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PUBLICATIONS

1. A Theoretical Description of the Radiative Decay Processes ($b^1\Sigma^+$, $a^1\Delta$) $\rightarrow$ $X^3\Sigma^-$ in NF.
D. R. Yarkony, J. Chem. Phys., *85*, 7261 (1986).

2. On the Radiative Lifetimes of the $b^1\Sigma^+$ and $a^1\Delta$ States in NCl.
D. R. Yarkony, J. Chem. Phys., *86*, 1642 (1987).

3. On the Characterization of the Dipolar Spin-Spin Interaction in Molecular Systems: A Symbolic Matrix Element Approach.
J. O. Jensen and D. R. Yarkony, Chem. Phys. Lett. *141*, 391 (1987).

4. On the Evaluation of Lifetimes for Spin-Forbidden Radiative Transitions Originating in Coupling to States Embedded in a Continuum. Application to CH^-.
B. H. Lengsfield, J. O. Jensen, and D. R. Yarkony, J. Chem. Phys. *88*, 3853 (1988).

5. On the Evaluation of Non Born-Oppenheimer Interactions for Born-Oppenheimer Wavefunctions V: A Body Fixed Frame Approach. Applications to Isotope Effects of Equilibrium Geometries and the Adiabatic Correction for the $X^1\Sigma^+$ State of LiH.
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6. On the Electronic Structure of the He^-H_2 System Characterization of, and Nonadiabatic Interactions Between, the $1^1A'$ and $2^1A'$ Potential Energy Surfaces.
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8. On the Quenching of Helium 2^3S: Potential Energy Curves for, and Nonadiabatic, Relativistic and Radiative Couplings Between, the $a^3\Sigma_u^+$, $A^1\Sigma_u^+$, $b^3\Pi_g$, $B^1\Pi_g$, $c^3\Sigma_g^+$ and $C^1\Sigma_g^+$ States of He_2.
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10. On the Characterization of Regions of Avoided Surface Crossings Using an Analytic Gradient Based Method
D. R. Yarkony, J. Chem. Phys. in press

11. Spin-Orbit Effects in the Decomposition Reaction $N_3H(X^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-, a^1\Delta)$
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12. Theoretical Studies of the Electronic Structure Aspects of Electronically Nonadiabatic Processes Using Analytic Gradient Techniques: Seams of Avoided Crossings in the Electronic Quenching Reaction $Na(^2P) + HCl \rightarrow NaCl + H(^2S)$
D. R. Yarkony, submitted to J. Phys. Chem. (Proceedings of " Forty Years of Quantum Chemstry", Oct. 1989)

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The goal of this research program was to consider the electronic structure aspects of radiative and radiationless decay processes related to the stability and formation of high energy density materials. In order to accomplish this goal a unique system of electronic structure algorithms, the BROOKLYN programs, has been developed. These programs provide advanced capabilities for the study of the electronic structure aspects of spin-forbidden and electronically nonadiabatic processes The methodology which we developed is based *exclusively* on large scale configuration state function expansions (10^5–10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of radiative and radiationless decay processes. Problems of particular relevance to the high energy density materials program include: (i) a study of the possible stability of the energetic maximum ionicity state $(HeH)^+$-H^-; (ii) a study of the spin-forbidden decay mechanism of the model azide system $N_3H(^1A') \rightarrow N_2(^1\Sigma_g^+) + NH(X^3\Sigma^-)$ and finally a study of the decay pathways for the metastable excited state of the helium atom, $He(2^3S)$, resulting from collisions with other (ground state) helium atoms.

Finally a new phase of program development has been initiated focusing on the efficient determination of regions of allowed and avoided crossings of potential energy surfaces using analytic gradient techniques. This program development, which will be completed during our present AFOSR sponsored research program, will provide powerful new tools for the study of spin-forbidden and electronically nonadiabatic processes.

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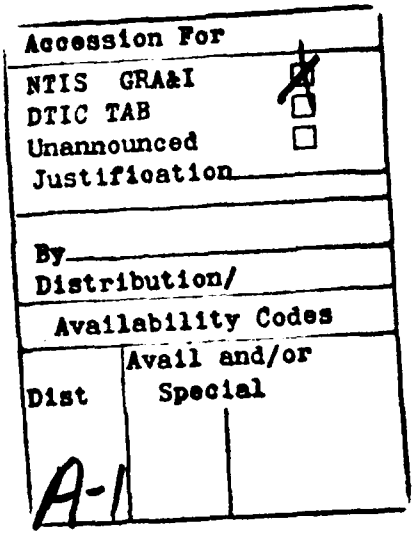

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SUMMARY

The goal of this research program was to consider the electronic structure aspects of radiative and radiationless decay processes related to the stability and formation of high energy density materials. In order to accomplish this goal a unique system of electronic structure algorithms, the BROOKLYN programs, has been developed. These programs provide advanced capabilities for the study of the electronic structure aspects of spin-forbidden and electronically nonadiabatic processes The methodology which we developed is based *exclusively* on large scale configuration state function expansions (10^5–10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of radiative and radiationless decay processes. Problems of particular relevance to the high energy density materials program include: (i) a study of the possible stability of the energetic maximum ionicity state $(HeH)^+$-H^-; (ii) a study of the spin-forbidden decay mechanism of the model azide system $N_3H(^1A') \rightarrow N_2(^1\Sigma_g^+) + NH(X^3\Sigma^-)$ and finally a study of the decay pathways for the metastable excited state of the helium atom, $He(2^3S)$, resulting from collisions with other (ground state) helium atoms.

Finally a new phase of program development has been initiated focusing on the efficient determination of regions of allowed and avoided crossings of potential energy surfaces using analytic gradient techniques. This program development, which will be completed during our present AFOSR sponsored research program, will provide powerful new tools for the study of spin-forbidden and electronically nonadiabatic processes.

TECHNICAL REPORT

One of the principal aspects of our research program has been the development of new theoretical tools for treating spin-forbidden and electronically nonadiabatic processes. These tools have then been used to study the stability and/or decay mechanisms of potential high energy density materials(HEDM's). We believe that as a result of computational limitations the electronic structure aspects of these important classes of chemical problems had received inadequate treatment. The methodology which we developed is based *exclusively* on large scale configuration state function expansions (10^5–10^6 terms). These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of radiative and radiationless decay processes. Below we outline the methods we have developed and their applications in the HEDM program

I: SPIN-FORBIDDEN CHEMISTRY

Our studies in the area of spin-forbidden chemistry employ the Breit-Pauli approximation[1] and consider those interactions which lift the 2S+1 degeneracy associated with the total electron spin quantum number, S. These interactions are the full microscopic spin-orbit interaction $\hat{H}^{so}$,

$$\hat{H}^{so} = \sum_{i=1}^{N} \mathbf{h}^{so}(i)\cdot \mathbf{s}_i + \sum_{i,j=1}^{N} \mathbf{h}^{soo}(i,j)\cdot\left(\mathbf{s}_i + 2\mathbf{s}_j\right) \qquad 1.1$$

and the dipolar spin-spin interaction $\hat{H}^{ss}$

$$\hat{H}^{ss} = \sum_{i,j=1}^{N} \mathbf{s}_i \cdot \mathbf{h}^{ss}(i,j)\cdot \mathbf{s}_j \qquad 1.2$$

where $\mathbf{h}^{so}(i)$, $\mathbf{h}^{soo}(i,j)$, and $\mathbf{h}^{ss}(i,j)$ are the microscopic spin-orbit, spin-other-orbit, and dipolar spin-spin interactions[1] and we write $\hat{H}^{BP} = \hat{H}^{so} + \hat{H}^{ss}$.

(A) Methodology

Our treatment of these interactions is *unique* in *two* ways. We use the symbolic matrix element methods originally introduced in the treatment of the nonrelativistic Born Oppenheimer hamiltonian $\hat{H}^0$ by Liu and Yoshimine[2] to evaluate the matrix elements of $\hat{H}^{so}$[3] and $\hat{H}^{ss}$[4] in the N-electron configuration state function (CSF) space. This enables the use of large scale CSF spaces (10^5–10^6 terms) to characterize these interactions. These spaces are one to two orders of magnitude larger than those accessible using previously existing methods[1,6] and have, as discussed below, improved significantly the reliability of theoretical work in this area.

The second unique aspect of our approach involves the manner in which the relativistic wavefunction is obtained from the zeroth order nonrelativistic [configuration interaction (CI)] wavefunction.[5] Within the context of the Breit-Pauli approximation the relativistic wavefunction,$\Psi(I)$, is obtained from the zeroth order nonrelativistic wavefunction, $\Psi^0(I)$, using perturbation theory. The commonly used approach had been[6] to determine the perturbation contribution to the relativistic wavefunction

$$\Psi(I) = \Psi^0(I) + \Psi^1(I) \qquad 1.3$$

from first order perturbation theory using a spectral resolution

$$\Psi^1(I) = \sum_K \frac{\left\langle \Psi^0(K) \middle| \hat{H}^{BP} \middle| \Psi^0(I) \right\rangle}{E^0(K) - E^0(I)} \Psi^0(K) \qquad 1.4$$

where $\Psi^0(K)$ satisfies the nonrelativistic Schroedinger equation

$$[\hat{H}^0 - E^0(I)]\Psi^0(I) = 0 \qquad 1.5$$

This procedure is unsatisfactory owing to the need to drastically truncate the sum in eq. 1.4. Instead we have introduced[5] a technique which allows $\Psi^1(I)$ to be determined *exactly*, within a given CSF space, as the solution of

$$[\hat{H}^0 - E^0(I)]\,\Psi^1(I) = -\hat{H}^{BP}\Psi^0(I) \quad . \qquad 1.6$$

The use of eq. 1.6 in lieu of eq. 1.4 has improved considerably our ability to predict radiative rates for spin-forbidden dipole-allowed processes.

Eq. 1.6 is only satisfactory when the electronic states in question are well separated. When one or more of the electronic states in eq. 1.4 is near to, quasidegenerate with, $\Psi^0(I)$ a generalization of eq. 1.6 is required. As part of this research program we have shown[7] how such a generalization can be derived from partitioning theory.[8] The description which emerges from this formalism expresses the electronic wavefunctions as linear combinations of dressed diabatic wavefunctions $[\Psi^d(I)]$

$$\Psi^d(I) = \Psi^0(I) + \Psi_Q^{1,d}(I) \qquad 1.7$$

where the dressing term, $\Psi_Q^{1,d}(I)$ represents the perturbation of the (diabatic) quasidegenerate state $\Psi^0(I)$ by states *outside* the quasidegenerate space and satisfies

$$\left[H^0 - E^0(I)\right]\Psi_Q^{1,d}(I) = -\hat{Q}\hat{H}^{BP}\Psi^0(I) \qquad 1.8$$

where $\hat{Q}$ projects onto the orthogonal complement of the quasidegenerate space. The quasidegenerate dressed diabatic states $\Psi^d(I)$ which are the analogues of the $\Psi(I)$ in eq. 1.3 are mixed by the Breit-Pauli interaction $\hat{H}^{BP}$. This mixing is given by a secular equation with the dimension of the quasidegenerate space which has the form:

$$\begin{pmatrix} H_{1,1}-E & H_{1,2} & \cdots & H_{1,M} \\ \vdots & H_{2,2}-E & & \\ H_{M,1} & & \ddots & H_{M,M}-E \end{pmatrix}\begin{pmatrix} \Psi^d(1) \\ \vdots \\ \Psi^d(M) \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \qquad 1.9$$

where $H_{I,J}=\left\langle \Psi^d(I)\middle|\hat{H}^0+\hat{H}^{BP}\middle|\Psi^d(J)\right\rangle$. Since the coupling between the states $\Psi^d(I)$ originates from a potential term $\hat{H}^{BP}$ rather than the derivative coupling terms to be discussed subsequently the $\Psi^d(I)$ are referred to as diabatic states.

Applications of the above described methodology in the area of spin-forbidden radiative decay are discussed below.

(B) Applications

(i) Radiative Decay in Nitrogen Halides, NF and NCl. Resolution of Significant Experimental Discrepancies

The lifetime with respect to spin-forbidden radiative decay is an important attribute when assessing the utility of a metastable species as an energy transfer agent in a chemical laser system. The $b^1\Sigma^+$ and $a^1\Delta$ states of the nitrogen halides NF and NCl are such metastable states as in each case the molecule has an $X^3\Sigma^-$ ground state. These systems have therefore been suggested as potential energy sources. This possibility motivated our theoretical studies of the spin-forbidden dipole-allowed radiative decay processes $(b^1\Sigma^+, a^1\Delta) \rightarrow X^3\Sigma^-$ in both NF and NCl.

Our study of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transition in NF revealed a key misconception concerning the nature of this transition. It had been previously reported[9] that $\mu_{\|}/\mu_{\perp} \sim 1/7$ based on Watson's[10] theoretical model of the experimental results of Douglas and Jones (DJ).[11] Here

$$\mu_{\|}=\left\langle \Psi\left(b^1\Sigma^+_{0+}\right)\middle|\hat{\mu}_0\middle|\Psi\left(X^3\Sigma^-_{0+}\right)\right\rangle \qquad 1.10a$$

and

$$\mu_{\perp} = \left\langle \Psi\left(b^1\Sigma^+_{0+}\right) \middle| \hat{\mu}_{-1} \middle| \Psi\left(X^3\Sigma^-_1\right)\right\rangle \qquad 1.10b$$

where $\hat{\mu}$ is the electronic dipole moment operator and $\Psi(I)$ (eq. 1.3) was obtained from eqs. 1.5–1.6. Although this result had been confirmed by SCF level calculations[9] it is in fact in error! Using the basic data of DJ and Watson's theoretical model we observed[5] that the correct ratio should be $\mu_{\|}/\mu_{\perp} \sim 7$, that is the inverse ratio had been reported! As a result of the confusion over the original experiment of DJ, Vervloet and Watson[12] reinvestigated the 0-0 band of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ emission using a Fourier transform spectrometer. Their result $\mu_{\|}/\mu_{\perp} \cong 3.8$ is in excellent agreement with our best theoretical estimate[13] $\mu_{\|}/\mu_{\perp} \sim 3.87$.

For the $a^1\Delta$ state of NCl the situation was much less subtle. In this case conflicting lifetime data for the $a^1\Delta \rightarrow X^3\Sigma^-$ transition had been reported.[14,15] Coombe and van Benthem[14a] had reported a lifetime of 205 nsec based on gas phase measurements. However shortly thereafter Becker and coworkers[15] reported a lifetime based on matrix isolation experiments of 1440 nsec (which extrapolates to a gas phase value of 2658 nsec). Our calculations (reported as a communication)[16] gave an estimated lifetime for the $a^1\Delta \rightarrow X^3\Sigma^-$ transition of 2400 nsec confirming the results of Becker et al.

(ii) Spin-Forbidden Radiative Decay Resulting from Coupling to Bound States Embedded in a Continuum. Application to the $a^1\Delta \rightarrow X\ ^3\Sigma^-$ Transition in CH^-

The previously noted work on the nitrogen halides not withstanding perhaps the most convincing demonstration of the power of the methodology we have introduced comes from our treatment[17] of the $a^1\Delta \rightarrow X^3\Sigma^-$ transition in CH^- a transition which had been studied experimentally by Lee's group at Berkeley.[18] This transition borrows intensity from $^3\Pi$, $^1\Pi$ states embedded in the ionization continuum of $CH(^2\Pi) + e^-$. Consequently traditional techniques for handling this problem based on the eigenstate expansion of $\Psi^1(I)$, eq. 1.4, are computationally intractable because of the *necessity* of obtaining a large number eigenstates, $\Psi^0(K)$ of $\hat{H}^0$. Consequently Lee and coworkers note in their work that a theoretical estimate of the lifetime of the

$a^1\Delta \rightarrow X^3\Sigma^-$ transition in CH^- "would be interesting but difficult given the presence of the ionization continuum." However our approach overcomes this difficulty since by obtaining $\Psi^1(I)$ directly from eq. 1.6 the correct contribution from *each* eigenstate is obtained.

A related problem concerns the determination of a molecular orbital space appropriate for the characterization of $\Psi^1(I)$, a function which contains contributions from highly excited states. We have developed a method to address this question based on the iterative natural orbital (INO)[19] procedure.

Our treatment of the spin-forbidden radiative transition $a^1\Delta \rightarrow X^3\Sigma^-$ in CH^- has been reported.[17] Using the INO procedure it was found that the optimum orbital space for describing $\Psi^1(I)$ includes a molecular orbital with character intermediate between the compact valence orbital and the diffuse orbital obtained from two alternative MCSCF procedures. This orbital space, the INO orbital space, was obtained from these two distinctly different starting points providing convincing evidence of the utility of this approach for obtaining molecular orbitals for use in the description of $\Psi^1(I)$. Using the INO orbital set a lifetime (τ) for the ground vibrational level of the $a^1\Delta$ state of 6.14($\pm$1.2)s was obtained. This value is in excellent agreement with the experimental value τ = 5.9(+0.8, –0.6)s reported by Okumura et al.[18] Note that agreement with experiment would have been *less satisfactory* (τ = 4.41s) if the INO optimized orbitals had *not* been used.

(iii) Spin-Forbidden Radiative Decay Involving Quasi-Degenerate States. Application to the $B^1\Sigma^+ \rightarrow a^3\Pi$ Transition in MgO.

As noted above when treating spin-forbidden radiative processes involving spin-allowed surface crossings or closely spaced PES's, that is spin-forbidden radiative decay involving quasidegenerate states, the straightforward first order perturbation treatment given by eqs. 1.4 or 1.6 is inappropriate. Instead the method outlined in eqs. 1.7–1.9 is required. This approach recognizes the special status of the quasidegenerate states while retaining the advantages inherent in the use of eq. 1.6 (rather than eq. 1.4) for treating the perturbation resulting from the remaining states.

Quasidegenerate perturbation theory was used to study[7] the spin-forbidden dipole-allowed $B^1\Sigma^+ \rightarrow a^3\Pi$ transition in MgO which had been investigated experimentally by Ip in R. W. Field's group at MIT.[20] In order to characterize this transition five (dressed) diabatic wavefunctions were determined

$$\Psi\left(B^1\Sigma^+_{0+}\right) = \Psi^0\left(B^1\Sigma^+_{0+}\right) + \Psi^1\left({}^3\Sigma^-_{0+}; B^1\Sigma^+_{0+}\right) + \Psi^1\left({}^3\Pi_{0+}; B^1\Sigma^+_{0+}\right) \qquad 1.11$$

$$\Psi\left(A^1\Pi_1\right) = \Psi^0\left(A^1\Pi_1\right) \qquad 1.12a$$

$$\Psi\left(a^3\Pi_1\right) = \Psi^0\left(a^3\Pi_1\right) + \Psi^1_Q\left({}^1\Pi_1; a^3\Pi_1\right) \qquad 1.12b$$

$$\Psi\left(X^1\Sigma^+_{0+}\right) = \Psi^0\left(X^1\Sigma^+_{0+}\right) + \Psi^1\left({}^3\Sigma^-_{0+}; X^1\Sigma^+_{0+}\right) + \Psi^1_Q\left({}^3\Pi_{0+}; X\,{}^1\Sigma^+_{0+}\right) \qquad 1.13a$$

$$\Psi\left(a^3\Pi_{0+}\right) = \Psi^0\left(a^3\Pi_{0+}\right) + \Psi^1_Q\left({}^1\Sigma^+_{0+}; a^3\Pi_{0+}\right) \qquad 1.13b$$

where the subscript Q indicates that the first order perturbation contribution (the dressing) is determined in a subspace orthogonal to the lowest state of the indicated symmetry which in the present circumstance is quasidegenerate with the zeroth order state being perturbed. The dressing terms (Ψ^1) give rise to an 'intrinsic' spin-forbidden transition moment for the $B^1\Sigma^+ \rightarrow a^3\Pi$ transition as they result in wavefunctions of mixed singlet-triplet character. The geometry dependent mixing of the pair of diabatic states in eq. 1.12 and (separately) the pair in eq. 1.13 is determined from a secular equation with hamiltonian $\hat{H}^0 + \hat{H}^{so}$ (eq. 1.9). This mixing gives rise to an additional contribution to the $B^1\Sigma^+ \rightarrow a^3\Pi$ transition moments.

Using this approach the parallel $\mu_{||}(B^1\Sigma^+_{0+}, v = 0; a\ {}^3\Pi_{0+}, v = n)$ and perpendicular $\mu_{\perp}(B^1\Sigma^+_{0+}, v = 0; a\ {}^3\Pi_1, v = n)$ components of the $B^1\Sigma^+ \rightarrow a^3\Pi$ transition moment were determined. The n = 0, 1 transitions had been observed experimentally.[20] The results for these transitions were found to be in good accord with the available experimental data. For example the calculated ratio F of the radiative rate for the $B^1\Sigma^+ \rightarrow a^3\Pi(0,0)$ transition and the $B^1\Sigma^+ \rightarrow a^3\Pi(0,0)$ transition is $F = 5.37 \times 10^{-3}$ which compares well with the estimate inferred from the work of Ikeda et al.[21], $F = 5.6 \times 10^{-3}$.

(iv) Lifetimes of Metastable (Potential Energetic) Species: The Quenching of Helium 2^3S

This study[22] was concerned with the lifetime of the metastable energetic species $He(2^3S)$ in liquid helium considering the possible role of nonadiabatic effects in the collisional quenching of this species, which energetic by 11eV with respect to the ground state atom. The electronic structure aspects of a nonadiabatic-radiative decay mechanism were analyzed. The basic issue was the lifetime of the $a^3\Sigma_u^+$ state of He_2 which correlates with $He(2^3S)$ and ground state helium. In the proposed mechanism the $a^3\Sigma_u^+$ state is coupled by relativistic, rotational and radiative interactions to the $A^1\Sigma_u^+$ state which serves as a gateway to the $X^1\Sigma_g^+$ (electronically quenched) state of He_2 through the spin-allowed dipole-allowed bound-free transition $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$.

State averaged MCSCF/second order CI wavefunctions for the ground $X^1\Sigma_g^+$ state, and the excited, $a^3\Sigma_u^+$, $A^1\Sigma_u^+$, $b^3\Pi_g$, $B^1\Pi_g$, $c^3\Sigma_g^+$, and $C^1\Sigma_g^+$ states (referred to here as the primary space) of He_2 were determined. Using these wavefunctions all interstate matrix elements of the form $\langle\Psi^0(J)\,|\,\hat{O}\,|\,\Psi^0(I)\rangle$ were determined for (i) $\hat{O} = \hat{H}^{BP} \equiv \hat{H}^{so} + \hat{H}^{ss}$ where $\hat{H}^{so}$ and $\hat{H}^{ss}$ are respectively the spin-orbit and dipolar spin-spin interactions in the Breit-Pauli approximation, (ii) $\hat{O} = \hat{L}$, where $\hat{L}$ is the total electronic orbital angular momentum operator and (iii) $\hat{O} = \hat{\mu}$ where $\hat{\mu}$ is the dipole moment operator.

In the nonrotating molecule these interactions give rise to the spin-forbidden dipole-allowed radiative transitions $(b^3\Pi_g, c^3\Sigma_g^+) \rightarrow A^1\Sigma_u^+$. However a complete description of these radiative decay processes requires consideration of interactions originating outside the primary space. Thus in this work the spin-forbidden, dipole-allowed perpendicular, $\mu_\perp(J, A^1\Sigma_{u0^+}^+)$, $J = c^3\Sigma_{g1}^+$, $b^3\Pi_{g1}$ and parallel, $\mu_{||}(b^3\Pi_{g0^+}, A^1\Sigma_{u0^+}^+)$, transition moments were determined using quasidegenerate perturbation theory.

The computed potential energy curves, coupling matrix elements and dipole moments permit a fully quantum mechanical analysis of the nonadiabatic-radiative quenching mechanism. However a preliminary phenomenological analysis of aspects of this process based on quasidegenerate perturbation theory indicated that this mechanism would not be competitive with the direct spin-forbidden radiative decay $a^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ studied previously by Chabalowski et. al.[23]

(v) Spin-forbidden Radiationless Decay: $N_3H(X^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-)$

Recently there has been considerable interest in the decomposition pathways of the homologous azides N_3-X for X=H[24-26], F [27], Cl [28-29] and Br [29-30], that is

$$N_3X(\tilde{X}\,^1A') \rightarrow NX(X^3\Sigma^-,a^1\Delta) + N_2(^1\Sigma_g^+) \qquad 1.14$$

as well as in the isovalent systems FNCO and NNOO[31]. Interest in these systems has been motivated in part by the potential of N_3F (fluorine azide) as a clean source of $NF(a^1\Delta)$. The approximately 1.5eV of energy in $NF(a^1\Delta)$[32] would then be available for use in a collisional energy transfer chemical laser system[27b] analogous to the oxygen-iodine laser system system.[33] Several recent experimental and theoretical studies[34-36] have focused on reaction 1 for X=H,D and contributed significantly to a detailed understanding of this reaction. The production of $NH(X^3\Sigma^-)$ in reaction 1 is clearly spin-forbidden. Alexander, Werner and Dagdigian (AWD),[26] in a recent theoretical study of the N_3H(hydrazoic acid) decomposition, noted three factors as being essential to the understanding of the electronic structure aspects of this process: (i) the location of the minimum energy singlet-triplet crossing which in this system represents the barrier to the spin-forbidden reaction, (ii) the gradients of the singlet and triplet potential energy surfaces at this crossing and (iii) the spin-orbit induced singlet-triplet coupling in the vicinity of the minimum energy crossing. Previous *ab initio* studies, including the study of AWD which motivated the present work, had provided considerable insight into the location and topology of the minimum energy crossing. However there had been no treatment of the spin-orbit induced coupling of the lowest singlet and triplet states in this key region using extended CI wavefunctions. To address this deficiency we undertook a study of the electronic structure aspects of the spin-forbidden decomposition reaction $N_3H(\tilde{X}\,^1A') \rightarrow NH(X^3\Sigma^-) + N_2(^1\Sigma_g^+)$ [37]. Using a flexible basis of better than double zeta-polarization quality and CI expansions of approximately 200,000 terms the spin-orbit (H^{so}) couplings between the lowest singlet state $\Psi_{1a'}(^1A') \equiv \Psi[1\,^1A'(0)]$ and the components of the lowest triplet state $\Psi_{1a'}(^3A'') \equiv i\,\Psi[1^3A''(0)]$, $\Psi_{2a'}(^3A'') \equiv i\,\{\Psi[1^3A''(1)] - \Psi[1^3A''(-1)]\}/\sqrt{2}$ were determined in the asymptotic region corresponding to N_2+NH, at the experimental[36] (planar) equilibrium geometry, and in the vicinity of the approximate minimum energy crossing. At the approximate minimum energy crossing we find $h_z^{so} \equiv \langle\Psi_{1a'}(^1A') \mid H^{so} \mid \Psi_{1a'}(^3A'')\rangle \approx 39.5\ cm^{-1}$ »

$h_y^{so} \equiv \langle \Psi_{1a'}(^1A') \mid H^{so} \mid \Psi_{2a'}(^3A'') \rangle \approx 0.456\ cm^{-1}$. The negligibility of h_y^{so} is attributed to the geometry of the N_3H moiety at the approximate minimum energy crossing and the absence of $NH(c^1\Pi)$ character in the $1^1A'$ state. The efficacy of h_z^{so} in promoting the spin-forbidden reaction 1 was estimated using a Landau-Zener model.[38] It was concluded that the spin-forbidden process would be significant only near threshold. This conclusion was attributable to both the small magnitude of h_z^{so} and the comparatively large gradient of ΔE with respect to the approximate reaction coordinate $R(N^2\text{-}N^3)$.

II: ELECTRONIC NONADIABATICITY INDUCED BY DERIVATIVE COUPLINGS

The decay of an electronically excited energetic species may involve a radiationless pathway. This pathway would in turn involve nuclear motion on more than one adiabatic Born-Oppenheimer potential energy surface (PES) with the coupling between the surfaces arising from derivative couplings of the form

$$g_\alpha(J, I, \mathbf{R}) = \left\langle \Psi^0_J(\mathbf{r}; \mathbf{R}) \left| \frac{\partial}{\partial R_\alpha} \Psi^0_I(\mathbf{r}; \mathbf{R}) \right\rangle_{\mathbf{r}} \right. \tag{1.15}$$

$$h_{\alpha,\beta}(J, I, \mathbf{R}) = \left\langle \Psi^0_J(\mathbf{r}; \mathbf{R}) \left| \frac{\partial^2}{\partial R_\alpha \partial R_\beta} \Psi^0_I(\mathbf{r}; \mathbf{R}) \right\rangle_{\mathbf{r}} \right. \tag{1.16a}$$

$$k_{\alpha,\beta}(J, I, \mathbf{R}) = \left\langle \frac{\partial}{\partial R_\alpha} \Psi^0_J(\mathbf{r}; \mathbf{R}) \left| \frac{\partial}{\partial R_\beta} \Psi^0_I(\mathbf{r}; \mathbf{R}) \right\rangle_{\mathbf{r}} \right. \tag{1.16b}$$

where the $\Psi^0_J(\mathbf{r}; \mathbf{R})$ are the adiabatic state wavefunctions obtained from the solution of eq. 1.5. The $\mathbf{g}(J, I, \mathbf{R})$ or first derivative nonadiabatic coupling matrix elements which (for real-valued wavefunctions) only couple PES's, that is $\mathbf{g}(I, I, \mathbf{R}) = 0$, are usually the quantities of principal concern with the $\mathbf{h}(J, I. \mathbf{R})$ and $\mathbf{k}(J, I, \mathbf{R})$, which both couple and modify PES's being required in full quantum mechanical adiabatic state treatments.

(A) Methodology

Over the last five years we have developed a unique system of computer algorithms[39-40] for evaluating **g**, **h** and **k** which provide significant computational advantages over previously existing[41] methods. We employ techniques which are applicable to large scale CI wavefunctions (10^5 -10^6 terms) developed from state averaged MCSCF[42] reference spaces enabling the evaluation of the derivative couplings using the same wavefunctions which yield reliable PES's. This is an extremely important aspect of our approach since the nonadiabatic coupling matrix elements are a sensitive function of the separation of the PES's and hence of the nuclear coordinates.

We derive our computational efficiency in two ways. The wavefunction derivatives required in eqs. 1.15 and 1.16 are evaluated using the same analytic gradient techniques employed in the evaluation of energy gradients.[39b] Thus we obtain savings in computational effort similar to the substantial savings achieved when analytic energy gradients replace energy gradients based on divided differences. A corollary of this approach is a unified system of programs for obtaining *both* derivative couplings and energy gradients.[39b]

The second source of computational efficiency obtains in our treatment of derivative couplings attributable to *overall* nuclear translation and rotation. For R_α an overall nuclear translation or rotation the derivative couplings matrix elements can be obtained from eqs. 1.15 and 1.16 *or* as matrix elements of electronic operators including the mass polarization operator and the total electronic angular momentum operator.[40] By replacing the nuclear derivative operator in eqs. 1.15 and 1.16 with these (body fixed frame) electronic operators the costly evaluation of orbital and CI coefficient derivatives can be avoided. Further this approach permits us to make maximal use of molecular point group symmetry when determining the adiabatic states an advantage which does not obtain if the nuclear derivative formulation is used exclusively. Finally the observation that for overall nuclear translations and rotations, alternative, independent computational paths to the same result exist - one exploiting gradient techniques and the second involving only matrix elements of electronic operators - provides a stringent test of the precision of both algorithms. A detailed discussion of these points can be found in reference 40.

(B) Applications

(i) The Energetic System: He + $H_2(B^1\Sigma_u^+)$

In the following we consider the stability of a proposed high energy density material with respect to radiationless decay. This study provides a clear demonstration of the power of theoretical methods to (quickly) assess the utility of a proposed energy storage system by determining the topology of the relevant potential energy surfaces (PES's) and the nonadiabatic interactions which couple them.

The $H_2(B^1\Sigma_u^+)$ state contains over 11 eV of energy relative to the $H_2(X^1\Sigma_g^+)$ ground state.[32] It has been suggested that the charge transfer structure $(HeH)^+ - H^-$ which consists of two stable moieties, HeH^+ and H^- might exist as a stable species on either the $2^1A'$ PES (as a maximum ionicity excited state - MIES[43] structure) or on the ground $1^1A'$ PES and thereby provide a chemical means of storing the electronic energy in the $B^1\Sigma_u^+$ state of H_2.

To address this question the 1, $2^1A'$ states of the $He–H_2$ system were characterized using *ab initio* MCSCF/second order CI wavefunctions.[44] These surfaces correlate with the $He(^1S)$ + $H_2(X^1\Sigma_g^+, B^1\Sigma_u^+)$ system states. This work provided the first extended treatment of the nonadiabatic interactions between the 1, $2^1A'$ states reporting first derivative nonadiabatic couplings (eq. 1.14) at over 100 nuclear configurations. Two extrema on the $2^1A'$ PES were determined at the CI level, a global minimum and a saddle point. In each case the character of the extremum was determined from the eigenvalues of the second derivative matrix. While this work built on previously reported theoretical treatments of these PES's,[45] both qualitative and quantitative differences with previous work were found. The predicted, entrance channel, saddle point on the $2^1A'$ PES gave a barrier of 1.5 Kcal/mol which is significantly lower than previous estimates.[45a] The global minimum on the $2^1A'$ PES corresponds to a charge transfer structure, $(HeH)^+–H^-$ and is stable by 38.99 Kcal/mol relative to the $He(^1S) + H_2(B^1\Sigma_u^+)$ asymptote. The structure and energy of this extremum are in qualitative accord with the previous *ab initio* results of Farantos et al.[43]

The most significant new finding in this work was the demonstration of the existence of a 'seam' for which the $1^1A'$ and $2^1A'$ PES's are nearly degenerate, $\Delta E \equiv E(2^1A') - E(1^1A') <$

0.001–0.5 Kcal/mol. This extended region of large nonadiabatic effects occurs for *general* C_s, rather that C_{2v} or $C_{\infty v}$ geometries, and includes the region of the minimum on the $2^1A'$ PES noted above. This feature of the 1, $2^1A'$ PES's should significantly influence the quenching of $H_2(B^1\Sigma_u^+)$ by He and alter expectations of the lifetime of the state corresponding to the global minimum on the $2^1A'$ PES.[46] It is anticipated that the lower entrance channel barrier noted above and the near degeneracy seam reported here will serve to increase the calculated quenching cross section[47] which is appreciably lower than the measured value.[48] The large nonadiabatic coupling between the $1,2^1A'$ wavefunctions in the vicinity of the global minimum on the $2^1A'$ PES will serve to decrease the predicted lifetime of this 'state'. To facilitate dynamical studies of these questions first derivative nonadiabatic coupling matrix elements were determined in the vicinity of the 'seam'.

The possible stability of the charge transfer structure $(HeH)^+–H^-$ on the $1^1A'$ PES was considered using a surface walking technique. In the vicinity of the above noted seam an exchange of the charge transfer structure between the 1, $2^1A'$ states is observed. Surface walks on the $1^1A'$ PES which follow the energy gradient from nuclear configurations corresponding to the charge transfer structure, $(HeH)^+–H^-$, were performed. In *no* case was a stable triatomic structure corresponding to a charge transfer configuration found.

C. Avoided and Allowed Surface Crossings

(i) Efficient Determination of Regions of (Avoided) Surface Crossings Using Analytic Energy Gradients

A key to the understanding of electronically nonadiabatic processes is the determination of the regions of nuclear configuration space for which the potential energy surfaces in question are closely spaced or actually cross. It is in these regions that nonadiabatic effects are most important. The location of such regions of coordinate space can be quite time consuming. Recent advances in analytic gradient techniques[49-53] have reduced considerably the labor required for determining single surface extrema. As part of this research effort we have begun the development of algorithms to bring comparable efficiencies to the determination of (avoided) surface crossings.[54] These algorithms utilize the same state averaged MCSCF/direct symbolic matrix CI wavefunctions

which are used to characterize the spin-orbit and spin-spin interactions. They are based on *analytic gradient* techniques thereby achieving the considerable efficiencies already available to us in the location of extrema on a single potential energy surface.

This project was motivated by our previous studies of spin-forbidden and electronically nonadiabatic decay pathways in polyatomic energetic materials As noted above we have considered (1) the mechanism of the spin-forbidden radiationless decay of hydrazoic acid $N_3H(X^1A') \rightarrow N_2 + NH(X^3\Sigma^-)$ and (2) the formation of the [unstable with respect to decomposition into $He+H_2(^1\Sigma_g^+)$] charge transfer state HeH^+-H^- from $He + H_2(B^1\Sigma_u^+)$. In order to characterize the electronic structure aspects of process (1) it was necessary to determine, in addition to the requisite spin-orbit coupling matrix elements, the *minimum energy crossing point* of the $1^1A'$ and $1^3A''$ potential energy surfaces. Similarly the elucidation of the mechanism of process (2) required the determination of the nonadiabatic coupling matrix elements between the $1^1A'$ and $2^1A'$ potential energy surfaces as well as a *seam of avoided crossings* [R(r), γ(r)] where r is the H_2 distance, R is the He-H_2 distance and γ is the He-H_2 angle. In the above noted studies the minimum energy crossing point and seam of avoided crossings were determined, somewhat tediously, by consideration of the individual potential energy surfaces. The analytic gradient driven algorithms for determining allowed and avoided crossings of potential energy surfaces would have reduced considerably the computational effort required to treat these problems.

These procedures have broad applicability. In particular these algorithms can be expected to find considerable use in the characterization of high energy density materials as these species are frequently characterized by locally stable regions of a potential energy surface which are isolated from more stable structures by (avoided) surface crossings.

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PUBLICATIONS

1. A Theoretical Description of the Radiative Decay Processes ($b^1\Sigma^+$, $a^1\Delta$) $\rightarrow$ $X^3\Sigma^-$ in NF.
   D. R. Yarkony, J. Chem. Phys., *85*, 7261 (1986).

2. On the Radiative Lifetimes of the $b^1\Sigma^+$ and $a^1\Delta$ States in NCl.
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3. On the Characterization of the Dipolar Spin-Spin Interaction in Molecular Systems: A Symbolic Matrix Element Approach.
   J. O. Jensen and D. R. Yarkony, Chem. Phys. Lett. *141*, 391 (1987).

4. On the Evaluation of Lifetimes for Spin-Forbidden Radiative Transitions Originating in Coupling to States Embedded in a Continuum. Application to CH^-.
   B. H. Lengsfield, J. O. Jensen, and D. R. Yarkony, J. Chem. Phys. *88*, 3853 (1988).

5. On the Evaluation of Non Born-Oppenheimer Interactions for Born-Oppenheimer Wavefunctions V: A Body Fixed Frame Approach. Applications to Isotope Effects of Equilibrium Geometries and the Adiabatic Correction for the $X^1\Sigma^+$ State of LiH.
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6. On the Electronic Structure of the He^-H_2 System Characterization of, and Nonadiabatic Interactions Between, the $1^1A'$ and $2^1A'$ Potential Energy Surfaces.
   J. K. Perry and D. R. Yarkony, J. Chem. Phys., *89*, 4945 (1988).

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8. On the Quenching of Helium 2^3S: Potential Energy Curves for, and Nonadiabatic, Relativistic and Radiative Couplings Between, the $a^3\Sigma_u^+$, $A^1\Sigma_u^+$, $b^3\Pi_g$, $B^1\Pi_g$, $c^3\Sigma_g^+$ and $C^1\Sigma_g^+$ States of He_2.
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10. On the Characterization of Regions of Avoided Surface Crossings Using an Analytic Gradient Based Method
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11. Spin-Orbit Effects in the Decomposition Reaction $N_3H(X^1A') \rightarrow N_2(X^1\Sigma_g^+) + NH(X^3\Sigma^-, a^1\Delta)$
    D. R. Yarkony, J. Chem. Phys., in press.

12. Theoretical Studies of the Electronic Structure Aspects of Electronically Nonadiabatic Processes Using Analytic Gradient Techniques: Seams of Avoided Crossings in the Electronic Quenching Reaction $Na(^2P) + HCl \rightarrow NaCl + H(^2S)$
    D. R. Yarkony, submitted to J. Phys. Chem. (Proceedings of " Forty Years of Quantum Chemstry", Oct. 1989)

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INTERACTIONS

The following invited talks were given by the principal investigator based on work performed during the course of this grant.

1. "Theoretical Studies of Spin-Forbidden Processes Within the Breit -Pauli Approximation"
   presented at: AFOSR/AFWL/SDIO Contractor's Conference
   AFGL, Hanscom AFB, MA
   15 October-17 October 1986

2. "Theoretical Studies of Spin-Forbidden Radiative Processes and Electronically Nonadiabatic Processes Using ab initio Electronic Structure Methods"
   presented at: High Energy Density Matter Contractors Conference 1987
   Rosslyn, VA
   May 1987

3. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes Relevant to the Structure and Stability of Potential High Energy Density Materials"
   presented at: High Energy Density Matter Contractors Conference
   Newport Beach, CA
   March 2, 1988

4. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes"
   presented at: ACS Middle Atlantic Regional Meeting
   Millersville State University
   Lancaster, PA
   May 26, 1988

5. "Theoretical Studies of Electronically Nonadiabatic Processes"
   presented at: Lawrence Livermore National Laboratory
   Livermore, CA 94550
   August 24, 1988

6 "Theoretical Studies of Electronically Nonadiabatic Processes"
   presented at: Astronautics Laboratory
   Edwards Air Force Base, CA 93523
   August 28, 1988

7. "Recent Advances in the Treatment of Spin-Forbidden and Electronically Nonadiabatic Processes: Theory and Application"
   presented at: * 32nd Okazaki Conference
   Institute for Molecular Science
   Myodaiji, Okazaki, Japan
   September 1988

8. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes"
   presented at: Keio University
   Yokohama, Japan

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* Plenary Lecture

September 30, 1988

9. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic processes"

   presented at: Division of Molecular Engineering
   Kyoto University
   Kyoto, Japan
   October 3, 1988

10. "Theoretical Studies of Electronically Nonadiabatic Processes"

    presented at: 1988 U.S. Army CRDEC Scientific Conference on Chemical Defense Research
    Aberdeen Proving Ground, MD
    November 15, 1988

11. "Decay Processes in Energetic Species: Theoretical Studies of the Electronic Structure Aspects of He(2^3S) Quenching and the Azide Decomposition Reaction $N_3H \rightarrow NH(X^3\Sigma^-) + N_2$"

    presented at: High Energy Density Materials Contractors Conference
    New Orleans, LA
    March 12-15, 1989

12. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes"

    presented at Argonne National Laboratory
    Argonne, IL
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13. "Theoretical Studies of Spin-Forbidden and Electronically Nonadiabatic Processes"

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