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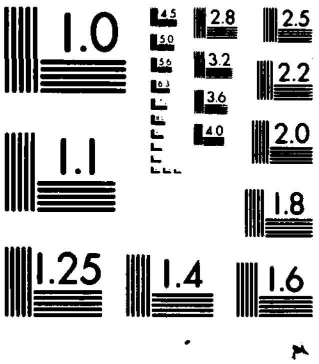

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We have made significant developments in the area of quantum chemical methodology. The majority of these developments were aimed at providing our group with state-of-the-art tools for use on the difficult chemical problems in which we are interested. Making use of our new theoretical tools, we have studied the electronic ~~studies~~ properties (stability, bonding character, shapes) of the ground and excited electronic states of several classes of molecular ions and novel reactive intermediates.

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Final Technical Report for

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prepared by

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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 proposal. 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 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. 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^-, Be_2^-, Be_3^-, Be_4^-, Mg_2^-, Mg_3^-, Mg_4^-, 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., $3p_{\sigma g}$ 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_2CC:, H_2CCC:, :, , and H_2CCCC: 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.

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(1979-1981)

"Lineshapes of charge-transfer spectra", by Jeanne McHale and Jack Simons.
J. Chem. Phys. 70, 4974-4981 (1979).

"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).

"Polarization Green's Function with Multiconfiguration Self-Consistent-Field Reference States", by Ajit Banerjee, John W. Kenney, III, and Jack Simons.
Int. J. Quantum Chem. XVI, 1209-1237 (1979).

"Analysis of the "charge resonance" transition in anthracene dimer anion" by Jeanne McHale and Jack Simons.
J. Chem. Phys. 72, 425 (1980).

"Should one use complex basis functions in coordinate rotation calculations on molecules", by Jack Simons.
J. Chem. Phys. 73, 992-993 (1980).

"Application of the Coordinate Rotation Method to Metastable Atom-Diatom Scattering Resonances", by Zlatko Bacic and Jack Simons.
Int. J. Quant. Chem. Symp. 14, 467-475 (1980).

"The Electronic Structure of Singlet Cyclopentadienylidene", by Ron Shepard and Jack Simons.
Int. J. Quant. Chem. 14, 349-353 (1980).

"Multiconfigurational Wavefunction Optimization Using the Unitary Group Method", by Ron Shepard and Jack Simons.
Int. J. Quant. Chem. 14, 211-228 (1981).

"The Coupled-Cluster Method with a Multiconfiguration Reference State", by Ajit Banerjee and Jack Simons.
Int. J. Quant. Chem. XIX, 207-216 (1981).

Line shapes of charge-transfer spectra

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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:tetracyanoethylene (Mes:TCNE) and anthracene:chloranil (AN:CA). Results are compared with those previously published for benzene:iodine (Bz:I_2), 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_2 CT spectrum is reinvestigated, and the question of which ionization potential of benzene is involved is addressed.

I. INTRODUCTION

In earlier publications[1–3] a theoretical formalism for describing electronic absorption spectra in condensed media was developed. By taking a suitable average[4] (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,[1] anthracene anions in glassy anthracene,[1] styrene and cyclooctatetraene anions,[2] NO_2^- in several strongly interacting solvents,[5] and to the benzene iodine charge-transfer spectrum.[2] In the charge-transfer (CT) case, the zeroth-order contribution to the line shape was shown to be given by

$$I_R^{(0)}(\omega)=\frac{N_D}{Z_v}\sum_{v_A,\bar{v}_A,v_D,\bar{v}_D} e^{-\beta E_v^{00}} \times F_{\delta\to\alpha}^2(v_A,\ \bar{v}_A,\ v_D,\ \bar{v}_D)\, r^2_{0_D\delta,R_A\alpha}\, G[\omega, \Delta E_{\delta\to\alpha}(R)+\Delta E_v, \sigma_{DA}] \qquad (1)$$

for a donor (D) at the origin and an acceptor (A) at R. $F_{\delta\to\alpha}(V_A, \bar{V}_A, V_D, \bar{V}_D)$ is a product of the Franck–Condon factors for the ionization of the donor molecule to give the donor cation and the addition of an electron to an acceptor molecule to give the acceptor anion. $r_{0_D\delta,R_A\alpha}$ is the transition dipole between the donor molecular orbital δ and the acceptor molecular orbital α, E_v^{00} is the initial vibrational energy of the unionized donor and acceptor, $\Delta E_{\delta\to\alpha}(R)$ and ΔE_v are the electronic and vibrational excitation energies, respectively, and $G[\omega, \omega', \sigma_{DA}]$ is a Gaussian of width σ_{DA} centered at ω'. The inhomogeneous broadening constant, σ_{DA}, can be expressed in terms of fluctuations in the energy levels of 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 Mes:TCNE 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,[6] 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:

$$I(\omega)\propto\int_0^\infty R^2\exp[-(\beta k/2)(R-R_{eq})^2]\, I_R(\omega)\, dR\,. \qquad (2)$$

R 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 π-π^* complexes Mes:TCNE and AN:CA. R_{eq} is the value of R corresponding to the equilibrium geometry of the donor–acceptor ground state, and β is $(k_B T)^{-1}$. The factor R^2 results from Mulliken's approximation that, neglecting overlap, the electronic transition dipole is proportional

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[b] Camille and Henry Dreyfus Teacher–Scholar, David P. Gardner Fellow.

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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.

I. Introduction

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated carbenes. Theoretical research in our laboratory[1] and theoretical and experimental work in other laboratories[1-5,13] 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.[3] 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.[4] 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-

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* Camille and Henry Dreyfus Teacher-Scholar, David P. Gardner Research Fellow, John Simon Guggenheim Fellow.

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Polarization Green's Function with Multiconfiguration Self-Consistent-Field Reference States

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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.

Le formalisme des fonctions de Green de polarisation dans la notation utilisant les superopérateurs de Goscinski et Lukman a été réétabli avec un état de référence MC-SCF pour obtenir le métrique des superopérateurs. Les avantages potentiels de cet état de référence plus général ainsi que certains points faibles inhérents associés aux états de référence utilisés traditionnellement dans les théories de perturbation Hartree–Fock ou Rayleigh–Schrödinger sont discutés brièvement. L'hermiticité des superopérateurs est analysée dans le cadre des états de référence MC-SCF. Utilisant une notion d'ordre propre à cet état de référence on présente des formules explicites et des procédés de calcul pour la réalisation de cette théorie des fonctions de Green, qui sont spécialisés pour inclure des termes consistants jusqu'au second ordre.

Der Formalismus für Green'sche Funktionen von Polarisierungstyp in der Superoperatorbezeichnung von Goscinski und Lukman wird mittels eines MC-SCF-Referenzzustands hergeleitet. Die möglichen Vorteile mit diesem allgemeineren Referenzzustand und gewisse mit den in den traditionellen Hartree–Fock- oder Rayleigh-Schrödinger-Störungstheorien verwendeten Referenzzuständen verbundene eigene Schwächen werden kurz diskutiert. Die Hermitizität der Superoperatoren wird im Rahmen des MC-SCF-Referenzzustands analysiert. Mittels eines für diesen Referenzzustand geeigneten Ordnungsbegriffs werden explizite Formeln und Rechnungsverfahren für die Implementierung dieser Theorie von Green'schen Funktionen vorgelegt und spezialisiert um Glieder bis zur zweiten Ordnung einzuschliessen.

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

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

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(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 excitation 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[1] 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 mobile electrons (formed by bleaching at 520 nm) with the σ-bonded dianthracene anion. According to Shida and Iwata, the charge resonance (CR) absorption involves as upper and lower states the symmetric and antisymmetric dimer anion wave functions, which are constructed from the ground-state molecule (ϕ_0) and anion (ψ_0) wave functions at sites 1 and 2:

$$\Phi_{00}^{\pm} = 1/\sqrt{2}\,(\phi_0^1\psi_0^2 \pm \psi_0^1\phi_0^2)\ . \tag{1}$$

Shida and Iwata calculated the intensities and positions of peaks in the spectrum of the dimer anion using the self-consistent-field molecular orbitals (SCF-MO's) of anthracene molecule as basis orbitals, assuming the short and long symmetry axes of the two molecules to be parallel, and estimating the intermolecular distance to be 3.4 Å or about twice the van der Waals' radius of a typical π system. They predict that the charge resonance absorption will occur at about 4000 cm^{-1}, compared to the experimentally observed energy of 5000 to 10 000 cm^{-1}.

In Sec. II, we show how the CR energy can be more reasonably accounted for in terms of the resonance energy of the lowest unoccupied molecular orbitals (LUMO's) on the neighboring anthracenes as well as in terms of the geometrical distortion energies of the planar anion and nonplanar molecule. This distortion energy, which shall be shown to make an important contribution to the CR energy, was not accounted for in the calculation of Shida and Iwata, who assumed planar geometries for both molecules in the dimer.

II. ANALYSIS OF THE CHARGE RESONANCE ENERGY ΔE_{CR}

In the following, we consider the CR transition to involve dimer states which can be described in terms of products of a ground-state anthracene molecule wave function $\psi_{1,2}^0(r, Q)$ and a ground-state anthracene anion wave function $\psi_{1,2}^-(r, Q)$. The subscripts refer to sites 1 and 2, which are assumed to be 3.4 Å apart. To consider the energy of the *vertical* CR transition, 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. Let the geometry which minimizes the energy of the molecule be represented by Q_p (planar), and that which minimizes the energy of the anion be given by Q_n (nonplanar). We consider the zeroth-order ground state to consist of a planar molecule at site 1 and a nonplanar anion at site 2:

$$\Psi_g^{(0)} = \psi_1^0(r, Q_p)\psi_2^-(r, Q_n)\ . \tag{2}$$

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

$$\Psi_e^{(0)} = \psi_1^-(r, Q_p)\psi_2^0(r, Q_n)\ . \tag{3}$$

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

$$\underline{H} = \begin{bmatrix} \langle\Psi_g^{(0)}|H|\Psi_g^{(0)}\rangle & \langle\Psi_g^{(0)}|H|\Psi_e^{(0)}\rangle \\ \langle\Psi_g^{(0)}|H|\Psi_e^{(0)}\rangle & \langle\Psi_e^{(0)}|H|\Psi_e^{(0)}\rangle \end{bmatrix}\ . \tag{4}$$

To simplify the calculation, zero overlap of wave functions on different sites is assumed. In this approximation, the H_{11} matrix element is just the sum of the ground-state equilibrium energies of an undistorted

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Should one use complex basis functions in coordinate rotation calculations on molecules?

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(Received 15 January 1980; accepted 28 March 1980)

In applying the coordinate rotation method[1] (CRM) to electron–molecule[2] scattering resonances, one attempts to find the complex eigenvalues (Z_α) corresponding to square integrable eigenfunctions (ψ_α) of the rotated Hamiltonian H_η. H_η is obtained from the conventional Hamiltonian by scaling the electronic coordinates $\mathbf{r}_i$ by the complex quantity $\eta(\mathbf{r}_i - \mathbf{r}_i\eta)$. For a diatomic molecule whose nuclei have charges Z_A, Z_B and positions $\mathbf{R}_A$, $\mathbf{R}_B$. H_η contains kinetic energy $(-\eta^2/2\sum_i^N \nabla \mathbf{r}_i^2)$, electron–electron interactions $(\eta\sum_{i<j}^N r_{ij}^{-1})$, and electron–nuclei interactions $(-\eta\sum_i^N Z_A|\mathbf{r}_i - \eta^{-1}\mathbf{R}_A|^{-1} - \eta\sum_i^N Z_B|\mathbf{r}_i - \eta^{-1}\mathbf{R}_B|^{-1})$. The desired resonance eigenvalues of H_η are usually found by expanding $\psi_\alpha(\mathbf{r})$ in some basis of square integral functions $(\psi_\alpha \cong \sum_k C_k(\eta)\phi_k(\mathbf{r}))$ which are themselves real and η-independent. If the basis set $\{\phi_k(\mathbf{r})\}$ is complete, this is a perfectly reasonable expansion to make. However, in practical applications of the CRM to electron–molecule scattering, the set $\{\phi_k\}$ usually consists of a finite number of $(N+1)$ electron Slater determinants involving molecular orbitals expressed in terms of atomic orbitals centered at $\mathbf{R}_A$ and $\mathbf{R}_B$. 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[3] 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 $\mathbf{r}_i = \mathbf{R}_A$, by $-\frac{1}{2}\nabla^2\mathbf{r}_i^2 - Z_A|\mathbf{r}_i - \mathbf{R}_A|^{-1}$ which, just as in the hydrogen atom, gives large (1*s*) amplitude in $\mathbf{r}_i$ space near $\mathbf{R}_A$. 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 $\mathbf{R}_A$, because of the strong influence of this part of the electron density on the total electronic energy. It is most common to employ either 1*s* Slater or "tight" contracted Gaussian basis functions centered at $\mathbf{R}_A$ and $\mathbf{R}_B$.

In considering the best choice of basis for treating the rotated H_η, it therefore seems important to guarantee that the resultant approximations to $\psi_\alpha(\mathbf{r})$ display high orbital amplitude *at points dictated by* H_η. Because the electron–nuclei interactions in H_η have singularities at $\mathbf{r}_i = \eta^{-1}\mathbf{R}_{A,B}$, it is probably quite importnat to include in any reasonable atomic orbital basis (Slater or Gaussian) functions centered at the *complex* positions $\eta^{-1}\mathbf{R}_A$ and $\eta^{-1}\mathbf{R}_B$. This is easily achieved in electron–atom problems by simply choosing the coordinate origin to be at the atomic nucleus; then $\eta^{-1}\mathbf{R}_A = \mathbf{R}_A = 0$. For molecules, this choice of origin does not remove the problem.

Because the most common procedures[1,2] for locating resonance energies (Z_α) within the CRM involve following eigenenergies of H_η as η is varied, all η-dependent atomic-basis integrals (one- and two-electron) arising in the computation (e.g., by configuration interaction) of Z_α need to be recomputed. We therefore suggest that one employ only a few (e.g., one per nucleus) "tight" basis functions centered at $\eta^{-1}\mathbf{R}_A$, $\eta^{-1}\mathbf{R}_B$, while using large numbers of atomic orbitals centered at $\mathbf{R}_A$, $\mathbf{R}_B$. The latter basis functions should be capable of describing the resonance wave function $\psi_\alpha(\mathbf{r})$ in the "valence" region and for values of $\mathbf{r}$ which are on the "exterior" of the target molecule. Moreover, only those integrals which involve the functions centered at $\eta^{-1}\mathbf{R}_{A \text{ or } B}$ need to be recomputed as η is varied.

If the basis $\{\phi_k\}$ is not able to describe high orbital amplitudes at $\eta^{-1}\mathbf{R}_{A,B}$ then spurious imaginary contributions[4] can arise in the desired resonance energies and even in the bound states which should be η-independent. We believe that the "compromise basis" described above has potential for eliminating the undesirable spurious features. Rescigno *et al.*[4] and Junker *et al.*[4] 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 $\eta^{-1}\mathbf{R}_{A,B}$, which essentially "undoes" the effort of rotating these N electrons in H_η). 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

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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_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_2^- rotational predissociation problem, the three-atom situation addressed here involves motion on a three-dimensional potential energy surface (H_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.

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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_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_2^- rotational predissociation problem, the three-atom situation addressed here involves motion on a three-dimensional potential energy surface (H_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.

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The Electronic Structure of Singlet Cyclopentadienylidene

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Abstract

We have carried out *ab initio* multiconfigurational self-consistent field calculations on the lowest singlet state of the carbene C_5H_4. We find that there are, along a restricted geometry deformation coordinate, two local energy minima corresponding to localized and delocalized π 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 ${}^1A_1$ states (within C_{2v} geometries) of methylene (CH_2), cyclopropenylidene (C_3H_2), and linear unsaturated carbenes can be described as a double excitation from an occupied a_1 orbital into a vacant b_1 orbital of the dominant configuration. A comparison [1] of the importance of this $a_1^2 \to b_1^2$ configuration in the cyclic C_3H_2 and the other systems [2, 3] shows that this correlation is less important in C_3H_2. In the C_3H_2 system, the b_1^2 configuration has 4π electrons and thus acquires antiaromatic character while the dominant a_1^2 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 delocation and hybridization.

In this brief report, the importance of aromatic factors is investigated for another cyclic carbene—cyclopentadienylidene. In contrast to the C_3H_2 carbene, both the delocalization effects and the aromatic nature of the $a_1^2 \to b_1^2$ configuration work in accord to increase the importance of this configuration. The result is that the b_1^2 configuration becomes not only more important than in CH_2 and C_3H_2 but it actually becomes the dominant configuration at some molecular geometries examined in this study.

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Multiconfigurational Wavefunction Optimization Using the Unitary Group Method

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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:

$$|\psi^{mc}\rangle = \sum_K C_K |K\rangle \tag{1}$$

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):

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The Coupled-Cluster Method with a Multiconfiguration Reference State

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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.

Das Verfahren mit gekoppelten "Clusters" für die Berechnung von Wellenfunktionen für gebundene Zustände eines Vielelektronensystems ist im Rahmen gewisser physikalisch angemessenen Näherungen erweitert worden, um einen multikonfigurationellen Referenzzustand zu erlauben. Mit dieser Erweiterung können Berechnungen der Elektronenstruktur von Systemen mit korrelierten abgeschlossenen oder offenen Schalen und mit einer potentiell einheitlichen Genauigkeit für alle Molekülgeometrien ausgeführt werden. Explizite Gleichungen werden mit einem multikonfigurationellen Referenzzustand für den Fall abgeleitet, wo der sogenannte Clusteroperator von seinem Ein- und Zweiteilchenkomponenten angenähert wird. Die Auswertung der erforderlichen Matrixelemente wird durch die Anwendung der Generatoren der unitären Gruppe erleichtert.

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.

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