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Effective Hamiltonian of Doubly Perturbed Systems

Hosung Sun†, Un Sik Kim and Yang Kim

Department of Chemistry, Pusan National University, Pusan 607, Korea *(Received July 20, 1985)*

When a molecule is perturbed by an external fied, the perturbed moecue can be described as a douby perturbed system. Hartree-Fock operator in the absence of the field is the zeroth order Hamiltonian, and a correlation operator and the external field operator are perturbations. The effective Hamiltonian, which is a projection of the total Hamiltonian onto a small finite subspace (usually a valence space), has been formally derived. The influence of the external field to the molecular Hamiltonian itself has been examined within an effective Hamiltonian framework. The first order effective expectation values, for instance electromagnetic transition amplitudes, between valence states are found to be easily calculated — by simply taking matrix elements of the effective external field operator. Implications of the terms in perturbation expansion are discussed.

1. Introduction

When a molecule is perturbed by an external field, various phenomena will be observed, for instance, Zeeman effect or Stark effect. Needless to say, it is important and interesting to understand such phenomena. Also when so called properties of molecules are desired, the property operator should be added to the molecular Hamiltonian like the external perturbation. Consequently, the perturbation method can be utilized to solve the problem. In the perturbation framework, the perturbed molecule is regarded as a doubly perturbed system. Since it is impossible to solve the molecular Hamiltonian (Hartree-Fock plus correlation operator) exactly, it is practical to consider the Hartree-Fock operator as the zeroth order part, and correlation and external field operators as two perturbations.

From the Kelly's initiative work to Bartlett's many-body perturbation approach[1-6], double perturbation problems have long been studied. However it still is a challenging problem as far as the convergence and efficiency of theoretical treatments are concerned. The difficulties in double perturbation method arise from, of course, the fact that there are two perturbations. Therefore the perturbation expansion is very complicated so that it is a formidable task to locate dominant terms.

In the present work we have the so called first order properties between molecular valence states in mind. The first order properties are expectation values of property operators truncated at the first order in perturbation expansion. Examples are dipole moments and oscillator strengths, etc. From now on we treat the property operator relating to properties of molecules as the second perturbation. Particularly we are interested in the effective property operator that spans only within a valence space and, therefore, describes the valence state properties.

Recently the ab initio effective Hamiltonian method for an isolated molecular system has been developed.[7-14] And the effective Hamiltonian has been extensively applied to various atomic and molecular systems.[15-19] Absolute energies, consequently excitation energies and various spectroscopic constants have been reported. Those applications confirm that the effective Hamiltonian itself is either a well formulated method or another good ab initio method for describing molecular electronic structures. However, to our knowledge, ab initio effective Hamiltonian for molecular properties has not been formulated yet. Only Brandow showed that any effective property operator can be obtained in terms of well-defined perturbation expansion.[12]

We derive a formal expression for an effective Hamiltonian which has the second perturbation of property operator. The derivation shows how the double perturbation manifests in an effective Hamiltonian. Next a simple first order (with repect to the property) effective Hamiltonian is obtained. From the comparison of the first order effective Hamiltonian with the exact one, we find that perturbation expressions for the first order molecular properties can be easily obtained. The diagramatic perturbation expansion technique may be useful for resumming expansion terms so that more practical (easily tractable in numerical calculations) expressions could be obtained.

Section 2 describes the doubly perturbed Hamiltonian and shows how the whole Hamiltonian can be transformed into an effective valence Hamiltonian. First order approximation with respect to property operator has been invoked to obtain a simple effective property operator in section 3. In section 4, comparisons of the exact and the first order effective Hamiltonian are provided. Explanation on relevant terms are also given in section 4. Section 5 summarizes the derivation and the meanings of the effective Hamiltonian of doubly perturbed systems.

2. Exact Effective Hamiltonian, H^{eff}

When an arbitrary operator, M is added to an molecular electronic Hamiltonian, H^0, the whole Hamiltonian, H is given as

$$H = H^0 + \lambda M \tag{1}$$

where λ is an expansion index. We call M a property operator throughout the paper. Then the full Schrödinger equation is

$$H\psi = E\psi \tag{2}$$

where E is the total energy of H.

Let us assume that the H^0 be exactly solved. H^0 is the zeroth order part and M is a perturbation when M is small. We project the whole Hamiltonian, H onto a small subspace P. Q space is the complimentary to it. The whole wavefunction, ψ can be represented as a linear superposition of some functions, ϕ of which are eigenfunctions of H^0, *i.e.*,

$$\psi = \sum_{i \in P} C_i \phi_i + \sum_{j \in Q} C_j \phi_j \tag{3}$$

we utilize a matrix representation where C_p designates the column vectors of C_i for $i \in P$ and C_Q for those $j \in Q$. The Schrödinger equation (2) can then be expressed in supermatrix form as

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} C_P \\ C_Q \end{pmatrix} = E \begin{pmatrix} C_P \\ C_Q \end{pmatrix} \tag{4}$$

where $H_{pp} = \langle \phi_i | H | \phi_{i'} \rangle$ for $i, i' \in P$, denotes the sub-block of the Hamiltonian matrix within P space, $H_{PQ} = \langle \phi_i | h | \phi_j \rangle$ for $i \in P$, $j \in Q$, that between P and Q, etc. E is a diagonal matrix of the total energy. Equation (4) can be rewritten as

$$H_{PP}\, C_P + H_{PQ}\, C_Q = E_{PP}\, C_P \tag{5}$$

$$H_{QP}\, C_P + H_{QQ}\, C_Q = E_{QQ}\, C_Q \tag{6}$$

where E_{PP} is a diagonal energy matrix within P space and E_{QQ} within Q space. From equation (6), we obtain

$$C_Q = (E_{QQ} - H_{QQ})^{-1} H_{QP} C_P \tag{7}$$

Substituting equation (6) into euqation (5) gives

$$H^{eff} C_P = [H_{PP} + H_{PQ} (E_{QQ} - H_{QQ})^{-1} H_{QP}] C_P = E_{PP} C_P \tag{8}$$

The H^{eff} is an effective operator of H, which acts only within a small and finite P space. Inserting equation (1) into equation (8), we readily find an expression for H^{eff}, *i.e.*,

$$\begin{aligned} H^{eff} = {} & (H^\circ + \lambda M)_{PP} + (H^\circ + \lambda M)_{PQ} (E_{QQ} - H^\circ_{QQ} - \lambda M_{QQ})^{-1} \\ & \times (H^\circ + \lambda M)_{QP} \end{aligned} \tag{9}$$

Since M is usually very small compared with the electronic energy part H°, the denominator in equation (9) can be expanded as

$$\begin{aligned} & (E_{QQ} - H^\circ_{QQ} - \lambda M_{QQ})^{-1} \\ & = [1_{QQ} - \lambda (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ}]^{-1} (E_{QQ} - H^\circ_{QQ})^{-1} \\ & = [1_{QQ} + \lambda (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} + \sum_{n=2}^{\infty} \lambda^n \\ & \quad \{(E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ}\}^n] (E_{QQ} - H^\circ_{QQ})^{-1} \end{aligned} \tag{10}$$

where 1_{QQ} is a unit matrix within Q space. M_{PP} is a sub-block of M matrix within P space, etc.

Substituting equation (10) into equation (9) and expanding the term in Σ, we easily find the second order expression for H^{eff}, *i.e.*,

$$\begin{aligned} H^{eff} = {} & H^\circ_{PP} + H^\circ_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} \\ & + \lambda [M_{PP} + M_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} \\ & \qquad + H^\circ_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QP} \\ & \qquad + H^\circ_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP}] \\ & + \lambda^2 [M_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QP} \\ & \quad + M_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} \\ & \quad + H^\circ_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QP} \\ & \quad + H^\circ_{PQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP}] \\ & + O(\lambda^3) \end{aligned} \tag{11}$$

When we consider only the first order properties, the expansion is truncated at the λ-term. As shown in equation (11), the H^{eff} is the total energy (E) dependent, which makes evaluation of H^{eff} *cumbersome and difficult.*

3. Effective Property Operator, M^{eff}

The molecular electronic Hamiltonian, H^0 in equation (1) can not be solved exactly. Therefore H^0 could be solved with a perturbation method. As H^{SCF} is the zeroth order part and V is a perturbation, H^0 can be written as

$$H^\circ = H^{SCF} + V \tag{12}$$

H^{SCF} is usually a one-electron Hartree-Fock Hamiltonian and V is a correlation operator. The Schrödinger equation is then

$$H^\circ \psi^\circ = E^\circ \psi^\circ \tag{13}$$

where ψ^0 is expressed in linear combinations of electronic determinantal wavefunctions, Φ^0. That is

$$\psi^\circ = \sum_{i \in P} C_i \Phi^\circ_i + \sum_{j \in Q} C_j \Phi^\circ_j \tag{14}$$

P and Q have the same meaning as those in equation (3). The energy E^0 is a molecular energy when external (property) operator M is absent. In supermatrix form, equation (13) again can be rewritten as

$$\begin{pmatrix} H^\circ_{PP} & H^\circ_{PQ} \\ H^\circ_{QP} & H^\circ_{QQ} \end{pmatrix} \begin{pmatrix} C^\circ_P \\ C^\circ_Q \end{pmatrix} = E^\circ \begin{pmatrix} C^\circ_P \\ C^\circ_Q \end{pmatrix} \tag{15}$$

Adopting the same projection operator formalism, $H^{0,\, eff}$ which is the effective Hamiltonian of H^0 within P space can be expressed as

$$H^{\circ,\, eff} C^\circ_P = [H^\circ_{PP} + H^\circ_{PQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP}] C^\circ_P = E^\circ_{PP} C^\circ_P \tag{16}$$

When a molecule is perturbed by a weak field M, M becomes another perturbation besides the correlation V. The first order (with respect to M) property involving the states ψ°_i and ψ°_j is, under the first order approximation, $\psi^{\circ\dagger}_i M \psi^\circ_j$. We will call the expectation value "property integral". Since the zeroth order wavefunctions,

$$\psi^\circ_i = C^\circ_{P,i} + C^\circ_{Q,j} \tag{17}$$

the property integral can be written as

$$\begin{aligned} \psi^{\circ\dagger}_i M \psi^\circ_j & = (C^\circ_{p,i} + C^\circ_{Q,j})^\dagger M (C^\circ_{P,i} + C^\circ_{Q,j}) \\ & = C^{\circ\dagger}_{P,i} M C^\circ_{P,j} + C^{\circ\dagger}_{P,i} M C^\circ_{Q,j} \\ & \quad + C^{\circ\dagger}_{Q,i} M C^\circ_{P,j} + C^{\circ\dagger}_{Q,i} M C^\circ_{Q,j} \end{aligned} \tag{18}$$

Similarly to equation (7), we know that

$$C^\circ_Q = (E^\circ_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} C^\circ_P \tag{19}$$

Substituting equation (19) into equation (18) gives

$$\begin{aligned} M^{eff} \equiv {} & M_{PP} + M_{PQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} \\ & + H^\circ_{PQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1} M_{QP} \\ & + H^\circ_{PQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1} M_{QQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1} H^\circ_{QP} \end{aligned} \tag{20}$$

and

$$\psi^{\circ\dagger}_i M \psi^\circ_j = C^{\circ\dagger}_{P,i} M^{eff} C^\circ_{P,j} \tag{21}$$

As shown in equation (20), M^{eff} is independent of the total energy E. It rather depends on the zeroth order energy E^0 under the first order approximation.

4. Comparison of H^{eff} with M^{eff}

The H^{eff} in equation (11) is dependent on the total energy E. To obtain E-independent M^{eff} from H^{eff}, we expand the denominator $(E_{QQ}-H^0_{QQ})^{-1}$ in equation (11). We define

$$E = E^\circ + \lambda E' \tag{22}$$

where E' is perturbation value due to the operator, M. Assuming that E' be much smaller than E^0,

$$\begin{aligned} (E_{QQ} - H^\circ_{QQ})^{-1} & = (E^\circ_{QQ} + \lambda E'_{QQ} - H^\circ_{QQ})^{-1} \\ & = (E^\circ_{QQ} - H^\circ_{QQ})^{-1} [1_{QQ} + \sum_{n=1}^{\infty} (-\lambda)^n \{E'_{QQ} (E^\circ_{QQ} - H^\circ_{QQ})^{-1}\}^n] \end{aligned} \tag{23}$$

We take the zeroth and first order part from H^{eff} in equation (11) and substitute equation (23) into equation (11). The results are then

$$
\begin{aligned}
H^{eff}=&H^{\circ}_{PP}+H^{\circ}_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}H^{\circ}_{QP}\\
&-\lambda H^{\circ}_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}E'_{QQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}H^{\circ}_{QP}\\
&+\lambda\,[M_{PP}+M_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}H^{\circ}_{QP}+H^{\circ}_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}M_{QP}\\
&+H^{\circ}_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}M_{QQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}H^{\circ}_{QP}]\\
&+O(\lambda^{2})
\end{aligned}
\tag{24}
$$

Recollecting equations (16) and (20), we find that

$$
H^{eff}=H^{\circ,eff}+\lambda M^{eff}-\lambda H^{\circ}_{PQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}E'_{QQ}(E^{\circ}_{QQ}-H^{\circ}_{QQ})^{-1}H^{\circ}_{QP}
\tag{25}
$$

Equation (25) is valid under the first order approximation. Operator M does not appear in the last term of equation (25). It means that the term is independent of *M*. Actually it only shifts the molecular energy level in the presence of *M*. Note that the first order energy can be evaluated with the zeroth order wavefunctions, C^0_p. Consequently the first order effective Hamiltonian within *P* space is

$$
C^{\circ\dagger}_{P,i}H^{eff}C^{\circ}_{P,j}\approx C^{\circ\dagger}_{P,i}H^{\circ,eff}C^{\circ}_{P,j}+\lambda C^{\circ\dagger}_{P,i}M^{eff}C^{\circ}_{P,j}
\tag{26}
$$

In another words, the property integral is identified as $C^{\circ\dagger}_{p,i}H^{eff}C^{\circ}_{p,j}$. This reduced form is identical with the first order M^{eff} given in equation (21). It implicitly means that the evaluation of first order properties can be performed by slightly altering perturbation expansion diagrams for equation (15).

The M_{pp} term in equation (24) is identified as the effective operator at Hartree-Fock level. The following three terms are effective property operators when a correlation is included. In Bartlett et al.'s many-body perturbation approach,[6] they treat the M as the first perturbation. That is, the M operator is included into $H^0=H^{SCF}+M$. V is the second perturbation. The present analysis implicitly shows that their approach minimize the energy-shift term (last term in equation (25)). Therefore, complexities arising from the presence of both correlation and property operator are nicely avoided.[10]

At this moment we should point out a practical validity of equation (26). To evaluate the first order property with repect to *M*, it is not necessary to know the exact C_p. Instead, a knowledge on C^0_p is sufficiently enough. However at least first order correction to C_p (or corresponding second order correction to property operator) is necessary to evaluate the second order property integrals. The perturbation expansion of C_p is interesting to study.

Another problem is how to obtain the unperturbed wavefunctions, *i.e.*, C^0_p. As mentioned before it is impossible to determine exact C^0_p. Only approximate C^0_p can be obtained via, say, perturbation expansion truncated at a certain order. It is not surely known that how much the use of truncated C^0_p (see equation (26)) affects the first order (with repect to M) properties. An approach of solving the problem is to use a diagramatic expansion method. Brandow[12] showed that the effective property integral, $C^{\circ\dagger}_{p,i}M^{eff}C^{\circ}_{p,j}$ can be determined exactly in the sense of effective matrix elements of M^{eff}. However, it should be further studied whether the first order part of exact H^{eff} (see equation (11)) can be approximated to the first order Hamiltonian (see equation (24)). It may be tentatively argued that diagrams which involve only one *M* operator are sufficient to determine one-electron properties (which means *M* is one-electron operator, for instance, dipole moment). Along the guideline, the diagramatic expansion technique should be studied in more detail.

5. Summary

It has been shown that theoretical investigation on molecular properties can be performed by using the double perturbation method. Furthermore the valence properties can be studied with the aid of the effective Hamiltoniam derived in this work. When the first order molecular properties are desired, a simple effective property operator, M^{eff} can be adopted for the purpose. The M^{eff} is found to adequately consist of a Hartree-Fock level term and correlation terms.

Unlike the higher order properties, *e.g.* polarizability, *etc.*, it has been found that the first order properties of a molecule, *e.g.* dipole moment, *etc.*, can be easily evaluated by simply altering the perturbation diagrams for the unperturbed molecule. An extensive derivation of the practical form of effective operator is currently under way.

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