Advances in
CHEMICAL PHYSICS

EDITED BY

I. PRIGOGINE

AND

STUART A. RICE

VOLUME XLVIII

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CHEMICAL PHYSICS

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

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ANALYSIS AND EVALUATION OF IONIZATION POTENTIALS, ELECTRON AFFINITIES, AND EXCITATION ENERGIES BY THE EQUATIONS OF MOTION—GREEN'S FUNCTION METHOD

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CONTENTS

I. INTRODUCTION

An accurate representation of the electronic structure of atoms and molecules requires the incorporation of the effects of electron correlation,[1] and this process imposes severe computational difficulties. It is, therefore, only natural to investigate the use of new and alternative formulations of the problem. Many-body theory methods[2–4] offer a wide variety of attractive approaches to the treatment of electron correlation, in part because of their great successes in treating problems in quantum field theory, the statistical mechanics of many-body systems, and the electronic properties of solids.

The pioneering work of Kelly[5] on atoms provided the first comprehensive utilization of many-body theory methods to describe electron correlation in these systems. These studies investigated the use of diagrammatic many-body perturbation theory, an approach that appeared to be quite different from the more traditional wave function methods. However, if a summation is made of the diagrams that Kelly found numerically to be the most important, the final result can then be shown to formally be equivalent to the sum-of-the-pairs wave function theories[6] that had previously been proposed by Sinanoğlu,[7] Nesbet,[8] and others. Thus, Kelly's work provided the first calculation of this sum-of-the-pairs variety. The framework of many-body perturbation theory also introduced a new vehicle for gaining physical understanding of the important processes in atomic electronic correlation. Furthermore, the work of Kelly has resulted in the introduction of a vast number of approximations and techniques that have had a wide impact on other approaches to electronic correlation.

Many-body Green's function–equations of motion methods[9, 10] appear to differ more strongly from wave function theories than does many-body perturbation theory. In wave function approaches it is necessary to evaluate energy differences, (excitation energies, ionization potentials, electron affinities, etc.) by determining the individual state energies and then evaluating their differences. On the other hand, the Green's function–equations of motion methods generate these energy differences directly.

There have also been other attempts to evaluate these energy differences directly.[11–13] These methods utilize Rayleigh-Schrödinger perturbation theory to express the energies for both states with a common orbital basis. When the perturbation series for the two state energies are subtracted, it is found that there is a considerable cancellation of identical terms from the individual series.

In all these direct energy difference methods the hope is that by a cancellation of common terms in the individual state energies, greater efficiency and accuracy can be achieved as compared with the traditional single state approaches. In addition, the equations of motion (EOM) and the many-body Green's function (MBGF) methods introduce a different operator algebra and outlook into the problem. This has the disadvantage of making the material quite incomprehensible to many practitioners of atomic and molecular quantum mechanics on one hand, but it also raises the possibility of the generation of new and useful insights into these electronic processes. These methods also introduce a new many-electron basis, to be called the many-body basis, which may be superior in some aspects, both conceptually and in terms of practical calculations, to the traditional configuration set. Throughout the discussion that follows we attempt to bridge the language gap between the many-body theory methods and the traditional wave function approaches by noting many of the strong parallels between the EOM method and traditional wave function theories, similarities that may often be obscured by the different formalism of the former.

A critical analysis of the Green's function–equations of motion method requires the resolution of the following questions: (*1*) Are these Green's function–equations of motion methods formally different from traditional wave function or many-body perturbation theory approaches? Even if they are not, these methods should still be of considerable utility because of the new insights and approaches afforded by them. (*2*) If indeed the answer to the first question is affirmative, it is of interest to determine the manner in which the many-body Green's function–equations of motion methods differ from the more traditional approaches. This is imperative if we are to be able to make meaningful comparisons of calculations that have been performed using the two types of theory. The reduction of these method types to a common language would thereby enhance our physical understanding of the important processes in determining the electronic structure of atomic and molecular systems. (*3*) It is also important to determine which types of systematic approximation can be utilized within the Green's function–equations of motion methods to provide results that are at least as accurate as those obtainable from the most sophisticated configuration interaction treatments now available.

These three questions have motivated a series of our studies of both the formal and computational aspects of the Green's function–equations of motion methods.

It is possible to provide a partial answer to question *1* without ever becoming enmeshed in the complicated details of Green's function–equation of motion theories. The simple reasoning is as follows.[14, 15] Any "black box" that produces the electronic energy levels of a many-electron system must somehow be related to the electronic Hamiltonian for the system or functions of this electronic Hamiltonian. Similarly, any theory that directly provides energy differences must be related to the only quantum mechanical operator whose eigenvalues are the energy differences. This operator is the Liouville operator L, which is defined by its action on an arbitrary operator A by

$$LA \equiv [H, A] = HA - AH$$

where H is the electronic Hamiltonian for the system and the square brackets denote the commutator as usual. Thus the equations of motion–Green's function methods must somehow differ from their wave function counterparts, which are based on the approximate solution of the eigenfunctions and eigenvalues of the electronic Hamiltonian H.

There have been a number of attempts to use Liouville operator techniques to directly evaluate energy differences. These attempts introduce the operator basis set, $\{|i\rangle\langle j|\}$, where $\{|i\rangle\}$ is a set of basis functions. The eigenfunctions of L are then represented as linear superposition of the basis operators,

$$A_\lambda = \sum_{i,j} C_{ij}^\lambda |i\rangle\langle j|$$

These attempts have considered simple problems like the anharmonic oscillator problem in a harmonic oscillator basis or the hydrogen atom in a Gaussian-type basis, generally with rather poor results. The reason for these difficulties is rather clear. Given N basis functions $\{|i\rangle\}$, there are N^2 basis operators $\{|i\rangle\langle j|\}$. Consequently, the equations for the eigenvalues and eigenvectors of L represent equations of rank $N^2 \times N^2$, as compared with the usual equations for the eigenfunctions and eigenvalues of H, which are of the much smaller dimension, $N \times N$. Hence this simple-minded Liouville operator approach merely compounds the mathematical difficulties already inherent in standard Hamiltonian methods.

The Green's function–equations of motion methods can be shown not to suffer from the N^2 problem of the naive use of Liouville operator methods. As discussed below, it is found that the corresponding Green's function–equations of motion methods are problems that generate matrices of dimension $2(N-1)$ when the original basis has been generated from all possibilities that arise from a given orbital basis set. Likewise, it can be shown that the Green's function method can be represented as particular subblocks (submatrices) of the resolvent of the Liouville operator, whereas the equations of motion methods consider the eigenvalues and eigenvectors of the Liouville operator in the same particular representation.

The one-electron Green's function has its poles at the ionization potentials and electron affinities of an atom or molecule, whereas the poles of the two-electron Green's function are located at the excitation energies.[9] Furthermore, the residues of the Green's function at these poles yield information about the transition amplitudes. Two main approaches have been followed in the evaluation of many-body Green's functions. The first involves the evaluation of a diagrammatic perturbative expansion for the Green's function,[16–35] and the latter looks for an approximate solution of the hierarchy of equations[3, 36–41] that the many-body Green's function obeys. The work of Cederbaum and co-workers[16–32] concerning the one-electron Green's function is a particularly noteworthy example of the diagrammatic technique. These investigators have developed a variety of approximations and have provided extensive numerical data concerning the importance of specific diagrams.

The propagator technique, which attempts to solve the hierarchy of equations for the many-body Green's function, has been facilitated by the use of inner projection techniques and the superoperator representation of Goscinski and Lukman.[42] Öhrn and co-workers[38–41] have applied these techniques to the evaluation of ionization potentials of atomic and molecular systems. Several authors[37, 43–48] have discussed the relationship between the EOM and MBGF approaches and have compared the various numerical schemes. Because these many-body EOM and Green's function methods are so closely related formally, the results obtained from one procedure provides information that is pertinent to all.

All calculations discussed here involve the use of a finite (therefore incomplete) set of analytical one-electron basis functions. A specific finite orbital basis set defines a finite set of N_e-electron wave functions or basis configurations that spans a finite-dimensional N_e-electron subspace of the full Hilbert space. Within this finite dimensional space any N_e-electron wave function can be expanded in terms of all the basis configurations (that have the correct symmetry). For almost all systems of interest, when reasonably accurate one-electron basis sets are used, this full N_e-electron basis expansion becomes prohibitively large, and accurate ways must be found of truncating the expansion. Much of the effort in electronic structure theory concentrates on devising better and more concise means of approximating the most important parts of the configuration space for the problem at hand. One of the central goals of this work is to systematically and critically investigate this problem for the equations of motion method.

The equations of motion method has its origins in nuclear physics, where Rowe[10] first developed it as a means of understanding nuclear energy level structure. McKoy and co-workers[49–55] refined the theory for the calculation of electron excitation energies and presented molecular calculations for a variety of different approximation schemes. Simons[56–65] and Yeager[66] independently developed the analogous EOM theory for ionization potentials and electron affinities. The present numerical work[67–72] deals mainly with the ionization potentials–electron affinity (IP–EA) variant of the EOM theory. However, because of the analogous nature of the excitation energy theory, many of the conclusions reached from the IP–EA calculations have immediate applicability to EOM excitation energy calculations. Some excitation energy calculations on simple systems are utilized here to illustrate important facets of the general theory.

Section II develops the EOM theory both for excitation energies and for ionization potentials and electron affinities. After the main EOM equations have been derived, the nature of a complete operator basis set in EOM calculations is determined and is shown to differ from the mathematically complete set. The many-body operator basis is described, and approximations introduced in practical calculations are discussed. There follows an explanation of the various divisions that are utilized to separate the IP–EA operator basis into primary and secondary subspaces. Numerical evidence, presented in Section III, indicates that the traditional division of the EOM operator space into primary and secondary subspaces (and the effectively equivalent partition in Green's function methods) for ionization potentials and electron affinities is not generally adequate. Section II also develops a more extensive IP–EA EOM theory, based on a generalized division of the operator space, which is introduced in view of the difficulties presented in Section III and of recent developments in configurational selection methods[72–75] for generating accurate approximations to the full configuration interaction matrix.

All IP–EA calculations given in Section III involve systems in which the initial state is a closed-shell state and a single determinant is used for a zeroth-order approximation to the ground-state wave function. This restriction to closed-shell ground states and single-determinant, zeroth-order wave functions has been common to nearly all EOM work, as well as to almost all the related propagator and diagrammatic Green's function calculations. In Section III.C, we present results on nitrogen that indicate the need for developing a satisfactory equation of motion—Green's function theory that allows for a multiconfigurational zeroth-order, ground-state wave function (corrected perturbatively). In Section III.F, excitation energy calculations are reported for beryllium, to compare results using a multiconfigurational reference state with the analogous calculations based on a reference wave function having a single determinant. These studies further substantiate the superiority of the multiconfigurational approach. In Section IV we briefly review current attempts[77–79] to devise an approximate theory that incorporates a multiconfigurational ground state and describe what we believe, based on our numerical evidence, to be necessary for a general, truly reliable, and accurate multiconfigurational equations of motion theory.

In Section III.A the differences between the IP–EA EOM methods of Simons[56] and Yeager[66] are analyzed numerically for nitrogen. Section III.B reports EOM ionization potentials for this gas using a series of different orbital basis sets. These results lead to the conclusion that EOM calculations using small basis sets are unreliable, much as is the case for configuration interaction and other traditional methods. This study is of interest because the early EOM results of Simons[57–65] appeared to indicate just the opposite; namely, that EOM calculations using small basis sets provided consistently accurate ionization potentials and electron affinities, presumably because of some cancellation of errors inherent in the method.

Section III.C presents results of a study of certain third-order terms in the EOM equation that had previously been neglected in IP–EA calculations. It is found that some of these terms are reasonably small but not negligible, whereas the inclusion of others in the EOM equation can cause a complete breakdown of the traditional perturbative EOM method for nitrogen when using the standard choice of the primary operator space.

Different choices of the primary space are shown to remedy the difficulties. In Section III.D the 15 to 40 eV photoelectron spectrum for nitrogen, including shake-up lines, is calculated, given the generalized definition of the EOM primary space. The peak intensities as well as peak positions are calculated.

In Section III.E, EOM ionization potentials and electron affinities are compared with accurate configuration interaction (CI) results for a number of atomic and molecular systems. The same one-electron basis sets are utilized in the EOM and CI calculations, allowing for the separation of basis set errors from errors caused by approximations made in the solution of the EOM equation. EOM results are reported for various approximations including those for the extensive EOM theory developed in Section II. Section III.F presents results of excitation energy calculations for helium and beryllium to address a number of remaining difficult questions concerning the EOM method.

Section IV summarizes the major conclusions of these investigations and outlines the extension and generalization of the EOM theory based on the results of our numerical studies.

II. THEORY

A. Derivation of the EOM Equations

Let $|0\rangle$ be the exact N_e-electron ground state of the Born-Oppenheimer Hamiltonian H for a given atomic or molecular system. Likewise, let $|\lambda\rangle$ be some exact excited state of interest for the same system with the same nuclear geometry. The corresponding state energies are denoted E_0 and E_λ, respectively. For excitation energy calculations $|\lambda\rangle$ is an excited N_e-electron state, whereas in ionization potential or electron affinity cases $|\lambda\rangle$ is an (N_e-1)-electron state or an (N_e+1)-electron state, respectively. The commutator of H with the operator $\tilde{O}_\lambda^\dagger=|\lambda\rangle\langle 0|$ is easily evaluated,

$$\begin{aligned}[H,\tilde{O}_\lambda^\dagger]&=H|\lambda\rangle\langle 0|-|\lambda\rangle\langle 0|H\\&=(E_\lambda-E_0)|\lambda\rangle\langle 0|\\&=(E_\lambda-E_0)\tilde{O}_\lambda^\dagger\end{aligned}\tag{1}$$

For IP (EA) calculations, it is necessary to define H to be the N_e-electron Hamiltonian when it acts on N_e-electron states and the $(N_e-1)[(N_e+1)]$-electron Hamiltonian when it operates on $(N_e-1)[(N_e+1)]$-electron states, and so on. This is simply accomplished by defining $H=\sum_M P_M H_M P_M$, where H_M is the M-electron Hamiltonian and P_M is the projection operator onto the space of all M-electron states. When H is expressed in second quantized notation,[2] it automatically has this property.

Equation 1 is an equation of the sort we are seeking; it yields the vertical energy difference $(E_\lambda - E_0)$ directly. One problem in calculating $E_\lambda - E_0$ from (1) is immediately obvious. $\tilde{O}_\lambda^\dagger$ involves $|\lambda\rangle$ and $|0\rangle$, and if these quantities are to be calculated separately, we have not gained anything from (1) over the traditional approach.

1. Primitive EOM Equations

One possible means of circumventing the problem of handling both $|\lambda\rangle$ and $|0\rangle$ is to expand $\tilde{O}_\lambda^\dagger$ in an appropriate set of basis operators,

$$\tilde{O}_\lambda^\dagger = \sum_i C_i^\lambda O_i^\dagger \tag{2}$$

and to determine equations governing the C_i^λ's. One such set of equations is readily obtained upon substituting (2) into (1) and multiplying from the left by the adjoint of one of the basis operators, yielding

$$\sum_j O_i[H, O_j^\dagger]C_j^\lambda = (E_\lambda - E_0)\sum_j O_i O_j^\dagger C_j^\lambda \tag{3}$$

which is an operator matrix eigenvalue equation with eigenvalues $(E_\lambda - E_0)$ and eigenvectors

$$C^\lambda = \begin{bmatrix} C_1^\lambda \\ C_2^\lambda \\ \vdots \end{bmatrix} \tag{4}$$

Equation 3 still presents problems. First, it is an operator equation. Most of the expertise that has been developed in electronic structure calculations has centered on equations involving matrix elements of operators, rather than the operators themselves. Second, and also important, the vast majority of the solutions of (3) are ones in which we have no interest. Within the limited orbital basis set approximation, there are only a finite number n of linearly independent N_e-electron states, or configuration functions, that can be formed. Within this basis, the "exact" N_e-electron energies $E_0, E_1, \ldots, E_{n-1}$ and the corresponding "exact" N_e-electron states, $|0\rangle, \ldots, |n-1\rangle$, are, respectively, the eigenvalues and eigenvectors of the $n \times n$ Hamiltonian matrix (i.e., the solutions of the complete CI problem for the finite orbital basis). For the excitation energy problem there are n^2 operators of the type $|\lambda\rangle\langle\lambda'|$ (where $|\lambda\rangle$ and $|\lambda'\rangle$ are exact N_e-electron states), and it follows that n^2 must be the dimensionality of the space that $\{O_i^\dagger\}$ spans. Hence (3) has n^2 solutions, whereas the original Schrödinger equation for the same finite orbital basis set has only n solutions. A similar difficulty with (3) persists for calculation of ionization potentials or electron affinities.

Despite these difficulties, Lasaga and Karplus[80] have discussed the calculation of excitation energies based on an operator equation related to (3). Simons and Dalgaard[81] have proposed a perturbation approach to a similar operator problem. To date, however, numerical applications have been limited to the analysis of the singlet excitation of ethylene in Pariser-Parr-Pople[82] (PPP) model, a two-level problem.[80]

Both difficulties with (3) are overcome by taking the ground-state expectation value of (3) to produce

$$\sum_j \langle 0|O_i[H,O_j^\dagger]|0\rangle C_j^\lambda = (E_\lambda - E_0)\sum_j \langle 0|O_iO_j^\dagger|0\rangle C_j^\lambda \tag{5}$$

To show that (5) has the desired n solutions as opposed to the n^2 solutions of (3), consider the specific set of basis operators, $\{O_i^\dagger\} = \{|\lambda\rangle\langle\lambda'|\}$, where the states $|\lambda\rangle$ and $|\lambda'\rangle$ are exact N_e-electron states. In terms of this operator basis set, the matrices $\langle 0|O_i[H,O_j^\dagger]|0\rangle$ and $\langle 0|O_iO_j^\dagger|0\rangle$ are readily found to be diagonal. If $O_j^\dagger = |\lambda\rangle\langle 0|$ and $\lambda \neq 0$, then (5) yields

$$\langle 0|O_j[H,O_j^\dagger]|0\rangle C_j^\lambda = (E_\lambda - E_0)\langle 0|O_jO_j^\dagger|0\rangle C_j^\lambda$$

If $O_j^\dagger = |\lambda\rangle\langle\lambda'|$ and $\lambda' \neq 0$ ($\lambda = 0, 1, \ldots, n-1$), then (5) trivially gives $0 = 0$. The remaining case is $O_j^\dagger = |0\rangle\langle 0|$, where the matrix element $\langle 0|O_jO_j^\dagger|0\rangle = 1$ while $\langle 0|O_j[H,O_j^\dagger]|0\rangle = 0$. Thus the operator $|0\rangle\langle 0|$ corresponds to a zero eigenvalue for (5). Therefore, only n basis operators, $|\lambda\rangle\langle 0|$, $\lambda = 0, 1, \ldots, n-1$, contribute nontrivially to (5).

2. *Double Commutator EOM Equations*

Actual numerical calculations introduce double commutator EOM equations[10] for excitation energies and for ionization potentials and electron affinities that, respectively, are

$$\sum_i \langle 0|[O_i,[H,O_j^\dagger]]|0\rangle C_j^\lambda = \omega_\lambda \sum_j \langle 0|[O_i,O_j^\dagger]|0\rangle C_j^\lambda \tag{6}$$

and

$$\sum_j \langle 0|\{O_i,[H,O_j^\dagger]\}|0\rangle C_j^\lambda = \omega_\lambda \sum_j \langle 0|\{O_i,O_j^\dagger\}|0\rangle C_j^\lambda \tag{7}$$

where $\{\ ,\ \}$ is the anticommutator, $\{A,B\}=AB+BA$. Equations 6 and 7 are just simple linear matrix eigenvalue equations with $\omega_\lambda = E_\lambda - E_0$ as eigenvalues and the C_j^λ's (which give $O_\lambda^\dagger$) as eigenvectors. Equations 6 and 7 are often derived by assuming that the adjoint of $O_\lambda^\dagger$ satisfies the annihilation condition

$$O_\lambda|0\rangle = 0 \tag{8}$$

in analogy with raising and lowering operators in the harmonic oscillator problem.[83] If (8) holds, it follows that

$$\langle 0|[H,O_\lambda^\dagger]O_i|0\rangle = \langle 0|O_\lambda^\dagger O_i|0\rangle = 0 \tag{9}$$

Combining (5) and (9) immediately yields (6) and (7). However, Herman and Freed[72] have shown that the annihilation condition (8) is, in general, not satisfied for the excitation energy problem when $|\lambda\rangle$ is of the same symmetry as $|0\rangle$. In fact, the equation $O_\lambda^\dagger|0\rangle = |\lambda\rangle$, which is usually taken to define $O_\lambda^\dagger$, does not hold for $O_\lambda^\dagger$'s that are general solutions of (6). These conclusions result from the realization that the set of operators $\{|0\rangle\langle 0|, |\lambda'\rangle\langle\lambda''|; \lambda',\lambda''\neq 0\}$ ($|\lambda'\rangle, |\lambda''\rangle$ are eigenstates of H) give only zero matrix elements when inserted for O_i or $O_j^\dagger$ in $\langle 0|[O_i,[H,O_j^\dagger]]|0\rangle$ and $\langle 0|[O_i,O_j^\dagger]|0\rangle$. Therefore, the most general $O_\lambda^\dagger$ that satisfies

$$\langle 0|[O_i,[H,O_\lambda^\dagger]]|0\rangle = \omega_\lambda \langle 0|[O_i,O_\lambda^\dagger]|0\rangle \tag{10}$$

is given by[72]

$$O_\lambda^\dagger = |\lambda\rangle\langle 0| + \alpha_{0,0}|0\rangle\langle 0| + \sum_{\lambda',\lambda''\neq 0} \alpha_{\lambda',\lambda''}|\lambda'\rangle\langle\lambda''| \tag{11}$$

for arbitrary values of $\alpha_{0,0}$ and $\alpha_{\lambda',\lambda''}$. This $O_\lambda^\dagger$ does not satisfy $O_\lambda^\dagger|0\rangle = |\lambda\rangle$ and $O_\lambda|0\rangle = 0$ but rather has

$$O_\lambda^\dagger|0\rangle = |\lambda\rangle + \alpha_{0,0}|0\rangle \tag{12}$$

and

$$O_\lambda|0\rangle = \alpha_{0,0}|0\rangle \tag{13}$$