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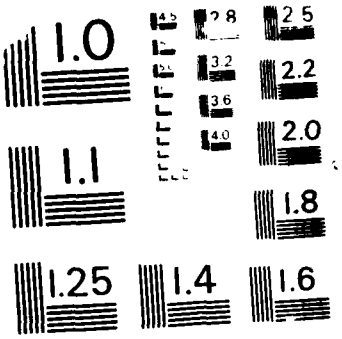

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MOLECULAR REACTION AND ENERGY TRANSFER RATE ESTIMATION FOR CHEMICAL-LASER ANALYSIS

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Final Report

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This report presents the results of an investigation of methods for estimation of reaction and energy transfer rates for collisions between electronically excited atoms and molecules of the sort typically present in energetic gases such as electronic-transition chemical-laser media. The research specifically dealt with ground- and excited-state electronic structure and energies of molecular collision complexes. The primary result of the investigation is a systematic method, within the context of electronic-structure theory, for estimation of potential energy surfaces for molecules in electronically excited states. The method focuses on overlap between atomic orbitals associated with shared electrons in molecules, depends upon the role of this overlap and its optimization in molecular electronic interactions, and is illustrated by the collision of $Na^*(3p, {}^2P)$ with $H_2(\sigma^2, {}^1\Sigma_g^+)$. The report includes an overview of methods for estimation of the dynamics and rates of molecular collisions in terms of the estimated excited-state electronic structure and energies, and also presents results of a study of

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19. ABSTRACT (Continued)

rational-fraction representations of interaction energies for the ground and A electronic states of N_2.

CONTENTS

I. INTRODUCTION

The understanding and quantitative characterization of the behavior of a molecular gaseous medium containing a large amount of energy are of crucial importance in numerous scientific and technological contexts. The particular composition of the gaseous medium and the means by which energy has been deposited into it can vary widely. The gaseous media can be interstellar clouds, planetary atmospheres, or those under study in the laboratory. The energy can, for example, come essentially continuously or in pulses from electric discharges, high intensity electromagnetic radiation, or nuclear or chemical reactions or explosions. Both radiative and nonradiative molecular rate processes will, in general, govern the disposal of that portion of the external supply of energy absorbed by the molecular constituents of the gas into their rotational, vibrational, electronic (i.e., rovibronic), and/or translational degrees of freedom. The former processes result in state-to-state exchange of energy between the gaseous molecules and surrounding electromagnetic radiation fields, and can lead to alteration of the number densities of the molecular species in the gas via photodissociation and photoionization. The latter processes result in state-to-state exchanges of energy among the molecules via nonreactive and reactive collisions, of which the latter also lead to changes in molecular species number densities in the gas.

Such energetic gases, supplied as they are with energy intermittently or continuously by external sources, are typically not in macroscopic states of equilibrium. Even if a gas is approaching equilibrium, the particular final macroscopic state is not essential to the analysis of this contract effort. The analysis rather centers around the population densities of the molecules in specific rovibronic states or sets of states, and the spectral and intensity properties of the radiation present, all as functions of time either during an approach to equilibrium, or during a sustained period of nonequilibrium in which energy pooling into, or population inversions between, specific molecular states may occur. Statistical mechanics is therefore largely inadequate for the characterization of gases under such conditions.

The foregoing paragraphs point to the complexity of the problem of characterization of energetic gaseous media. The number of microscopic state-to-state molecular rate processes are legion. In the absence of practical constraints, the characterization of the energy degradation in a gas may proceed by means of an ideal experimental approach or an ideal theoretical approach. The ideal experimental approach would consist either of precise monitoring of molecular population densities in all the accessible rovibronic and translational states, and of the intensity and spectral properities of radiation, for the actual energetic gas as a function of time, or of accurate measurement (i.e., under rovibronically and translationally state-resolved molecular-beam conditions) of the rates of all processes. The latter experimental data would provide all of the ingredients for rate-equation calculations of the time evolution of the molecular rovibronic state populations. The ideal theoretical approach would consist, in principle, of the accurate quantum-dynamical calculation of the rates of all possible radiative and nonradiative state-to-state processes, followed by the corresponding rate-equation calculations.

The ideal experimental and theoretical approaches just described are actually not so far from the realm of possibility. State-of-the-art molecular-beam experimental techniques and quantum-dynamical theories and calculational schemes are becoming increasingly more capable of accurate analysis of given state-to-state radiative and nonradiative molecular rate processes. The limiting factors tend to be cost and time. Detailed measurements or calculations are usually only feasible for a relatively small number of the many rates of state-to-state processes in an energetic gaseous medium. On the other

hand, in typical energetic molecular gases only a few state-to-state radiative and nonradiative processes have rates that are large enough to significantly influence the degradation of energy. In this regard large enough rates refer to those within an order of magnitude of gas kinetic or larger. Processes whose rates are several orders of magnitude smaller than gas kinetic play only minor roles in energy disposal.

In view of the preceding discussion it is clear that an efficient and accurate analysis of energy disposal in energetic gases would be greatly facilitated by quick methods of reliable estimation of mechanisms and rates for the various possible state-to-state reactive and nonreactive processes. Rate estimates of mere order-of-magnitude reliability would serve to identify the molecular rate processes of most importance to energy disposal. Rate-equation analysis of the time evolution of molecular state populations based upon these estimated rates would then provide an initial, albeit approximate, characterization of the energetic gas. Furthermore, the estimates of the mechanisms at the molecular rovibronic level of the various state-to-state reactive and nonreactive collision processes would provide a basic insight into the reason the rates of some processes are large while those of others are small. This becomes particularly important to applications in which achievement of selective channeling of energy into specific molecular states is the goal. A knowledge of why, as opposed to if, channeling has or has not occurred provides a much better framework for assessment of the best means for its achievement and/or optimization. Finally, those molecular rate processes identified by such estimates as the ones that primarily control energy disposal in a given gas are logical candidates for further, more thorough, experimental and/or theoretical investigations of the sort that will lead to improved characterization of the behavior of the gas. This could mean tremendous savings in time, effort and money which otherwise might be used up by state-of-the-art experimental or theoretical studies, or even by literature searches, on molecular rate processes that are of minor consequence to the behavior of some particular energetic gas of interest.

The research of this report consists of an investigation into general methods of reliable estimation of mechanisms and rates of inelastic and reactive molecular collisions that occur particularly in energetic gaseous media. Because of the high energy content of the gases, molecules in electronically excited states play a dominant role in energy disposal. The investigation therefore focused on collisions and reactions of electronically excited molecules. The goal was achievement of reliable estimates of mechanisms and rates of molecular dynamical processes as quickly as possible with minimum need for literature search or calculations requiring more than a good hand calculator. The ideal of this goal would be methods of estimation that depend upon little more than reference to the Periodic Table and recourse to back-of-the-envelope calculations. Success in the development of such methods of estimation of physical quantities hinges in large measure upon the soundness of physical principles and basic knowledge of molecular electronic structure and dynamics that provide the basis for the methods.

Since collisions and reactions of electronically excited molecules were the primary focus of this research effort, the investigation centered around the situation of gases that can be characterized by macroscopic states of equilibrium with respect to all except electronic degrees of freedom. In other words, the analysis will apply to gases, for which statistical equilibrium of translational, rotational and vibrational degrees of freedom at some temperature T applies, but whose atomic and molecular constituents are electronically excited (by some means) with electronic excitation energies well in excess of kT (k is the Boltzmann constant), the energy per degree of freedom associated with the macroscopic state of equilibrium. The result of the research is a systematic procedure for analysis of

all the possible reactive and/or nonreactive collisions of electronically excited atoms and molecules for a given gas.

The procedure resulting from this research effort for analysis of collisions of electronically excited atoms and molecules follows three basic steps. The first step consists of a determination, for a particular pair of collision partners, of the possible electronic structure of the molecular complex they form upon collision, and, for each electronic state of the molecular collision complex, the possible electronic states of products of the collision for both reactive and nonreactive cases. This step depends upon an analysis in terms of the shared electrons in the molecule, and of one-electron orbital descriptions of electronic structure for the least symmetrical forms of the molecular collision complex. The second step consists of assessment of the bonding and antibonding character of the electronic states. The investigation here consisted of development of a method for estimation of the electronic energy surfaces for those electronic states likely to play an appreciable role in the collision. In this method molecular electronic interaction energies are represented by atom-atom pair contributions that are characteristic of the atom-atom pairs as they exist in the actual molecular environment rather than in isolation. The assessment of the perturbative influence that the environment of a molecule has on its atom-atom pairs was in terms of electronic atomic orbital overlap and its fundamental role in molecular electronic structure. The third step of the overall analysis is the calculation of approximate rates for the various possible reactive and nonreactive collision processes. The electronic energy surfaces provided by the second step of the analysis serve as input for the rate calculations, which could be based upon transition-state or classical trajectory descriptions of the dynamics of the elastic, inelastic or reactive molecular collisions. The rate calculations depend also upon use of Landau-Zener analysis to describe nonadiabatic electronic transitions that occur during collision.

The major part of this investigation centered around the second step of the above analysis, namely, the systematic estimation of electronic structure and interaction energies of molecules in electronically excited states. The major portion of this report gives a detailed account of methods for estimation of molecular electronic structure and interaction energies. Time limitations of the period of technical effort prevented a full development of methods for rate calculations of the third step in the above analysis.

II. A REVIEW OF THEORY FOR ATOMIC AND MOLECULAR GROUND- AND EXCITED-STATE ELECTRONIC STRUCTURES AND ENERGIES

The description of wave functions for systems of many electrons in terms of products of one-electron wave functions, i.e., spin orbitals, represents the backbone of electronic structure theories for atoms, molecules and solids. Of the numerous excellent treatments of this subject the books by Slater (Refs. 1 - 5) provide a complete and detailed account. The book, *Coulson's Valence* , by McWeeny (Ref. 6), while less detailed, also provides a good foundation in terms of basic physical principals and understanding. These and most other treatments stress the ground-state electronic structure of molecules in stable geometries. The research of this contract effort, however, centers primarily around excited-state molecular electronic structure and collisional interaction of molecules governed by excited electronic states. The investigation at the outset, therefore, consisted of a thorough review of fundamentals of the spin-orbital description of electronic structure. This section of the report consists of this review, which lays the foundation for the results presented by Sec. III.

Each spin orbital is a product of a spatial function, or orbital $u(\vec{r})$, that depends on the position $\vec{r}$ of an electron, and a spin function $\alpha(s)$ or $\beta(s)$, that depends on the spin coordinates $s = \frac{1}{2}$ or $-\frac{1}{2}$ of an electron. Here $\alpha(\beta)$ refers to an electron whose component of spin angular momentum along a specified direction is $+(-)\hbar/2$ (where $\hbar$ is the Planck constant divided by 2π). According to convention, spin up refers to the + case, spin down refers to the - case, and $\alpha(s) = \delta_{s,\frac{1}{2}}$ while $\beta(s) = \delta_{s,-\frac{1}{2}}$. Implicit in a product of a given set of N spin orbitals corresponding to a system of N electrons is a particular assignment of the space-spin coordinates of the electrons to the various spin orbitals. Owing to the indistinguishability of electrons, one assignment of electronic coordinates to a set of spin orbitals is equivalent to another, and thus there are many equivalent product wave functions for a given set of spin orbitals. Furthermore, because electrons are Fermions, and obey the the Pauli exclusion principle, an electronic wave function should be antisymmetric under interchange of the space-spin coordinates of any two electrons. An electronic wave function corresponding to a given set of spin orbitals, therefore, is that particular linear combination of all equivalent product wave functions which is antisymmetric in electronic coordinates. Such a linear combination corresponds to a so-called determinantal wave function $D(1,2,...,N)$ where $(1,2,...,N)$ is shorthand notation for the space-spin coordinates $(\vec{r}_1 s_1, \vec{r}_2 s_2, ..., \vec{r}_N s_N)$ of the N electrons.

A determinantal wave function constitutes a configuration of the electrons. An actual state of an N-electron system, $\psi(1,2,...,N)$ can be well approximated often by a single determinantal wave function, or, in the case of spin-orbital degeneracy and/or symmetry constraints imposed by certain geometrical arrangements of the nuclei in a molecule, by a linear combination of a few determinantal wave functions. Such linear combinations of configurations allow for so-called configuration interaction in the description of an electronic state. The greater the amount of configuration interaction, the greater the degree to which the corresponding electronic wave function accounts for the detailed correlations in electronic motions. Of formal, but not practical, importance is the fact that an electronic state can be exactly represented by a linear combination of *infinitely many* configurations, i.e., by complete configuration interaction, which accounts for all correlations of electrons.

Adequate physical descriptions of systems of electrons are often provided by simple representations of electronic states in terms of one or a few determinantal wave functions (Ref. 6). Such physical descriptions form the basis for the analysis of this research effort

of ground and excited electronic states of quasi-molecules that form during molecular collisions and reactions. In general, there are many spin orbitals for an N-electron system, each of which corresponds qualitatively to a possible spatial wave function or orbital, u, of a representative electron of spin up or spin down as it moves with some total one-electron energy ϵ under the influence of the Coulomb potential provided by the nuclei and an average potential provided in a collective way by all of the other electrons. A spin orbital that describes bound motion of a representative electron is characterized by a one-electron energy $\epsilon < 0$, whose magnitude is an approximate measure of the amount of energy necessary to remove the representative electron from the overall system of N electrons in a state described by configurations which include the particular spin orbital. There are also spin orbitals that describe unbound motions of electrons, and whose one-electron energies $\epsilon > 0$ lie in the continuum.

As mentioned above, a configuration of a system of N electrons corresponds to an assignment of the electrons to a particular set of N spin orbitals, the occupied ones. The remaining spin orbitals remain unoccupied. Thus, for a set of spin orbitals, approximate wave functions for ground- and excited-state electronic structure can be specified by assignments of values 0 or 1 to occupation numbers n_i for each spatial orbital u_i of a given spin state. Accommodation of all electrons requires $\sum_{i\uparrow} n_i + \sum_{i\downarrow} n_i = N$, where $\sum_{i\uparrow}$ ($\sum_{i\downarrow}$) means summation over all spatial orbitals u_i of spin up (down). Occupation of the spin orbitals of lowest one-electron energies leads to the configurations that approximate ground electronic states, and successive promotion of electrons out of the ground-state spin orbitals into spin orbitals of higher one-electron energies leads to configurations that approximate various excited electronic states. This procedure constitutes an Aufbau, or building up, principle for electronic states. In any configuration, assignment of the spatial coordinates of two electrons of opposite spin states to a single orbital of one-electron energy ϵ does not violate the Pauli exclusion principle.

There are numerous methods for determination of sets of approximate spin orbitals. Most methods rely upon self-consistent-field (SCF) treatments of the electronic structure. Such SCF treatments lead to one-electron Schrödinger equations that should be satisfied by the spin orbitals. The orbitals associated with electrons of spin up satisfy in general different one-electron Schrödinger equations from the orbitals associated with electrons of spin down. The one-electron Schrödinger equations are of the type,

$$h^{1(1)}(1;G)u_i(1;G) = \epsilon_i(G)u_i(1;G), \tag{1}$$

where each u_i is an orbital associated with an electron of spin up (spin down) in a particular configuration. In Eq. (1) the geometry of the nuclei in a molecule is indicated by G, which collectively refers to the positions of the nuclei. For example, in the case of a molecule consisting of M nuclei, $G \equiv (\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M)$. The one-electron Hamiltonians of Eq. (1) have the form,

$$h^{1(1)}(1;G) = -(\hbar^2/2m_e)\nabla^2 - e^2[\sum_{I=1}^{M} Z_I/r_{1I}] + V^{1(1)}(1;G), \tag{2}$$

in which, on the right of the equation, the first term accounts for the kinetic energy of an electron (where m_e denotes its mass), the second term accounts for the Coulomb potential energy of an electron at $\vec{r}_1$ due to the nuclei in their geometry G (where nucleus I consists

of Z_I protons, e is the charge of an electron, and $r_{iI} = |\vec{r}_i - \vec{R}_I|$), and the last term accounts for the effective Coulomb and exchange interaction of an electron of spin up (spin down) at $\vec{r}_i$ with all the other electrons. This last term depends upon the configuration, i.e., the assignment of occupation numbers to the spin orbitals. The exchange part of $V^{f(i)}(1;G)$, furthermore, is in general a nonlocal operator, and is dependent on each u_i that appears in Eq. (1). That is, electrons of a given spin state in different orbitals experience different exchange interaction with the other electrons for a given configuration. This difference in exchange interaction is accounted for explicitly by the Hartree-Fock approximation, according to which the one-electron Schrödinger equations of the type of Eq. (1) result from minimization of the total electronic energy for a single configuration. Various quite good statistical approximations to the exchange interaction lead, however, to local exchange operators in $V^{f(i)}(1;G)$ that still depend upon the spin state with which the orbitals in Eq. (1) are associated, but do not depend upon each u_i itself. These statistical exchange approximations represent in various ways the average exchange interaction between electrons as they occupy some set of spin orbitals.

Electronic spin and its role in electronic structure require careful consideration, especially in the context of excited electronic states. As discussed above, the orbitals u_i and corresponding one-electron energies ϵ_i associated with electrons of one spin state differ in general from their counterparts associated with electrons of the opposite spin state. These differences, when they do exist, are usually small. The assumption that the orbitals and one-electron energies associated with spin-up electrons are identical to those associated with spin-down electrons is therefore a good one as an initial approximation. This approximation corresponds to spin degeneracy of the orbitals. An electronic shell refers to a single nondegenerate orbital, or a set of degenerate orbitals, of energy ϵ.

The spin degeneracy approximation is usually a good one, but it can become severe in two cases; whenever the electrons of one spin state greatly outnumber those of the opposite spin state, and whenever one-electron energies are separated by amounts less than the differences in exchange interaction energy between electrons of spin up and spin down. The former case, which applies to electronic states of the largest net spins possible, frequently occurs for systems of a few electrons, such as the He atom for example (Ref. 7), for which states and configurations where all the electrons are in the same spin state are not uncommon. The latter case applies in particular to Rydberg-like spin orbitals whose one-electron energies exhibit dense spacing near the continuum limit. The relative ordering of one-electron energies of spin orbitals can become important in connection with the correlation between the one-electron energies and spin orbitals of reactants and/or products of a collision, and the one-electron energies and spin orbitals of the quasi-molecule that forms during the collision.

The electronic structure of atoms forms a fundamental starting point for analyses of the electronic structure of molecules. An atomic orbital (AO) centered on one of the nuclei of a molecule can serve as a contribution to representations of a molecular orbital (MO) in terms of linear combinations of AOs, or can enter into so-called valence-bond configurations that account approximately for molecular electronic structure. Due to the spherical symmetry of an isolated atom, the positions $\vec{r}$ of electrons relative to an atom's nucleus (of atomic number Z) are best designated by spherical-polar coordinates (r, θ, ϕ), and the orbitals factor into products of radial and angular wave functions. The radial wave functions, $P_{nl}(r)/r$, are characterized by the so-called principle quantum numbers, $n = 1, 2, \ldots$, which basically specify the one-electron energies, and by the numbers, $l = 0, 1, \ldots, n - 1$, which specify, for given n, the possible states of electronic orbital angular momentum. The magnitude of the orbital angular momentum corresponding to a given value of l is $\sqrt{l}\sqrt{l+1}\hbar$. The angular wave functions are the spherical harmonics,

$Y_{lm}(\theta,\phi)$, which describe states of angular momentum, whose magnitude is specified by l, and whose component along the z axis is $m\hbar$, where, by convention, s, p, d, f, ..., etc. denote, respectively, $l = 0, 1, 2, 3, ...$, etc., and for given l the allowable values of m are $-l, -l + 1, ..., l$.

Figure 1 depicts schematically, as a function of r, the atomic effective potentials for a one-electron Schrödinger equation such as Eq. (1), and for angular momentum states corresponding to $l = 0$, 1, and 2. Figure 1 also shows one-electron energies for orbitals corresponding to n = 1, 2, and 3, and the radial charge densities $|P_{nl}(r)|^2$ for electrons that may occupy these orbitals. The radial charge density plots appear relative to their corresponding one-electron energies for the sake of clarity, and Fig. 1 makes no distinction between the one-electron energies and radial charge densities associated with electrons of spin up and down. The energy scale in Fig. 1 is not necessarily linear, for typically (at least for electronic ground states) differences of an order of magnitude exist between ϵ_{1s} and $\epsilon_{2s,2p}$, $\epsilon_{2s,2p}$ and $\epsilon_{3s,3p,3d}$, etc. The one-electron energy-level scheme at the left of Fig. 1 explicitly depicts the fact that, for atoms, orbitals of the same n and l, but different $m = -l, -l + 1, ..., l$, are degenerate. The vertical arrows in the one-electron energy-level scheme at the left of Fig. 1 show one way of designation of a configuration of the electrons. In Fig. 1 the configuration designated by the vertical arrows corresponds to the ground state of the Na atom. By convention such an arrow pointing up (down) indicates occupation of the corresponding orbital by an electron of spin up (down). Another convention for designation of the configuration indicated by the one-electron energy levels and arrows of Fig. 1 is ($1s^2 2s^2 2p^6 3s^1$, ^1S), which specifies each orbital and its electron occupation number as a superscript. The notation, ^1S, identifies the overall electronic configuration. This written designation for the Na atom would be $Na(1s^2 2s^2 2p^6 3s^1, {}^1S)$. In this example of the ground state of Na, the 1s, 2s and 2p shells are closed in the sense that all of their spin orbitals are occupied by electrons in the configuration. The 3s shell is, on the other hand, open in the sense that it is occupied by only one electron, which may have spin up or down. The 3p, 3d, ..., etc. shells are, for the ground state of Na, empty in the sense that they are unoccupied by electrons. These shells are, however, available for configurations which describe excited electronic states of Na.

Figure 1 shows how the 1s electronic charge radially falls largely inside the 2s and 2p electronic charge, which in turn falls largely inside the 3s, 3p, and 3d electronic charge, etc. When an atom in some electronic state approaches another atom or molecule, the electrons that primarily participate in the resulting interaction, down to atom-atom separations on the order of a few Bohr radii (the Bohr radius is 0.52918 Å), will be those characterized by the AOs of the atom's electronic configuration whose maximum radial charge densities are furtherest from the nucleus. Approximate descriptions of molecular electronic structure in terms of the electronic structure of constituent atoms, therefore, require realistic descriptions of the radial parts of AOs of ground- and excited-state configurations of any given atom, in particular over regions of r for which their radial charge densities are maximum. The thrust of the investigation of this contract effort is development of such an approximate description of molecular electronic structure that is physically realistic yet simple, that involves minimal computational complexity, and that by all means avoids recourse to full SCF calculations based on Eq. (1).

Slater, as early as 1930, carried out an analysis of the radial parts of AOs based on then available SCF calculations for atoms, and arrived at empirical rules (Refs. 1 and 8) for the characterization of radial atomic wave functions. These rules afford a measure of self-consistency among the AOs for a given electronic configuration [though not at the level of self-consistent solutions to Eq. (1)] in that they approximately account for the

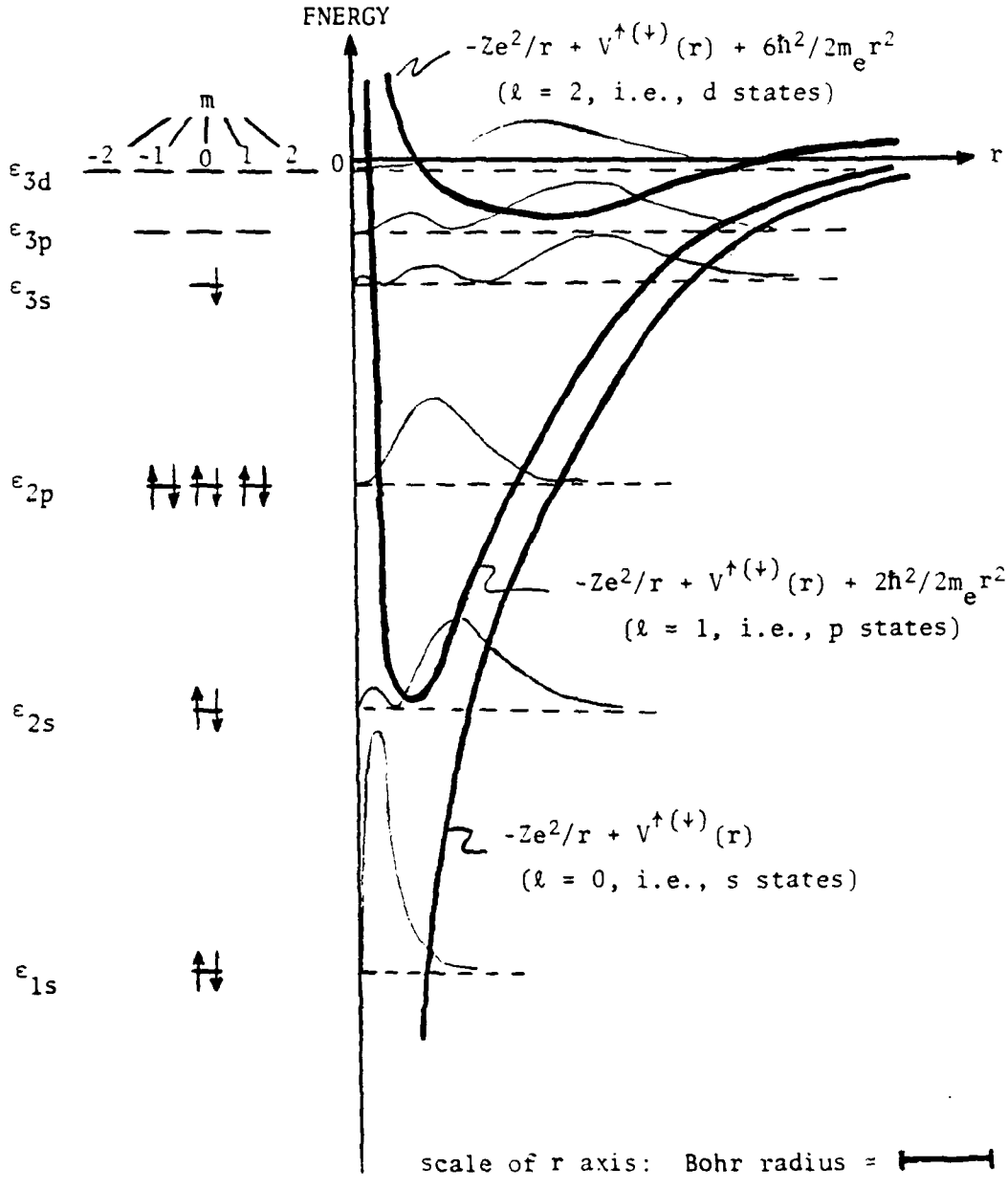

Figure 1

Schematic illustration of atomic effective potentials for one-electron Schrödinger equations corresponding to s, p, and d angular momentum states, and of one-electron energies and radial charge densities of 1s, 2s, 2p, 3s, 3p, and 3d orbitals.

way electrons near the nucleus screen the nuclear Coulomb attraction for electrons further away from the nucleus. Slater found that the functions,

$$g_n(r) = r^{n-1} e^{Z_{eff} r/n}, \tag{3}$$

provide good descriptions of the radial parts of AOs in just those regions of r where their radial charge densities are maximum. In this function Z_{eff} is an effective nuclear charge related to the actual nuclear charge, Z, by $Z_{eff} = Z - \rho$, where ρ, the screening constant, accounts for screening of the nuclear charge by electrons nearer the nucleus than a particular electron whose radial behavior is being represented by Eq. (3).

Slater found that screening constants differ very little for AOs within certain groups. These groups of AOs follow a progression in terms of principle and angular momentum quantum numbers. The groups, in this progression, are (1s), (2s,2p), (3s,3p), (3d), (4s,4p), (4d), (4f), etc. Slater's rules (Refs. 1 and 8), for a given configuration, i.e., for a given assignment of electrons to the AOs, prescribe the following contributions to ρ for an occupied AO in a given group: 1) nothing for any electrons that occupy AOs of groups later in the progression than the given group; 2) an amount 0.35 (except for the 1s group where the amount is 0.30) for each of the electrons, save one, which occupy AOs of the given group: 3) an amount 0.85 for each electron that occupies an AO of the group immediately preceding the given group in the progression, and an amount 1.00 for each electron that occupies an AO in the remaining groups preceding the given group, if the given group contains AOs of s or p type; and 4) an amount 1.00 for each electron that occupies an AO of the groups preceding the given group in the progression if the given group contains AOs of d or f type. Since Slater proposed these rules there have been analyses of a similar nature based upon more accurate and sophisticated SCF calculations of atomic electronic structure than were available in 1930. These latter analyses (Refs. 5 and 9) involve more complicated prescriptions for estimating ρ, and lead to refinements in descriptions of radial parts of AOs. These refinements, like those provided by detailed SCF calculations of atomic structure, are not crucial to the goal of development of estimations of molecular electronic structure.

The preceding discussion and review establishes the framework that supports the method stemming from the investigation of this contract effort by which molecular electronic structure and the electronic potential energy surfaces corresponding to the various electronic states of molecules may be estimated. The goal is a simple, but qualitatively and quantitatively realistic, description of electronic structure of a molecule formed by combination of two generally electronically excited constitutes, which may be atoms or other molecules. Any and all geometries of the nuclei of the molecules, as opposed to just those geometries that are most symmetrical, are of importance since the electronic structure under consideration is that of molecules under collision conditions in which the nuclei do not remain in symmetrical geometries as they move.

The approach of this investigation follows analyses made long ago by Pauling, Slater, Mulliken, Hückel and Hund. An early paper by Mulliken (Ref. 10) gives a good overview of these analyses, and serves as motivation for the present analysis. The starting point of this analysis is the approximation that electrons of a molecule fall into two basic groups, those that are and those that are not shared by the constituent atoms of the molecule. As an atom collides with another atom or molecule the unshared electrons of this atom are those that play a relatively minor role in its interaction with the collision partner. Any of the electrons of the atom that essentially maintain atomic-like

character in the environment of the resulting molecule that forms by collision fall into this category. An unshared electron of this sort occupies an MO in resulting molecular electronic configurations that differs so slightly from a pure AO of the particular atom that this AO adequately represents the MO. Such an AO typically has a one-electron energy large in magnitude (i.e., it describes electrons that are tightly bound to the atom). Another category of unshared electrons consists of the electrons that belong to a closed shell in the electronic configurations that describe the isolated atomic constituent. The electrons of this category are unshared primarily because, according to the Pauli exclusion principle, electrons in closed shells tend to be avoided by other electrons. The essential behavior of this latter category of unshared electrons may or may not conform to the molecular environment.

The electrons of the isolated atomic constituent under consideration that are not unshared belong to the group of shared electrons in the overall molecule. Clearly, an atomic constituent will have all unshared electrons if its electronic configuration is purely closed shell. In this case the shared electrons of the overall molecule, if there are in fact any, will come from the atom's collision partner (atom or molecule). If all the electrons of an overall molecule are unshared, then the electronic interaction energy between the two constituents of the molecule is basically repulsive, as in the case of interaction between two noble gas atoms in their ground electronic states. If, on the other hand, there are shared electrons in the overall molecule, then not only does their behavior conform to the overall molecule, but also they occupy MOs that can be adequately described by a linear combination of AOs (MOs), each of which belongs to either an empty or a partially closed shell of an atomic (molecular) constituent. In particular, such an AO belongs, in configurations of an atomic constituent under consideration, to the occupied shell of highest (i.e., least negative) one-electron energy; or, if the occupied shell of highest one-electron energy is closed, to the unoccupied shell next higher in one-electron energy. This description of molecular formation is consistent with the observation in the above discussion that the electrons which predominantly participate in the interaction of an atom with another atom or molecule are those characterized by the atom's most accessible and energetically favorable AOs, whose radial charge densities are concentrated furtherest from the nucleus.

The foregoing analysis of electronic structure for an atom in collision with a molecule applies equally well to the case of one molecule in collision with another molecule Reference to AOs of the atomic constituent under consideration need only be replaced by reference to MOs of the molecular constituent under consideration. The MOs that characterize shared electrons of a molecule may, therefore, be represented by linear combinations of appropriate AOs of its atomic constituents and/or appropriate MOs of its molecular constituents. Any such linear combination is, however, decomposable into AO contributions alone. These several ways of treatment of molecular electronic structure are important ot descriptions of formation (breakup) of electronically excited molecules from (into) various possible constituent atom and/or molecules that may or may not be electronically excited.

The MOs of the shared electrons of a molecule formed by interaction of two atomic or molecular constituents should ideally be SCF solutions of an appropriate one-electron Schrödinger equation such as Eq. (1). The present analysis follows the book by McWeeny (Ref. 6), and relies upon an approximate description of these MOs guided by Eq. (1). The following discussion will concern the case of two atoms, A_1 and A_2, which, upon collision, form a diatomic molecule with the internuclear separation denoted by R. The two atom's AOs, of the sort described above, whose linear combinations represent MOs, u, of the shared electrons of the resulting diatom, are u_1 and u_2, and

$$u(\vec{r};R) = C(R)[u_1(\vec{r}) + \lambda(R)u_2(\vec{r})], \tag{4}$$

where C(R) is a normalization constant given by

$$C(R) = [1 + \lambda^2(R) + 2\lambda(R)S_{u_1,u_2}(R)]^{-1/2}, \tag{5}$$

in which $S_{u_1,u_2}(R)$ is the so-called overlap of orbitals u_1 and u_2 and is given by

$$S_{u_1,u_2}(R) = \int_{(R)} d^3r\ u_1(\vec{r})u_2(\vec{r}). \tag{6}$$

In Eq. (6) the symbol below the integral sign indicates the geometry of the diatomic molecule's nuclei (specified in this case simply by the internuclear separation, R) which determines the condition under which the two AOs overlap. For simplicity the AOs u_1 and u_2 are real functions. The position vector $\vec{r}$ locates a shared electron in the molecule. The requirement that u of Eq. (4) satisfy the appropriate one-electron Schrödinger equation of Eq. (1) (with neglect of electron spin) forces $\epsilon(R)$, the one-electron energy corresponding to u, to satisfy the secular equation,

$$[h_{u_1,u_1}(R) - \epsilon(R)][h_{u_2,u_2}(R) - \epsilon(R)] - [h_{u_1,u_2}(R) - \epsilon(R)S_{u_1,u_2}(R)]^2 = 0, \tag{7}$$

in which (for i, j = 1, 2)

$$h_{u_i,u_j}(R) = \int_{(R)} d^3r\ u_i(\vec{r})h(\vec{r};R)u_j(\vec{r}), \tag{8}$$

where $h(\vec{r};R)$ is the one-electron Hamiltonian of Eq. (2) in the case of a diatomic molecule whose nuclear geometry is specified by the internuclear separation R.

The diagonal matrix element, $h_{u_1,u_1}(R)$, of Eq. (8) represents the energy an electron confined to AO u_1 would have in the presence of both atoms at internuclear separation R. An analogous statement applies to $h_{u_2,u_2}(R)$. Thus, $h_{u_1,u_1}(R)$ corresponds approximately to the energy ϵ_1 of an electron in AO u_1 of an isolated atom A_1, with a correction, that may be quite small, due to the presence of atom A_2, and vice versa. The off-diagonal matrix elements, $h_{u_1,u_2}(R) = h_{u_2,u_1}(R)$, are the so-called bond integrals. These bond integrals and the overlap, $S_{u_1,u_2}(R)$, depend upon the mutual behavior of the two AOs, u_1 and u_2, for a given molecular geometry, and the condition for appreciable overlap of two AOs insures that the corresponding bond integral is also appreciable [compare Eqs. (6) and (8)]. This condition is met by two AOs if they share regions of space over which they both exhibit values that are of the same sign and of appreciable magnitude. There are two solutions to Eq. (7), $\epsilon_+(R)$ and $\epsilon_-(R)$, given by

$$\epsilon_{\pm}(R) = (\tfrac{1}{2})[1 - S^2_{u_1,u_2}(R)]^{-1} \times$$

$$\times \Big[h_{u_1,u_1}(R) + h_{u_2,u_2}(R) - 2h_{u_1,u_2}(R)S_{u_1,u_2}(R)$$

$$\pm \sqrt{[h_{u_1,u_1}(R) + h_{u_2,u_2}(R) - 2h_{u_1,u_2}(R)S_{u_1,u_2}(R)]^2 - 4[1 - S^2_{u_1,u_2}(R)][h_{u_1,u_1}(R)h_{u_2,u_2}(R) - h^2_{u_1,u_2}(R)]}\Big] \quad (9)$$

The two one-electron energies, $\epsilon_+(R)$ and $\epsilon_-(R)$, specify two MOs, $u_+(\vec{r};R)$ and $u_-(\vec{r};R)$, or, correspondingly, two values, $\lambda_+(R)$ and $\lambda_-(R)$, for the mixing coefficients and two values, $C_+(R)$ and $C_-(R)$, for the normalization constants of Eq. (4) [see Eq. (5)].

The role of overlap in MO formation is evident in Eq. (9). In the following analysis of molecular electronic structure overlap plays an exclusive role. The fundamental ingredients of electronic structure exhibited by Eq. (9) provide the framework upon which this analysis rests. Of the two MO one-electron energies, $\epsilon_+(R)$ exceeds $\epsilon_-(R)$. Consequently, upon approach of two atoms, an electron with behavior described by orbital u_+ acquires a larger share of the total molecular energy than an electron described by orbital u_-. In other words, when electrons occupy orbital u_+, the two atoms approach each other at greater expense to their energy of relative motion than they do when electrons occupy orbital u_-. The term antibonding, therefore, appropriately applies to ϵ_+ and u_+, and, correspondingly, the term bonding applies to ϵ_- and u_-. Since both the bond and overlap integrals vanish in the separated-atoms limit (i.e., the limit $R \rightarrow \infty$), the antibonding and bonding one-electron energies satisfy the following limiting relationships: $\epsilon_+(R\rightarrow\infty) \simeq h_{u_1,u_1}(R\rightarrow\infty) = \epsilon_1$, and $\epsilon_-(R\rightarrow\infty) \simeq h_{u_2,u_2}(R\rightarrow\infty) = \epsilon_2$, where ϵ_1 and ϵ_2 are the isolated-atom one-electron energies for AOs u_1 and u_2, respectively, and where $\epsilon_2 \leq \epsilon_1$ in keeping with $\epsilon_+(R) \geq \epsilon_-(R)$.

In the case of a heteronuclear diatomic molecule, where the atoms A_1 and A_2 have different nuclear charges, whenever $S_{u_1,u_2}(R) \simeq 0$, then $h_{u_1,u_2}(R) \simeq 0$ as well and, according to Eq. (9), $\epsilon_+(R) \simeq h_{u_1,u_1}(R)$ and $\epsilon_-(R) \simeq h_{u_2,u_2}(R)$. The earlier discussion about h_{u_1,u_1} and h_{u_2,u_2} then implies that $\epsilon_+(R) \simeq \epsilon_1$ and $\epsilon_-(R) \simeq \epsilon_2$ are good approximations. In this situation $u_+(\vec{r};R) \simeq u_1(\vec{r})$ [i.e., $C_+(R) \simeq 1$ and $\lambda_+(R) \simeq 0$] and $u_-(\vec{r};R) \simeq u_2(\vec{r})$ [i.e., $C_-(R) \rightarrow 0$ and $\lambda_-(R) \rightarrow \infty$ such that $C_-(R)\lambda_-(R) \rightarrow 1$]. In other words, u_+ and u_- are the atomic-like MOs described earlier. The electrons in such atomic-like MOs are quite energetically neutral towards approach of the two atoms, since one-electron energies remain fairly constant near ϵ_1 or ϵ_2. On the other hand, two MOs, u_+ and u_-, which are comprised of AOs that appreciably overlap, are consequential to the mutual interaction of two atoms. In the case of two AOs that appreciably overlap, under the condition that $\epsilon_-(R)$ lies much closer to $h_{u_2,u_2}(R) \simeq \epsilon_2$ than to $h_{u_1,u_1}(R) \simeq \epsilon_1$, and vice versa for $\epsilon_+(R)$, Eq. (9) reduces to

$$\epsilon_-(R) \simeq h_{u_2,u_2}(R) - [h_{u_1,u_2}(R) - h_{u_2,u_2}(R)S_{u_1,u_2}(R)]^2[h_{u_1,u_1}(R) - h_{u_2,u_2}(R)]^{-1} \quad (10)$$

and

$$\epsilon_+(R) \simeq h_{u_1,u_1}(R) + [h_{u_1,u_2}(R) - h_{u_1,u_1}(R)S_{u_1,u_2}(R)]^2[h_{u_1,u_1}(R) - h_{u_2,u_2}(R)]^{-1}. \quad (11)$$

This result shows that, for large differences between $h_{u_1,u_1}(R) \simeq \epsilon_1$ and $h_{u_2,u_2}(R) \simeq \epsilon_2$, $\epsilon_+(R)$ and $\epsilon_-(R)$ differ very little from ϵ_1 and ϵ_2, respectively. Thus, for an MO to be

of consequence to the interaction of two atoms, it must be represented by a linear combination of two AOs whose one-electron energies are fairly close in value.

Another important situation occurs when atoms A_1 and A_2 are of the same nuclear charges, and the corresponding diatomic molecule is homonuclear. Here the two AOs may be identical. Certainly the combination of such identical AOs will be most consequential to the formation of the diatom, since such AOs have identical one-electron energies (i.e., $\epsilon_1 = \epsilon_2$). In this case, with $a(R) \equiv h_{u_1,u_1}(R) = h_{u_2,u_2}(R)$, $b(R) \equiv h_{u_1,u_2}(R)$, and $S(R) \equiv S_{u_1,u_2}(R)$, Eq. (9) becomes

$$\epsilon_{\pm}(R) = [a(R) \pm b(R)][1 \pm S(R)]^{-1}, \tag{12}$$

and also [see Eqs. (4) and (5)],

$$u_{\pm}(\vec{r};R) = \frac{-[-u_1(\vec{r}) \pm u_2(\vec{r})]}{\sqrt{2[1 \pm S(R)]}}. \tag{13}$$

The reflection symmetry of MOs of homonuclear diatomic molecules is exhibited by Eq. (13). The $\pm$ combination of u_1 and u_2 (which are identical, but centered on different atomic sites) persists even if S(R) becomes negligible. This is a reminder that all MOs must reflect the symmetry of the nuclear framework of a molecule, since the one-electron Hamiltonians of Eq. (2) (of which each MO should be an eigenfunction) are invariant with respect to that symmetry.

The preceding considerations and analysis lead to the following conclusions. Molecular orbitals come in bonding-antibonding pairs, $u_{\pm}(\vec{r};R)$, the bonding one of which to some degree describes electrons that energetically favor the approach of two atoms, and the antibonding one of which , to roughly the same degree, describes electrons that energetically oppose the approach of the two atoms. If, for a given bonding-antibonding pair of MOs, u_+ is occupied by as many electrons as u_- in a molecular electronic configuration, the net bias of those particular electrons on the approach of the two atoms is approximately neutral. This is consistent with the earlier observation that an AO which contributes to representations of MOs of shared electrons in a molecule is either the occupied one of highest one-electron energy in the electronic configuration of the atom, or, if the occupied one of highest one-electron energy belongs to a closed shell, the unoccupied one next higher in one-electron energy. Furthermore, the bonding-antibonding pair of MOs for the shared electrons essentially determines, as far as electronic energy is concerned, the amount of attraction or repulsion two atoms experience when they interact.

All of the analysis beginning with Eq. (4) applies equally well to the interaction of an atom A_1 and a molecule M_2, or of two molecules, M_1 and M_2. In the case of atom-molecule or molecule-molecule interactions, R refers to the separation of the centers of mass of the two interacting partners, and the geometry of the nuclei is specified collectively by R, and by G_i and G, the nuclear geometry of molecule M_i and of the overall resulting molecule, respectively.

III. ESTIMATION OF MOLECULAR ELECTRONIC GROUND- AND EXCITED-STATE INTERACTION ENERGIES

The one-electron energies, $\epsilon_{\pm}(R,G)$, of the previous section of this report constitute an approximation only to that part of the potential energy in a molecule due to the interaction of the electrons with themselves and with the nuclei. This is evident from the terms in the one-electron Hamiltonian of Eq. (2). The total potential energy of interaction, $U_{\pm}(R,G)$, corresponds to $\epsilon_{\pm}(R,G)$ plus the Coulomb repulsions between the nuclei, which means

$$U_{\pm}(R,G) = \epsilon_{\pm}(R,G) + e^2 \sum_{\text{pairs}(I,J)} \frac{Z_I Z_J}{R_{IJ}}, \tag{14}$$

where R_{IJ} is the separation between nuclei I and J.

According to the foregoing analyses the approximate assessment of electronic ground- and excited-state interaction energies of molecules depends upon estimation of the bonding and antibonding energies, $\epsilon_{\pm}(R,G)$, of corresponding pairs of MOs for shared electrons in electronic configurations of molecules. The method of estimation of $\epsilon_{\pm}(R,G)$, therefore, is of crucial importance to this investigation. The investigation led to a method of estimation that involves approximation of $\epsilon_{\pm}(R,G)$ as a sum of contributions, $\epsilon_{IJ}(R_{IJ},G)$, from all atom-atom pairs, (I,J), in the molecule. Each such contribution, $\epsilon_{IJ}(R_{IJ},G)$, is an appropriate bonding or antibonding energy of the corresponding diatomic molecule, but not necessarily in isolation. That is, each atom-atom pair contribution to $\epsilon_{\pm}(R,G)$ is modified in a well-defined and appropriate way by the presence of the other atoms in the molecule. The key to this scheme is AO overlap and its role in descriptions of molecular interactions.

Interaction energies of pairs of atoms in ground and excited electronic states are clearly fundamental in this approach to descriptions of molecular interaction energies. Many electronic ground- and excited-state interaction energies of atom-atom pairs already have been well characterized by means of spectroscopic and/or scattering measurements (Ref. 11) and by means of detailed SCF or configuration-interaction calculations of molecular electronic structure and energies (Ref. 12). In the case of bonding interaction energies the characterization is usually in terms of their long-range behavior, the internuclear separations at which their minima occur, the values of these minima relative to the electronic energies of the separated atoms, and the first few derivatives of the interaction energies at the minima (which characterize the vibrational/rotational energy spectra of the diatoms). Many model, parameterized, potential-energy functions are available that describe the behavior of given diatomic interaction energies over the whole range, or over limited ranges, of internuclear separation, R. The usefulness of such model potential functions depends upon *a priori* information about the interaction energy itself from experimental data or detailed electronic structure calculations. Adjustment of the parameters of a model potential function is governed by the condition that the function should conform as well as possible to already existing experimental or calculational data about the interaction energy.

The use of available experimental or calculational information on an atom-atom interaction energy of interest is of vital importance in this investigation. The ground- and A excited-state interaction energies of the N_2 molecule, for which spectroscopic data and corresponding RKR potentials exist (Refs. 13 and 14), serve as examples in this

regard. Part of the present investigation involved representation of these two interaction energies by functions consisting of ratios of polynomials in R. These rational-fraction, or so-called Padé, functions give excellent fits to the corresponding RKR potential functions, and have the advantage of being analytic in R over its entire range. The results of this phase of work appear in detail in the next section. The remainder of this section deals with adequate characterization of diatomic electronic interaction energies, $\epsilon_{\pm}(R)$, even when no experimental or calculational information about them is available. The goal is achievement of adequate estimates of atom-atom interaction energies in ways that obviate, in the first instance at least, the expense of such detailed experiments or calculations. Central to the analysis is development of ways for estimation of the degree to which interaction energies of isolated atom-atom pair are modified by the presence of other atoms that may surround the pair in a molecular environment.

The approach for estimation of molecular interaction energies arising from this investigation centers around the role of AO overlap in the characterization of bonding and antibonding electronic states of molecules. The ground and first excited electronic states of the H_2 molecule provide a prototype of bonding-antibonding one-electron energies. The AOs that combine to form the bonding-antibonding MO pair that describes the shared electrons are two 1s Hydrogen atomic orbitals, each of one-electron energy ϵ_{1s} in an isolated H atom, and each centered on and spherically symmetrical about an H nucleus with radial parts given by $g_1(r) = \exp(-r)$ [see Eq. (3)]. In terms of these orbitals [in Eq. (4)] the bonding-antibonding MO pairs, $u_{\pm}(\overline{r};R)$, of Eq. (13) have corresponding one-electron energies, $\epsilon_{\pm}(R)$, of Eq. (12) that are described by well-known expressions that are analytical in R (Ref. 3) and can be represented by a series expansion in powers of R and the overlap S(r).

Guided by an analysis of this series expansion, A. Corvo* recently developed a method for analyzing $\epsilon_{\pm}(R)$ for diatoms strictly in terms of the overlap of the two AOs which combine to describe the bonding-antibonding MO pair occupied by the shared electrons. In particular, Corvo considers the series expansion of $U_{\pm}(R)$ corresponding to Eq. (14) for the case of H_2, and also the corresponding expansions of the kinetic energy and effective Coulomb and exchange energy parts of $U_{\pm}(R)$. The kinetic energy part of $U_{\pm}(R)$ comes from the average of $u_{\pm}(\overline{r};R)$ with respect to $-(\hbar^2/2m_e)\nabla_1^2$ of Eq. (2), and the effective Coulomb and exchange energy part comes from the average of $u_{\pm}(\overline{r};R)$ with respect to $-e^2(\frac{1}{r_{11}}+\frac{1}{r_{12}}) + V(1;R)$, which is the effective Coulomb and exchange interaction of Eq. (2) for the case of H_2. The kinetic and effective Coulomb and exchange energies each exhibit a local extremum as a function of R for H_2, the former showing a minimum and the latter a maximum (Ref. 3). And, of course, the energy of the bonding (ground) electronic state exhibits a minimum for H_2 as well. Corvo found a strong similarity between the values of R at which $U_-(R)$ and its kinetic and effective Coulomb and exchange energy parts achieve their respective extrema, and the values of R at which certain functions of the overlap of the form, $R^kS^{k'}(R)$, achieve their respective extrema. Here k and k′ are integers, and the case, $k = k'$, applies to $U_-(R)$ and its minimum. In particular, the R for which RS(R) is extreme [i.e., for which $S(R) + RdS(R)\ dR = 0$] is very nearly the same as the R for which $U_-(R)$ is minimum in the case of H_2. The cases, $k \neq k'$, apply to the kinetic and effective Coulomb and exchange energies and their extrema. Encouraged by these results for H_2, Corvo applied this criteria to many homonuclear and heteronuclear diatomic molecules in ground electronic states and,

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for many cases, also in excited electronic states. The diatoms and electronic states he studied are those for which considerable spectroscopic data exists, and he found the criteria to be remarkably successful, especially for prediction of the values of R for which bonding interaction energies obtain their minimum values.

Corvo continued his analysis based on the series expansion of $\epsilon_-(R)$ for H_2 in integer powers of R and S(R). He proposed a representation of $\epsilon_\pm(R)$ in terms of a three-parameter function which depends on powers of R and S(R); namely,

$$\epsilon_\pm(R) = \epsilon_0 + H_\pm R^{K_\pm R^2} \left[S^{L_\pm R^2}(R) \right], \tag{15}$$

in which the parameters $H_\pm$, $K_\pm$ and $L_\pm$ are adjustable, and ϵ_0 refers to ϵ_1 in the case of $\epsilon_+(R)$ and to ϵ_2 in the case of $\epsilon_-(R)$ see Eqs. (9)-(11). Corvo found that Eq. (15) provides a *reliable representation* of bonding interaction energies, $\epsilon_-(R)$, as specified by data from spectroscopic measurement not only for the ground electronic state of H_2 but also for some of its electronically excited states and for the ground and some excited electronic states of several other diatomic molecules. The form of Eq. (15) exhibits a single product of a noninteger power of R and a noninteger power of S(R) and therefore, depending on R, represents in a global way various portions of the series expansion of $\epsilon_\pm(R)$ in integer powers of R and S(R). Furthermore, Eq. (15) represents $\epsilon_\pm(R)$ directly in terms of the overlap, $S_{u_1,u_2}(R)$, which, in light of earlier discussion, is a decisive indicator of both the qualitative and quantitative behavior of $\epsilon_\pm(R)$. Though the theoretical underpinings of Corvo's analysis, including Eq. (15), are already substantial, they still require some additional fortification. His analysis has certainly proven itself reliable on the basis of success *in application* to known electronic interaction energies of many diatomic molecules. The approach here relies on it as a sound basis for estimation of molecular ground and excited electronic state interaction energies.

According to the estimation of $\epsilon_\pm(R,G)$ for a molecule in terms of a sum of atom-atom contributions, $\epsilon_{IJ}(R_{IJ},G)$, for each (I,J) pair of atoms comprising the molecule,

$$\epsilon_\pm(R,G) \simeq \sum_{\text{pairs(I,J)}} \epsilon_{IJ}(R_{IJ},G), \tag{16}$$

so that Eq. (14) becomes

$$U_\pm(R,G) \simeq \sum_{\text{pairs(I,J)}} \epsilon_{IJ}(R_{IJ},G) + \frac{e^2 Z_I Z_J}{R_{IJ}}. \tag{17}$$

The overall molecule may be comprised of two atoms, an atom and a molecule, or two molecules. That is, $u_1(\vec{r})$ and $u_2(\vec{r})$ of Eq. (4) may be two AOs, an AO and an MO, or two MOs. In the latter two cases an isolated molecular constituent's MO is resolvable into its AO components.

A crucial and original aspect of the present method is the use of the condition of maximum net AO overlap in the overall molecule as the basis for specification of orientations of these AO components and for specification of pair interaction energies, $\epsilon_{IJ}(R_{IJ},G)$ of Eq. (17) in a way descriptive of the atoms and atom-atom pairs, not in isolation, but rather in the molecular environment itself. That is, all AOs and atom-atom pair interaction energies associated with the shared electrons of an overall molecule satisfy, in this

method, mutual compatibility to one another on the basis of the criterion that the net overlap of the AOs in the molecule be maximum. This criterion is consistent with the qualitative connection between the degree of AO overlaps and the degree of lowering (raising) of one-electron energies of bonding (antibonding) MO pairs.

Collisions of a Na atom in its (3p, ^{2}P) excited electronic state with an H_2 molecule in its ground electronic state provides a specific example that will explain the precise nature of the overall approach. A least symmetrical geometry of the NaH_2 molecular complex corresponds to the most general collisional situation. Figure 2 shows that situation schematically. The two H atoms of the H_2 molecule (whose internuclear separation is R_{H_2}) are indicated by H_a and H_b. The 1s AOs of H_a and H_b are denoted by $1s_a$ and $1s_b$, respectively. The internuclear separation between the Na nucleus and the nucleus of $H_a(H_b)$ is $R_a(R_b)$.

The dominant configuration of the ground electronic state of an isolated H_2 molecule consists of a closed-shell in which the MO, $\sigma \propto 1s_a + 1s_b$, is occupied by two electrons, one of spin up and the other of spin down. That is, the occupied MO of highest one-electron energy in ground-state H_2 belongs to a closed shell, the electrons of which are fairly stable (due to the Pauli exclusion principle) against being shared by the molecular complex formed by ground-state H_2 and Na*(3p,^{2}P). Thus, in this case the shared electrons of the NaH_2 molecule come essentially from the Na atom. According to previous discussion in Sec. II, the MO of ground-state H_2 contributing the largest component to the MO which describes the shared electrons of NaH_2 is not the MO σ, but rather the MO, $\sigma^* \propto 1s_a - 1s_b$, which is the unoccupied MO of lowest one-electron energy in the ground-state configuration of H_2. This is indicated in Fig. 2 by the (+) sign for the $1s_a$ AO and the (-) sign for the $1s_b$ AO.

The occupied AO of highest one-electron energy in the electronic configuration of Na*(3p,^{2}P) is the 3p AO, which does not belong to a closed shell for this configuration, whose designation, in detail, is ($1s^2 2s^2 2p^6 3s^0 3p^1$, ^{2}P). Of the AOs of Na*, therefore, this 3p AO should contribute the largest component to the MO that describes the shared electrons of NaH_2, and these shared electrons are in this case essentially a single electron that occupies the 3p AO of Na*(3p,^{2}P) before it approaches H_2 in the formation of NaH_2. The bonding-antibonding MO pair for the shared electron of NaH_2 is thus approximated by

$$u_{\pm}^{(NaH_2)} \simeq C_{\pm}^{(NaH_2)} \left[3p^{(\gamma)} + \lambda_{\pm}^{(NaH_2)} \sigma^* \right], \tag{18}$$

in which $3p^{(\gamma)}$ denotes the Na* 3p AO whose orientation in the NaH_2 molecule is indicated by γ, the angle between the axis of the 3p AO and the NaH_b bond axis. Figure 2 shows this for the bonding (- sign) case of Eq. (18). The mixing coefficients $\lambda_{\pm}^{(NaH_2)}$ of Eq (18) have precise definition when the MOs, $u_{\pm}^{(NaH_2)}$, of Eq. (18) correspond to actual solutions of a one-electron Schrödinger equation of Eq. (1) appropriate for this excited-state configuration of NaH_2 [see the above discussion in connection with Eq. (9)]. In practice estimations of such mixing coefficients are possible in terms of the one-electron energies, ϵ_{3p} and ϵ_{σ^*}, of Na*(3p,^{2}P) and $H_2(\sigma^2, {}^1\Sigma_g^+)$, respectively, but the mixing coefficients are not of critical importance to this analysis.

The criterion of maximum net overlap of AOs for the molecule governs the value of γ, or, correspondingly, the orientation of the 3p AO in the NaH_2 molecule. For a given geometry of the nuclei, the net AO overlap in the molecule as a function of γ, is

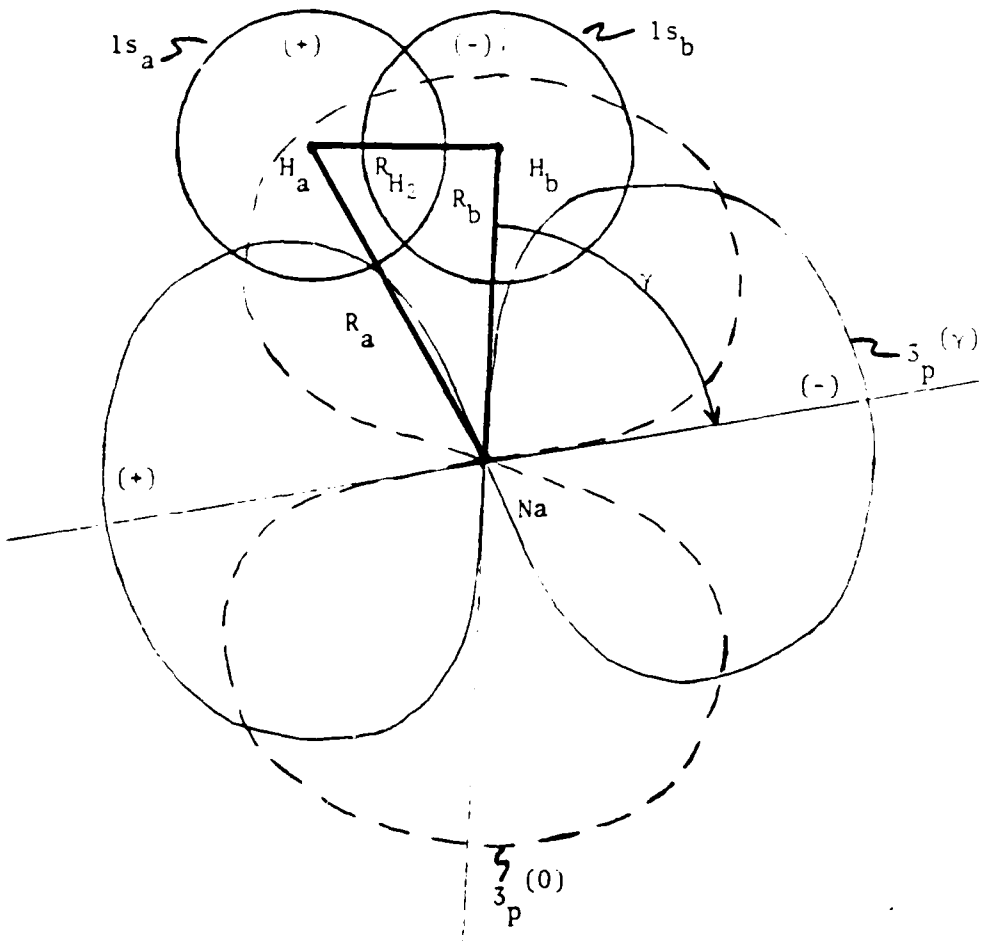

Figure 2

Schematic illustration of the atomic orbitals in connection with the shared electrons of the NaH_2 molecule formed by interaction of $Na^*(3p, {}^2P)$ and $H_2(\sigma^2, {}^1\Sigma_g^+)$. Explanation of the various labels appears in the text.

$$S_{net}(R_a,R_b,R_{H_2},\gamma) = S_{1s_a,3p^{(\gamma)}}(R_a) + S_{1s_b,3p^{(\gamma)}}(R_b) + S_{1s_a,1s_b}(R_{H_2}). \quad (19)$$

The appropriate value of γ is then the one for which S_{net} is maximum. In other words, upon approach of $Na^*(3p,^2P)$ to the H_2 molecule the 3p AO orients itself, to good approximation, so as to satisfy the condition of maximum AO overlap in the resulting NaH_2 molecule.

The specification of pair interaction energies of Eq. (17) that are characteristic of atom-atom pairs, not in isolation but in the molecular environment, is a crucial result of this research effort. The case of NaH_2 is a good example for the explanation of this specification. The estimation, in terms of atom-atom pair interaction energies as in Eq. (17), is of the molecular bonding-antibonding interaction energies, $U_\pm^{(NaH_2)}(R_a,R_b,R_{H_2},\gamma)$, corresponding to the bonding-antibonding MO pair, $u_\pm^{(NaH_2)}$, of Eq. (18). In Fig. 2 the orientation that the 3p AO of Na^* would have in the case of the bonding interaction of $Na^*(3p,^2P)$ and hydrogen atom, H_b, in the absence of hydrogen atom, H_a, is indicated by $3p^{(0)}$. The bonding-antibonding interaction energies of this isolated pair of Na^* and H atoms is denoted by $\epsilon_\pm^{(NaH)_0}(R)$, where R here refers to the internuclear separation of the two atoms. Based upon available experimental data or detailed electronic structure calculations for this particular diatomic interaction energy, $\epsilon_\pm^{(NaH)_0}(R)$ may be represented by analytical functions, according to the procedures described in the next section, or by functions of the form of Eq. (15) that directly involve the overlap which, in the case of the $Na^*(3p,^2P)$ - H_b atom-atom pair, is $S_{3p^{(0)},1s_b}(R_b)$. The use of Eq. (15) for descriptions of atom-atom pair interaction energies is attractive because it directly provides an approximate account of the role of AO overlap in diatomic interactions. Furthermore, Eq. (15) involves only a few parameters. In cases of atom-atom pair interactions for which no experimental data or calculations exist, information about the separated and united atoms or analysis, in terms of the virial theorem, of the relationship between the total electronic interaction energy and its kinetic and average Coulomb and exchange energy components can lead to an adequate determination of these few parameters. Forms such as Eq. (15) embody much of the essential physics of atom-atom interactions and are very promising for purposes of estimation. The parameters of Eq. (15) for $\epsilon_\pm^{(NaH)_0}(R)$, the example at hand, are denoted by $H_\pm^{(0)}$, $K_\pm^{(0)}$, and $L_\pm^{(0)}$, respectively, and

$$\epsilon_\pm^{(NaH)_0}(R) \simeq \epsilon_0 + H_\pm^{(0)} R^{K_\pm^{(0)} R^2} \left(S_{3p^{(0)},1s}(R)\right)^{L_\pm^{(0)} R^2}, \quad (20)$$

where ϵ_0 refers to the greater (lesser) of $(\epsilon_{3p}, \epsilon_{\sigma^*})$ for the bonding (antibonding) situation.

Each Na - H pair in the molecular environment will exhibit an interaction energy that reflects the presence of the other H atom. The allowance, in the present approach, for the orientation angle, γ, of the Na^* 3p orbital to adjust so as to maximize the net AO overlap accounts approximately for these influences of the molecular environment. This means that in the NaH_2 molecule the overlap is $S_{3p^{(\gamma)},1s_a}(R_a)$ for the $Na^*(3p,^2P)$ - H_a atom-atom pair and $S_{3p^{(\gamma)},1s_b}(R_b)$ for the $Na^*(3p,^2P)$ - H_b atom-atom pair. Each of these overlaps differs from the corresponding isolated atom-atom pair overlap, $S_{3p^{(0)},1s}(R)$. The simplest means, by which the influence of the molecular environment on the atom-atom pair interaction energies can be accounted for in terms of these overlap differences, is replacement, in Eq. (20), of $S_{3p^{(0)},1s}(R)$ by $S_{3p^{(\gamma)},1s_{a(b)}}(R_{a(b)})$. In this approximation the

parameters, $H_{\pm}^{(0)}$, $K_{\pm}^{(0)}$, and $L_{\pm}^{(0)}$, which are characteristic of the isolated $Na^*(3p,^2P)$ - H interaction, remain unchanged in the description of the corresponding interaction in the NaH_2 molecule, and the overlap alone accounts for the molecular environment. This is reasonable because the influence due to molecular environment on an atom-atom pair manifests itself primarily in terms of the distortion, due to the other nearby atoms, of the electronic charge clouds and their overlaps associated with the interaction. The approximation for the bonding-antibonding interaction energies for a molecule consisting of $Na^*(3p,^2P)$ and $H_2(\sigma^2,{}^1\Sigma_g^+)$ as constituents is

$$U_{\pm}^{(NaH_2)}(R_a,R_b,R_{H_2},\gamma) \simeq \epsilon_{\pm}^{(NaH_a)}\gamma(R_a) + \epsilon_{\pm}^{(NaH_b)}\gamma(R_b) + \epsilon_{-}^{(H_2)}(R_{H_2}) + e^2\left(Z_H Z_{Na}(R_a^{-1} + R_b^{-1}) + Z_H^2 R_{H_2}^{-1}\right), \quad (21)$$

where $\epsilon_{-}^{(H_2)}(R_{H_2})$ is the antibonding interaction energy of an isolated H_2 molecule corresponding to its σ^* MO. The pair interaction energy, $\epsilon_{-}^{(H_2)}(R_{H_2})$, contributes to both the bonding and antibonding interaction energy of Eq. (21). This example illustrates the general principle that the pair interaction energies of Eq. (17) associated with the AOs of two atoms of the same molecular constituent of an overall molecule correspond to the bonding (antibonding) combination of these two AOs if they combine in a bonding (antibonding) way in the representation of the molecular constituent MO that participates in the description of shared electrons of the overall molecule. All other pair interaction energies of Eq. (17) correspond to bonding or antibonding combinations of the respective AO pairs depending upon whether the description is of the bonding (U_-) or antibonding (U_+) molecular interaction energy, respectively.

The preceding example of the interaction of $Na^*(3p,^2P)$ and $H_2(\sigma^2,{}^1\Sigma_g^+)$ illustrates the basic method, resulting from this research effort, for estimation of molecular electronic interaction energies. This approach is systematic, and its application is straight forward. It accounts for the perturbative influence of the molecular environment or the AOs and pair interaction energies of atoms in a molecule to the extent that p, d, f, ... AOs are involved. This is illustrated by the above example of NaH_2. Unlike p, d, f, ... AOs, the s AOs have no directional properties and, therefore, are neutral by themselves with respect to alignment for maximization of AO overlap. Thus, for molecules whose shared electrons are described by linear combinations of s AOs only, the method, in the simple version outlined above, uses unperturbed atom-atom pair interaction energies in Eq. (17).

IV. RATIONAL-FRACTION REPRESENTATION OF THE INTERACTION POTENTIALS OF THE NF DIATOMIC MOLECULE IN ITS GROUND AND A ELECTRONIC STATES

The reaction, $NF(a,^1\Delta) + N(^2D) \rightarrow N_2(?) + F,^2P)$, was examined to see which electronic states of N_2 might be found taking into account energy and electron spin. Eventually, eleven states of diatomic nitrogen including the ground (X) state and metastable (A) state are possible products. Of the eleven only a $^7\Sigma_u^+$ and the A' $^5\Sigma_g^+$ states are spin-forbidden products. Radiative transitions to the X state are forbidden from all ten excited states. Among spin-allowed product states of N_2, the $^1\Sigma_g^+$ and a' (v = 0) states as well as the A state are metastable.

Potential curves V(R) as a function of internuclear separation R were sought for the X and A states of N_2. These V(R) are for incorporation in N_2F potential surfaces. For the X state we sought a V(R) - V(∞) in the form of a rational fraction of the form (1/R)[L/(L + S)]. Here the integer L is the degree of the numerator polynomial. The minimum value of L is 1 since there is one zero in V(R) - V(∞) at finite R. Two constraints were applied to the coefficients. The first numerator coefficient, p_0, was constrained so that $p_0/R = (Ze)^2/R$ with nuclear charge Z = 7 for nitrogen. The highest numerator and denominator coefficients were constrained to have a ratio $p_L, q_{L+5} = -C_6$. Here C_6 is the long-range potential coefficient in V(R) - V(∞) = $-C_6/R^6$ as R $\rightarrow \infty$. In the intermediate R region, the fraction coefficients were least squares fitted to the RKR curves (based on vibrational states v = 0 to 21) from Jain and Sahni (Ref. 13) and from Benesch, et al. (Ref. 14). The best (1/R)[1/6], (1/R)[2/7], and (1/R)[3/8] fits to the Jain and Sahni potential were essentially identical. The root-mean-square error at all v = 0 to 21 turning points was 19.8 cm^{-1}; the RKR procedure (Ref. 15) cannot be relied upon to be more accurate. The error in the predicted V(∞) from the three identical rational fractions was only 2.69%.

A third constraint, V(∞) = D_e = 79,850 cm^{-1} (Ref. 16), was used in a (1/R)[1/6] fitting to Jain's and Sahni's ground-state experimental V(R). In a sense, this results in the best V(R) available for the ground state of N_2 over the entire domain $0 \leq R < \infty$. With this V(R) the WBK method was used to extract all bound vibrational levels. Sixty-three bound states were derived. The v = 62 level occurs at 79,846.8 cm^{-1}, 3.2 cm^{-1} below dissociation.

For the A electronic state, a rational fraction of the form V(∞) + (1/R)[L/L + 5] was fitted to the same p_0 and (p_L/q_{L+6}) as for the ground state. The Benesch, et al. RKR turning points (Ref. 14) were used for the 14 experimentally known vibrational states. The root-mean-square discrepancy in vibrational energies was only 7.0 cm^{-1} but V(∞) was 8.7% high. Again a third constraint, V(∞) = D_e = 29,640 cm^{-1}, produced a fitted V(R) on (0, ∞) of sufficient reliability to warrant extracting first-order WBK vibrational eigenenergies. Thirty eight levels were found for the A state. The v = 37 energy is 1.8 cm^{-1} below the dissociation limit for two ground-state N atoms.*

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* A paper entitled "Vibrational Potential Representation for the X and A Electronic States of N_2" is to be read at the 40th Symposium on Molecular Spectroscopy, June 17 - 21, 1985 at Ohio State University

V. OUTLINE OF OVERALL ESTIMATION METHODS

The preceding sections have presented results of an initial investigation into methods for reliable estimation of electronic structure associated with inelastic and reactive molecular collisions between electronically excited species. The emphasis has been on energetic gaseous media that can be characterized by macroscopic states of equilibrium with respect to all except electronic degrees of freedom. Such gases are typical of electronic-transition chemical-laser media, in which statistical equilibration of translational, rotational and vibrational degrees of freedom at some temperature, T, applies, but whose atomic and molecular constituents are electronically excited via chemical reaction with electronic excitation energies well in excess of thermal energies. In addition to the foregoing results for estimation of molecular excited-state electronic structure and energies, this research effort has also led to the outline of a conceptually and calculationally simple, yet systematic, procedure for analysis of the dynamics of all the possible reactive and/or nonreactive collisions of electronically excited atoms and molecules for a given gas. The overall procedure includes the estimations of electronic structure and energies, as described by the preceding sections, and consists of three basic steps, an overview of which follows.

The first step of the procedure is the determination of the possible electronic structure of the molecular complex formed by collision and, for each electronic state of the molecular collision complex, the possible electronic states of products of the collision for both reactive and nonreactive processes. This first step is based on descriptions of one-electron orbitals of molecular collision complexes by simple linear combinations of orbitals of reactants and of products (Refs. 6, 10 and 17), and on correlation of reactant and product orbitals with those of the least symmetrical geometry of the molecular collision complex (Refs. 17 and 18). Symmetrical, collinear or frozen geometries of molecular collision complexes represent only a small domain of the geometries accessed by the nuclei during a collision. In other words, quasi-molecules that form during collision of atoms and molecules spend some, if not most, of their existence in geometries of least symmetry. Thus, the least symmetrical molecular collision complex is the lowest common denominator for correlations of reactant and product electronic structure (Refs. 18 and 19). Conservation of electronic spin angular momentum during molecular collisions holds to a great extent, since interaction between electronic spin and orbital angular momenta tends to be small for molecules. So electronic spin criteria are reliable and expeditious for correlation of reactant and product states. These spin considerations do not, however, lead to a great deal of discrimination as to which spin-allowed product states are most likely to result from a collisional process (Ref. 18).

The second step consists of the analysis of molecular orbitals for shared electrons of the collision in terms of their bonding or antibonding character (Refs. 6 and 10), as described in detail in Secs. II and III. The electronic configurations in the reactant channel that are antibonding do not enter into such analyses because they mediate collisions with typically strongly repulsive intermolecular electronic energy surfaces and, hence, govern essentially elastic scattering. The bonding (and also weakly antibonding) configurations in the reactant channel are the ones that govern inelastic and reactive, as well as possible elastic, scattering. In the product channel those antibonding configurations, whose repulsive electronic potential energy surfaces exhibit avoided crossings with electronic energy surfaces of the collision complex that are bonding or weakly antibonding in the reactant channel, have possible roles in mediating inelastic or reactive molecular collision processes. Product-channel bonding or weakly antibonding configurations, that have electronic energies which match or are close to reactant-channel

bonding or weakly antibonding electronic energy surfaces, also can mediate inelastic and reactive processes.

The overall procedure up to this point already provides useful information about a given molecular collision on the basis simply of information about atomic- and molecular-orbital structure and electronic energies of precollision and postcollision partners. Such information for atoms and small molecules of the type that often form the basis of electronic-transition chemical-laser schemes, are usually available from spectroscopic studies (Ref. 11). The interaction potential energies of N_2 in its ground and A electronic states have served as examples of this sort in the present study, which has led to representations for these potential energies in terms of rational fractions as described in Sec. IV. In addition, the methods described by Secs. II and III provide a simple but powerful and general means for estimation of the structure and energies of excited electronic states of molecules in the absence of appropriate or sufficient spectroscopic or calculational information. These methods depend upon the fundamental role of atomic-orbital overlap in the characterization of bonding and antibonding electronic interaction energies. The estimation of the interaction energy for a given configuration of a molecule in some geometry is in terms of a sum of atom-atom pair contributions that reflect the perturbative influence of the molecular environment on the basis of AO overlap optimization. The calculation of AO overlaps is relatively simple and routine (Ref. 20), so this step of the procedure poses no difficulties. These estimates of electronic energy surfaces provide a useful characterization of their topology, an assessment of the location and magnitude of energy barriers to reaction, and also an assessment of avoided crossings of one electronic surface with another.

The final step of the overall procedure for analysis of molecular collision dynamics is estimation of rates for the various inelastic and reactive outcomes of a collision of specific electronically excited atoms or molecules. Here the use of elementary transition-state theory of chemical reactions (Ref. 21) and of Landau-Zener theory in the case of nonadiabatic electronic transitions in molecular collisions (Ref. 22) provides the simplest and most appropriate approach. The application of these two theories depends upon a knowledge of the electronic energy surfaces, as provided by the previous two steps. The application of transition-state theory, for example, in the case of a reaction governed by a particular electronic state, would involve the calculation of the relevant partition function for the molecular collision complex based upon the topology of the corresponding electronic surface near the reaction barrier. The Arrhenius factor, $e^{-E_A/kT}$, is determined by the energy, E_A, of the reaction barrier (Ref. 21). Furthermore, the molecular geometry of a reaction barrier specifies whether it occurs early or late in a reaction process. Reactions governed by early barriers have appreciable rates only for vibrationally cold reactants and lead to vibrationally hot products, while just the opposite holds for reactions governed by late barriers (Ref. 23). Finally, estimates of the topology of two electronic energy surfaces near avoided crossings lead, via the Landau-Zener formula, to corresponding estimates of the probability of occurrence during collision of electronic transitions between the corresponding electronic states (Ref. 22).

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