ENERGETICS OF IONIZATION AND EXCITATION PROCESSES (U)

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**MICROCOPY RESOLUTION TEST CHART**
Energetics of Ionization and Excitation Processes

John P. Simons

University of Utah
Salt Lake City, UT

U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27099

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19. KEY WORDS

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20. ABSTRACT

We have made significant developments in the area of quantum chemical methodology. The majority of these developments were aimed at providing our group with state-of-the-art tools for use on the difficult chemical problems in which we are interested. Making use of our new theoretical tools, we have studied the electronic states (stability, bonding character, shapes) of the ground and excited electronic states of several classes of molecular ions and novel reactive intermediates.
Final Technical Report for
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prepared by
John P. Simons, Professor of Chemistry
University of Utah
Salt Lake City, Utah

During the three years this U.S. Army Research Office Contract, we
have achieved even more than was included in our original research pro-
posal. The attached list of published articles which have resulted from
Army support attest to this fact.

We have made significant developments in the area of quantum chemi-
cal methodology. The majority of these developments were aimed at providing
our group with state-of-the-art tools for use on the difficult chemical
problems in which we are interested. Drs. Robert Donnelly, Ron Shepard,
and Ajit Banerjee have been instrumental in these achievements.

Making use of our new theoretical tools, we have studied the electronic
studies (stability, bonding character, shapes - of the ground and excited
electronic states of several classes of molecular ions and novel reactive
intermediates. Included in our investigations were
1) Anions of polar molecules such as LiH\(^-\), BeO\(^-\), LiF\(^-\), and NaH\(^-\). These ions have stable \( ^2\Sigma \) ground states and metastable \( ^2\Pi \) excited states.

2) Small cluster anions such as Li\(_2^\cdot\), Be\(_2^\cdot\), Be\(_3^\cdot\), Be\(_4^\cdot\), Mg\(_2^\cdot\), Mg\(_3^\cdot\), Mg\(_4^\cdot\), and Be Mg\(^-\). The alkaline earth clusters involve the interaction of closed-shell atoms (e.g., Mg is \( 3s^2 \)) which gives rise to very weak interaction energies for the neutral clusters (e.g., Mg\(_2^+\)). However, the addition of an "extra" electron to the lowest empty bonding orbital (e.g., \( 3p\_\sigma^\text{g} \) for Mg\(_2^+\)) gives rise to increased interaction energy and, hence, increased stability for the cluster anion.

3) Unsaturated carbenes which possess low-energy singlet and triplet states whose chemical reactivity patterns vary substantially. H\(_2^\cdot\)CC:, H\(_2^\cdot\)CCC:, \( \text{C}_2\), \( \text{C}_3\), and H\(_2^\cdot\)CCCC: have all been studied. Our goal was to understand the effect of delocalization and aromaticity on the relative energetic stability of the singlet and triplet states.
Publications Acknowledging U.S. Army Research Support

(1979-1981)


"Electronic structure of the Lowest $^1A_1$ and $^3B_1$ States of Cyclopropenylidene", by Ron Shepard, Ajit Banerjee, and Jack Simons. JACS 101, 6174 (1979).


Line shapes of charge-transfer spectra

Jeanne McHale and Jack Simons

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

(Received 9 January 1979)

The theoretical description of condensed-media line shapes of electronic transitions, as developed in earlier papers, is applied to the charge-transfer (CT) spectra of the complexes mesitylene-tricyanoethylene (Me₃TCNE) and anthracene-chloranil (AN:CA). Results are compared with those obtained previously for benzene:iodine (Bz:I), and the factors which contribute to line broadening (inhomogeneous broadening, the Franck-Condon profile, and donor–acceptor vibrational motion) are discussed. The results of an attempt to determine the contributions to the line shape made by intermolecular orbital couplings are presented. In addition, the Bz:I, CT spectrum is reinvestigated, and the question of which ionization potential of benzene is involved is addressed.

1. INTRODUCTION

In earlier publications a theoretical formalism for describing electronic absorption spectra in condensed media was developed. By taking a suitable average (over the solvent molecules' coordinates) of the electric dipole correlation function, the intensity of absorption $I(\omega)$ can be decomposed into zeroth-, first-, and second-order contributions, each of which contains the effects of localized intramolecular dipole transitions as well as those of intermolecular charge transfer. The first- and second-order contributions, which modify the zeroth-order dipole strength, contain the so-called “resonance” and “fluctuation” integrals, respectively, which depend upon the coupling between orbitals on neighboring molecules and fluctuations thereof. The theory has been successfully applied, in a parameterized form, to the spectra of excess electrons in ethanol glass, anthracene anions in glassy anthracene, styrene and cyclooctatetraene anions, NO₃⁻ in several strongly interacting solvents, and to the benzene iodine charge-transfer spectrum. In the charge-transfer (CT) case, the zero-order contribution to the line shape was shown to be given by

$$I(\omega) = \sum_{\alpha \beta} e^{i\mathbf{d} \cdot \mathbf{R}} \sigma_{\alpha \beta} \left[ a_{\alpha}^T \mathbf{U}_{\alpha \beta} \mathbf{U}_{\beta \alpha} a_{\beta} \right]$$

where $a_{\alpha}$ and $a_{\beta}$ are the donor and acceptor molecular orbitals as was shown in Ref. 1.

The first- and second-order parts of $I(\omega)$ have been found in this laboratory to make negligible or small contributions to the line shape in the cases studied previously. In order to further clarify the importance of these terms, a study of the concentration dependence of the Me₃TCNE CT spectrum was undertaken. Since the donor for this complex is totally miscible in common inert solvents, and since the existence of a ternary complex involving two donor molecules has previously been reported, it was hoped that by increasing the mesitylene concentration, the effects of coupling between orbitals on different donor molecules could be observed. In another attempt to search for such donor–donor orbital interactions, the spectrum of AN:CA was also recorded, but in a more limited concentration range.

It is important to note that Eq. (1) gives the absorption intensity for a fixed donor–acceptor separation $R$. However, an important reason for the experimental fact that typical CT spectra are very broad is that, due to the Coulombic interaction term in the excited state energy, the absorption frequency is strongly dependent on the donor–acceptor intermolecular distance. It has been found in this laboratory that, while Eq. (1) alone is sufficient to explain the width of spectra which arise from localized transitions in, for example, styrene and cyclooctatetraene anions, it is unable to fully account for the width of CT spectra. In order to model the homogeneous broadening brought about by intermolecular vibrational motion, a thermal average of the above intensity expression must be performed, using a Boltzmann weighting involving the ground-state donor–acceptor potential described here in terms of the harmonic force constant, $k$, for donor–acceptor stretching:

$$I(\omega) = \int_0^\infty R^2 \exp \left[ -\frac{\beta k}{2} (R - R_0)^2 \right] I(\omega) dR .$$

In this equation is the charge separation in the excited state, which is assumed to be equal to the donor–acceptor center-of-mass distance for the v-v' complex Me₃TCNE and AN:CA. $R_0$ is the value of $R$ corresponding to the equilibrium geometry of the donor–acceptor ground state, and $\beta$ is $(k T)^{-1}$. The factor $R^2$ results from Mulliken's approximation that, neglecting overlap, the electronic transition dipole is proportional...
Electronic Structure of the Lowest $^1A_1$ and $^3B_1$ States of Cyclopropenylidene

Ron Shepard, Ajit Banerjee, and Jack Simons*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received April 16, 1979

Abstract: Multiconfiguration self-consistent field calculations have been performed at several geometries on the lowest $^1A_1$ and $^3B_1$ states of cyclopropenylidene. The effects of hybridization and electron correlation are analyzed at the various geometries. These model prototype calculations reveal strong correlation effects in the aromatic singlet state as well as a singlet-triplet potential surface crossing which may play a role in the chemical reactivity of analogous chemical reactions involving insertion of singlet or triplet reagents into triple bonds. It is demonstrated that multiconfigurational wave functions are absolutely necessary to obtain a qualitative description of the two spin states of these unsaturated carbenes.

1. Introduction

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated carbenes. Theoretical research in our laboratory and theoretical and experimental work in other laboratories has focused on the very important question of singlet-triplet energy differences of isolated carbenes. Indeed, postulation of one-step stereospecific addition of singlet carbenes and two-step nonstereospecific addition of triplet carbenes to olefins has played a dominant role in the experimental determination of the spin state of carbenoid intermediates. In this report, we attempt to gain a fundamental understanding of a particular carbene reaction that appears to involve a nonstereospecific singlet addition of a cyclic carbene. Diphenylcyclopropenylidene appears to insert into both dimethyl maleate and dimethyl fumarate to produce the same spiropentene, thereby suggesting a triplet-like mechanism. However, the carbene itself is gen-
Polarization Green's Function with Multiconfiguration
Self-Consistent-Field Reference States

AJIT BANERJEE, JOHN W. KENNEY, III, AND JACK SIMONS*
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstracts

The polarization Green's-function formalism in the superoperator notation of Goscinski and Lukman is re-derived using a multiconfiguration self-consistent-field (MC-SCF) reference state to establish the superoperator metric. The potential advantages of employing this more general reference state in Green's-function theories and certain inherent weaknesses associated with the traditional Hartree-Fock or Rayleigh-Schrödinger perturbation theory reference state choices are briefly discussed. The Hermiticity of the superoperators is analyzed within the framework of the MC-SCF reference state. Using a concept of order appropriate for this reference state choice, explicit formulas and computational procedures for the implementation of this Green's-function theory are presented and specialized to include terms consistent through second order.

I. Introduction

In the last decade, Green's-function approaches to the direct calculation of electronic excitation energies and other spectral properties have been employed with considerable success to many atomic and molecular systems [1-18]. Electron attachment and detachment processes (i.e., ionization processes) also have been studied extensively with Green's-function methods [9-11, 19-27]. This paper focuses on the development of a new Green's-function approach in which the

* Camille and Henry Dreyfus Fellow.

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Analysis of the "charge resonance" transition in anthracene dimer anion

Jeanne McHale and Jack Simons

Chemistry Department, University of Utah, Salt Lake City, Utah 84112
(Received 20 August 1979; accepted 24 September 1979)

The experimentally observed "charge resonance" transition of anthracene dimer anion is explained in terms of the resonance interaction of the lowest unoccupied orbitals of neighboring anthracene molecules. The distortion energies of the anthracene molecule and anion are shown to make an important contribution to the CR energy. The numerical estimate of the resonance integral, based on the experimental absorption energy of the dimer anion, is shown to be related to that which is appropriate for a calculation of electron mobility in crystalline anthracene.

I. INTRODUCTION

Shida and Iwata have studied the electronic absorption spectra of γ-irradiated solutions of dianthracene in a low-temperature (77 °K) matrix of methyltetrahydrofuran (MTHF). Dianthracene is a composite molecule made up of two anthracene molecules in a sandwich configuration, with σ bonds connecting the equivalent 9 and 10 positions of each molecule. Shida and Iwata bleached dilute γ-irradiated solutions of dianthracene and observed the resulting optical absorption spectrum to be very nearly a superposition of the spectra of the isolated anthracene molecule and anthracene anion. In addition, a broad absorption occurring between about 5000 and 10 000 cm⁻¹ (-0.6-1.2 eV) with a peak at 6000 cm⁻¹ (0.72 eV) was observed. Since the absorption in this region was unlike the doublet that would have been observed for dianthracene anion, and because the rest of the spectrum showed peaks which could be assigned to anthracene molecules and anions, Shida and Iwata explained the absorption commencing at 5000 cm⁻¹ in terms of a "charge resonance" transition of a weakly interacting anthracene dimer anion involving an anthracene molecule and anion which are no longer held together by σ bonds.

The dimer anion results from the reaction of which minimizes the energy of the molecule being represented by the internal coordinates Q. The subscripts refer to sites 1 and 2, which are assumed to be 3.4 Å apart. To consider the geometry which minimizes the energy of the molecule, we must keep in mind that the equilibrium geometry, denoted by the internal coordinates Q, is not necessarily the same for the anion as for the molecule. The geometry which minimizes the energy of the molecule will be represented by Q, (planar), and that which minimizes the energy of the anion be given by Q, (nonplanar). We consider the zeroth-order ground state to consist of a planar molecule at site 1 and a nonplanar anion at site 2:

$$\phi^{0}_1(r, Q_1) = \phi^{0}(r, Q, Q_1)$$  \hspace{1cm} (3)

The zeroth-order excited state is composed of a planar anion at site 1 and a nonplanar molecule at site 2:

$$\psi^{0}_2 = \psi_{2}(r, Q_1, Q_2)$$  \hspace{1cm} (3)

If these two states are allowed to interact, the perturbed ground- and excited-state energies are obtained by diagonalizing the configuration interaction (CI) matrix $H$:

$$H = \begin{bmatrix} \langle \phi^{0}_1 | H | \phi^{0}_1 \rangle & \langle \phi^{0}_1 | H | \phi^{0}_2 \rangle \\ \langle \phi^{0}_2 | H | \phi^{0}_1 \rangle & \langle \phi^{0}_2 | H | \phi^{0}_2 \rangle \end{bmatrix}$$  \hspace{1cm} (4)

To simplify the calculation, zero overlap of wave functions on different sites is assumed. In this approximation, the $H_{12}$ matrix element is just the sum of the ground-state equilibrium energies of an undistorted
Should one use complex basis functions in coordinate rotation calculations on molecules?

Jack Simons

Chemistry Department, University of Utah, Salt Lake City, Utah 84112
(Received 15 January 1980; accepted 28 March 1980)

In applying the coordinate rotation method (CRM) to electron–molecule scattering resonances, one attempts to find the complex eigenvalues \( (Z_e) \) corresponding to square integrable eigenfunctions \( \psi_e \) of the rotated Hamiltonian \( H_r \). \( H_r \) is obtained from the conventional Hamiltonian by scaling the electronic coordinates \( r \) by the complex quantity \( \eta = r - R, \eta \).

For a diatomic molecule whose nuclei have charges \( Z_A \), \( Z_B \) and positions \( R_A \), \( R_B \), \( H_r \) contains kinetic energy \( \eta^2 / 2 M \nabla (r_1) \), electron-electron interactions \( \eta^2 / 2 \nabla (r_1, r_2) \), and electron-nuclei interactions \( -\eta^2 / 2 \nabla (Z_A, r_1) \), \( -\eta^2 / 2 \nabla (r_1, Z_A) \), \( -\eta^2 / 2 \nabla (Z_B, r_2) \), \( -\eta^2 / 2 \nabla (r_2, Z_B) \).

The desired resonance eigenvalues of \( H_r \) are usually found by expanding \( \psi_e (r) \) in some basis of square integrable eigenfunctions \( \{ \phi_e \} \) which are themselves real and \( \eta \)-independent. If the basis set \( \{ \phi_e \} \) is complete, this is a perfectly reasonable expansion to make. However, in practical applications of the CRM to electron–molecule scattering, the set \( \{ \phi_e \} \) usually consists of a finite number of \( (N+1) \) electron Slater determinants involving molecular orbitals expressed in terms of atomic orbitals centered at \( R_A \) and \( R_B \). This set is certainly not complete, so it is quite natural to ask whether it is even reasonable to employ this particular choice of basis.

It is well known that the lowest energy eigenfunctions of the unscaled Hamiltonian \( H(\eta = 1) \) possess high amplitude near each of the two nuclei. This arises because the Schrödinger equation is dominated, for \( r_A = R_A \), by \( -\nabla^2 Z_A / 2 r_A - Z_A / 2 r_A \), which, just as in the hydrogen atom, gives large (is) amplitude in the space near \( R_A \). In choosing atomic orbital basis sets for use in standard variational calculations on \( H(\eta = 1) \), it is important to include functions which properly represent the locally high amplitudes near \( R_A \), because of the strong influence of this part of the electron density on the total electronic energy. It is most common to employ either Slater or “tight” contracted Gaussian basis functions centered at \( R_A \) and \( R_B \).

In considering the best choice of basis for treating the rotated \( H_r \), it therefore seems important to guarantee that the resultant approximations to \( \psi_e (r) \) display high orbital amplitude at points dictated by \( H_r \). Because the electron–nuclei interactions in \( H_r \) have singularities at \( r_A = \eta R_A \), it is probably quite important to include in any reasonable atomic orbital basis (Slater or Gaussian) functions centered at the complex positions \( \eta R_A \) and \( \eta R_B \). This is easily achieved in electron–atom problems by simply choosing the coordinate origin to be at the atomic nucleus; then \( \eta R_A = R_A = 0 \). For molecules, this choice of origin does not remove the problem

Because the most common procedures for locating resonance energies \( (Z_e) \) within the CRM involve following eigenenergies of \( H_r \) as \( \eta \) is varied, all \( \eta \)-dependent atomic–basis integrals (one- and two-electron) arising in the computation (e.g., by configuration interaction) of \( Z_e \) need to be recomputed. We therefore suggest that one employ only a few (e.g., one per nucleus) “tight” basis functions centered at \( \eta R_A \), \( \eta R_B \), while using large numbers of atomic orbitals centered at \( R_A \), \( R_B \). The latter basis functions should be capable of describing the resonance wave function \( \psi_e (r) \) in the “valence” region and for values of \( \eta \) which are on the “exterior” of the target molecule. Moreover, only those integrals which involve the functions centered at \( \eta R_A \) or \( \eta R_B \) need to be recomputed as \( \eta \) is varied.

If the basis \( \{ \phi_e \} \) is not able to describe high orbital amplitudes at \( \eta R_A \), it then spurious imaginary contributions can arise in the desired resonance energies and even in the bound states which should be \( \eta \)-independent. We believe that the “compromise basis” described above has potential for eliminating the undesirable spurious features. Rescigno et al. and Junker et al. have, in fact, already employed an approach which is similar to that being proposed here. For example, Rescigno et al. employ a Slater determinant basis in which the \( N \) “bound” orbitals of the target atom are not even rotated (in our language, this would be analogous to expanding the \( N \) bound orbitals in terms of the basis orbitals centered at \( \eta R_A \), which essentially “undoes” the effect of rotating these \( N \) electrons in \( H_r \)). Only the “active” \( N + 1 \)st orbital is rotated. There is only a slight difference between what we are proposing and what
Application of the Coordinate Rotation Method to Metastable Atom–Diatom Scattering Resonances

ZLATKO BAČIĆ* AND JACK SIMON†
Chemistry Department, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract

The procedure for applying the coordinate rotation device to the coupled-channel scattering equations is presented. Results of applications of the method to resonances occurring in low-energy atom–diatom collision processes are presented. In particular, rotational Feshbach resonances in model (homogeneous) potentials which have also been studied by Grabenstetter and Le Roy are examined within this novel approach.

1. Introduction

The so-called coordinate rotation method (CRM) [1] has been used successfully to study scattering resonances in electron–atom and electron–molecule collisions [2, 3]. More recently, it has also been used to study rotational predissociation in H\textsubscript{2} [4]. In the present work, we report the first application of this technique to resonances which occur in closed-shell atom–diatom collisions. Unlike the H\textsubscript{2} rotational predissociation problem, the three-atom situation addressed here involves motion on a three-dimensional potential energy surface (H\textsubscript{2} involves only a one-dimensional curve). As a result, the diatom’s internal (vibrational–rotational) energy and (rotational) angular momentum must be explicitly coupled to the corresponding quantities of the incident atom. The proper coupling of energy and angular momentum (asymptotic) basis functions yields the usual set of coupled-channel equations. These coupled differential equations, upon application of the coordinate rotation device, give rise to a set of coupled-complex differential equations for the components of the scattering wavefunction which correspond to various channels.

In Sec. 2 we obtain the set of coupled-channel differential equations for a closed-shell atom–diatom collision and we demonstrate how these equations are transformed upon coordinate rotation. In Sec. 3, we indicate how the resulting coupled-complex differential equations can be solved either by a finite difference method or by an expansion of the (radial) scattering wave amplitudes in terms of square-integrable basis functions. A method for identifying the desired metastable resonance energy (which is complex) and its accompanying wavefunction is also outlined in Sec. 3. Section 4 contains our concluding remarks.

* University of Utah Graduate Research Fellow.
† Camille and Henry Dreyfus Fellow and John Simon Guggenheim Fellow.

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Application of the Coordinate Rotation Method to Metastable Atom–Diatom Scattering Resonances

ZLATKO BAČIĆ* AND JACK SIMON†
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* University of Utah Graduate Research Fellow.
† Camille and Henry Dreyfus Fellow and John Simon Guggenheim Fellow.
The Electronic Structure of Singlet Cyclopentadienylidene

RON SHEPARD* AND JACK SIMONS†

Chemistry Department, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract

We have carried out ab initio multiconfigurational self-consistent field calculations on the lowest singlet state of the carbene C₅H₄. We find that there are, along a restricted geometry deformation coordinate, two local energy minima corresponding to localized and delocalized σ bonds having 4π and 6π electrons, respectively. The role of 4n + 2 resonance in determining the nature of the electronic structure and reactivity of this carbene is analyzed and compared with that of other carbenes.

1. Introduction

In previous studies of the electronic structure of linear and cyclic carbenes [1–3], the importance of orbital hybridization of the electron-deficient carbene carbon, electron delocalization, and electron correlation have been investigated in order to gain a basic understanding of the nature of these important reaction intermediates. The most important correlation configuration of the 1A₁ states (within C₂ᵥ geometries) of methylene (CH₂), cyclopropenylidene (C₃H₂), and linear unsaturated carbenes can be described as a double excitation from an occupied a₁ orbital into a vacant b₂ orbital of the dominant configuration. A comparison [1] of the importance of this a₁ → b₂ configuration in the cyclic C₃H₂ and the other systems [2, 3] shows that this correlation is less important in C₃H₂. In the C₃H₂ system, the b₂ configuration has 4π electrons and thus acquires antiaromatic character while the dominant a₁ configuration has 2π electrons and hence possesses aromatic stability because it satisfies the "4n + 2 rule." This indicates that for this cyclic carbene the aromatic nature of the correlation configuration must be considered along with the effects of delocalization and hybridization.

In this brief report, the importance of aromatic factors is investigated for another cyclic carbene—cyclopentadienylidene. In contrast to the C₃H₂ carbene, both the delocalization effects and the aromatic nature of the a₁ → b₂ configuration work in accord to increase the importance of this configuration. The result is that the b₂ configuration becomes not only more important than in CH₂ and C₃H₂ but it actually becomes the dominant configuration at some molecular geometries examined in this study.

* Present address: Battelle Memorial Institute, Columbus, Ohio 43201.
† Camille and Henry Dreyfus Fellow, John Simon Guggenheim Fellow.
Multiconfigurational Wavefunction Optimization Using the Unitary Group Method

RON SHEPARD and JACK SIMON
Chemistry Department, University of Utah, Salt Lake City, Utah 84112, U.S.A.

Abstract

We have successfully used graphical unitary group methods to implement efficiently both multiconfigurational self-consistent field and configuration interaction ab initio quantum chemical computer programs. We indicate how these group theoretic methods improve efficiency and we demonstrate their utility on the ground and excited states of a model problem for which a full-configuration interaction calculation can be performed.

I. Introduction

Using the exponential-\(i\)-lambda (EIL) method [1] for wavefunction optimization and the graphical unitary group method [2] for the calculation of one- and two-particle density matrix elements, we have performed multiconfiguration self-consistent field (MCSCF) calculations on the ground and excited states of the Be atom at several levels of sophistication as a model calculation. We show how the global convergence problems of the EIL method may be overcome in these cases. We further show that although completely flexible configuration selection is not easily achieved within the unitary group formalism which we have implemented, limited distinct row tables based only on occupation restrictions are easily constructed. The resulting configuration lists are neither so large that chemical insights are lost nor are they so restrictive that chemical accuracy is sacrificed. We show how the graphical unitary group method may be used to construct efficiently the matrix elements required in the EIL MCSCF method without explicitly performing the two-particle density matrix construction. Because the EIL method possesses very good local convergence properties, not only accurate energy expectation values but also very accurate MCSCF wavefunctions are reported.

The MCSCF wavefunction is a multiconfiguration wavefunction:

\[
|\psi^{mc}\rangle = \sum_{K} C_{K} |K\rangle
\]  

(1)

where both the configuration mixing coefficients \(C_{K}\) and the orbitals are optimized to give the lowest energy expectation value. A property of the MCSCF wavefunction is that it satisfies the generalized Brillouin theorem [3] (GBT):
The Coupled-Cluster Method with a Multiconfiguration Reference State

AJIT BANERJEE AND JACK SIMONS*
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Abstracts

The coupled-cluster approach to obtaining the bond-state wave functions of many-electron systems is extended, with a set of physically reasonable approximations, to admit a multiconfiguration reference state. This extension permits electronic structure calculations to be performed on correlated closed- or open-shell systems with potentially uniform precision for all molecular geometries. Explicit coupled cluster working equations are derived using a multiconfiguration reference state for the case in which the so-called cluster operator is approximated by its one- and two-particle components. The evaluation of the requisite matrix elements is facilitated by use of the unitary group generators which have recently received wide attention and use in the quantum chemistry community.

Le procédé des amas couplés pour obtenir des fonctions d'onde pour les états liés d'un système à \( N \) électrons a été généralisé dans le cadre d'un nombre d'approximations raisonnables du point de vue physique, pour utiliser un état de référence multiconfigurationnel. Cette extension permet des calculs de la structure électronique pour des systèmes à couches fermées ou ouvertes correlées avec une précision qui est uniforme pour toutes les géométries moléculaires. Des équations explicites sont obtenues avec un état de référence multiconfigurationnel dans le cas où le soi-disant opérateur d'amas est remplacé par ses composantes à une et deux particules. Le calcul des éléments matriciels nécessaires est facilité par l'utilisation des générateurs du groupe unitaire.


1. Introduction

A cluster expansion formalism was developed by Coester [1] for treating \( N \)-fermion nuclear systems. Cizek [2] and others [3] expressed this formalism such that it was more suitable for electronic structure calculations on closed-shell systems and actually applied the resulting equations in an ab initio framework to the ground states of a few closed-shell molecules [4]. More recently, attempts have been made to extend the formalism to open-shell systems [5, 6] and Freeman et al. [7] have applied the method to the uniform electron gas.

* Camille and Henry Dreyfus Teacher-Scholar, John Simon Guggenheim Fellow.