonal metric) is hand-
led as a perturbation. As this perturbation is energy- and state-dependent,
one has to use the nonlinear Rayleigh-Schrödinger perturbation theory. The
state-dependence of the perturbation causes the theory to be also non-Her-
mitian.

OVERLAP AS A NONLINEAR PERTURBATION

We start from the standard (generalized) eigenvalue equation written in a non-or-
thogonal metric

$$\boldsymbol{H}^0\ \boldsymbol{c}_j = E_j\ \boldsymbol{S}\ \boldsymbol{c}_j \tag{1}$$

where $\boldsymbol{H}^0$ and $\boldsymbol{S}$ are Hermitian matrices (Hamiltonian and overlap), $\boldsymbol{c}_j$ and E_j are the
eigenvectors and eigenvalues of $\boldsymbol{H}^0$.

Solution of Eq. (1) is possible by numerous techniques. The standard solution is
either to diagonalize matrix $\boldsymbol{S}^{-1/2}\ \boldsymbol{H}^0\ \boldsymbol{S}^{-1/2}$ or to use the Choletsky decomposition tech-
nique.[1] Alternatively, one may find the right eigenvectors of the nonsymmetric matrix
$\boldsymbol{S}^{-1}\boldsymbol{H}^0$ (biorthogonal formalism). However, in many applications, especially in the field
of intermolecular interactions, the overlap and the interaction terms of the Hamil-

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[1] Also at: Quantum Theory Group, Institute of Physics, Technical University, Budapest, Hungary

tonian appear simultaneously and are expected to be of the same order of magnitude. In such situation, it may be of interest to treat overlap as a sort of *perturbation*. This makes it necessary to develop an »expanded« formalism in which terms linear, quadratic (and so on) in the off-diagonal overlap matrix elements appear in the first, second (and so on) orders of the perturbation expansion , respectively. Such an expansion can be done *e.g.* as follows.

Writing S as

$$S = (I + s)$$ (2)

with I being the unit matrix, Eq. (1) is rearranged as

$$(H^0 - E_j s) c_j = E_j c_j$$ (3)

Assuming the S does not differ too much from I, that is, the offdiagonal overlaps are not very large, the second term in Eq. (3) can be considered as a perturbation relative to H^0. This perturbation is, however, energy- and state-dependent, thus the perturbative solution of Eq. (3) requires special consideration. The state-dependency means that the perturbing matrix itself depends on the energy E_j (and so the solution c_j) which makes the problem nonlinear.

NONLINEAR PERTURBATION THEORY

In a somewhat different context, nonlinear perturbation theories have already been developed.[2-4] Here, we apply a similar idea but investigate a more general situation, when a nonlinear perturbation appears along with a »conventional« perturbational term of the Hamiltonian V. So assuming that a zeroth order problem

$$H^0 c_j^0 = E_j^0 c_j^0$$ (4)

has already been solved, we aim to develop a perturbative solution of

$$[H^0 + \lambda (V - E_j s)] c_j = E_j c_j$$ (5)

where λ is a formal perturbation parameter. An equation of similar structure has recently been introduced in the context of analyzing nearly additive interactions.[5]

For the solution of Eq. (5), we expand the exact energies and eigenvectors into a power series of λ:

$$E_j = \sum_{\mu=0} \lambda^\mu E_j^{(\mu)}$$ (6)

and

$$c_j = \sum_{\nu=0} \lambda^\nu c_j^{(\nu)}$$ (7)

The latter equation can be rewritten in the intermediate normalization and expanding the vectors c in terms of the zeroth order states as

$$c_j = c_j^{(0)} + \sum_{\nu=1} \lambda^\nu \sum_{k=1} d_{jk}^{(\nu)} c_k^0 \tag{8}$$

where the matrices $\boldsymbol{d}^{(\nu)}$ contain the expansion coefficient at the order ν.

The perturbation theory then proceeds in the usual manner. Substituting expansions (6 – 8) into Eq. (5), and collecting the terms of a given order in λ, we get the following results:

First order

For the eigenvalues:

$$E_j^{(1)} = V_{jj} - E_j^0 s_{jj} \tag{9}$$

while the eigenvectors are determined by the expansion coefficients $d_{jk}^{(1)}$, for which we get

$$d_{jk}^{(1)} = \frac{V_{kj} - E_j^{(0)} s_{kj}}{E_j^{(0)} - E_k^{(0)}} \tag{10}$$

In the above two equations, we used the standard notation for the matrix elements V_{kj} and s_{kj}. As usual for the first order results, Eqs. (9) and (10) do not show any »nonlinearity effects«, the latter being expected to appear from the second order only. In fact, formulae (9) and (10) agree with those obtained by nonlinear PT for overlap effects in the theory of localized orbitals,[6] where we introduced a notation for the *overlap-corrected interaction* $\boldsymbol{G}$, which is defined by the matrix elements

$$G_{jk}^i = V_{jk} - E_i^{(0)} s_{jk} \tag{11}$$

Note that matrix $\boldsymbol{G}$ is not symmetric. Definition (11) is the same as that used in Ref. 6, except that now we have introduced a separate superscript i to indicate state-dependency. With this notation, Eqs. (9–10) can be rewritten as

$$E_j^{(1)} = G_{jj}^j \tag{12}$$

and

$$d_{jk}^{(0)} = \frac{G_{kj}^j}{E_j^{(0)} - E_k^{(0)}} \tag{13}$$

Second Order

For the eigenvalues one obtains:

$$E_j^{(2)} = \sum_{k \neq j} \frac{G_{jk}^j - G_{kj}^j}{E_j^{(0)} - E_k^{(0)}} - G_{jj}^j s_{jj} \tag{14}$$

The first term of this result has a well-known structure, characteristic of a second-order energy correction. The second term arises from the non-linearity of the problem.

(It vanishes if the normalization of the state under study is not changed by the perturbation, *i.e.* if $s_{jj} = 0$).

We do not detail the second order contribution to the eigenvectors as one can use the general recursion formulae reported below for arbitrary orders.

Recursion formulae for order ρ

The ρ-th order of energy is

$$E_j^{(\rho)} = -E_j^{(\rho-1)} s_{jj} + \sum_{k \neq j} d_{jk}^{(\rho-1)} G_{ik}^j - \sum_{k \neq j} \sum_{\mu=1}^{\rho-2} d_{jk}^{(\mu)} E_j^{(\rho-\mu-1)} s_{jk} \qquad (15)$$

The ρ-th order contributions to the expansion coefficients $d_{jl}^{(\rho)}$ are:

$$d_{jl}^{(\rho)} = \left[E_j^{(\rho-1)} s_{lj} - \sum_{k \neq j} d_{jl}^{(\rho-1)} G_{lk}^j + \sum_{k \neq j} \sum_{\mu=1}^{\rho-1} d_{jk}^{(\rho-\mu-1)} E_j^{(\mu)} s_{lk} + \right.$$

$$\left. + \sum_{\mu=1}^{\rho-1} d_{jl}^{(\rho-\mu)} E_j^{(\mu)} \right] \left[E_l^{(0)} - E_j^{(0)} \right]^{-1} \qquad (16)$$

DISCUSSION

In the preceding section, we presented recursive relations for the perturbational corrections to the energy and wave function in the case when the perturbation consists of a usual (linear) term and a term proportional to the energy sought, the latter representing nonlinear perturbation. As it was mentioned, such a problem is topical in the field of intermolecular interactions when the overlap between the orbitals of the interacting molecules is not neglected.

Explicit handling of overlap in intermolecular interaction theories can be managed in several different manners. One can either turn to a biorthogonal formalism,[7] or one can orthogonalize the overlapping MOs directly. This latter procedure was followed by Kvasnička et al.,[8] based on the theory by Basilewsky and Beerenfeld.[9] These authors developed a many-body approach where the difference between the integral lists of the interacting and the non-interacting problems represented the perturbation. The integral list for the interacting case was written down in a Löwdin-orthogonalized basis. This theory can be converted to its overlap-expanded version by inserting the Taylor-series of matrix $S^{-1/2}$ into the expression of the transformed orbitals. In this manner one obtains a perturbation operator containing terms of different orders. As the order parameter of this partition is the same λ as used in Eq. (5), the formulae presented here could have been obtained alternatively by expanding the results of Kvasnička et al.[8] in terms of intermolecular overlap and interaction. However, it appears to us that an analysis of certain problems characteristic of the quantum chemistry of intermolecular interactions like the basis set superposition error (for a review see *e.g.*[10] will be manageable in the perturbational formalism presented in this paper.

Note added in proof. —Recently our attention has been called to the following papers related to the present aproach: J. N. Silverman and Y. Sobouti, *Astron. Astrophys.* **62** (1978) 355; J. N. Silverman, *J. Phys. A.* **16** (1983) 3741.

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SAŽETAK

Prekrivanje kao smetnja

István Mayer i Péter R. Surján

S izvandijagonalnim dijelom matrice prekrivanja može se postupiti kao sa smetnjom. Kako ta smetnja ovisi o energiji i o stanju, mora se uporabiti nelinearan Rayleigh-Schrödingerov račun smetnje. Ovisnost smetnje o stanju dovodi do toga da teorija prestaje biti hermitska.