

PROPAGATOR CALCULATIONS ON MOLECULAR  
IONIZATION AND EXCITATION PROCESSES

BY

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To Karen

Come my Way, my Truth, my Life

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## TABLE OF CONTENTS

		Page
	ACKNOWLEDGEMENTS.....	iii
	LIST OF TABLES.....	vi
	ABSTRACT.....	viii
	INTRODUCTION.....	1
CHAPTER ONE	ELECTRON BINDING ENERGIES.....	3
	1.1 The electron propagator.....	3
	1.2 An uncorrelated propagator.....	4
	1.3 Toward correlated electron propagators.....	6
	1.4 Approximations.....	9
	1.5 Approximate propagator expressions.....	11
	1.6 Vertical and adiabatic electron affinities of Cl <sub>2</sub> .....	13
	1.7 The vertical electron affinity of CN.....	22
	1.8 The ionization energies of NH <sub>2</sub> <sup>-</sup> .....	29
	1.9 The ionization energies of PH <sub>2</sub> <sup>-</sup> .....	32
	1.10 The transition operator method.....	38
	1.11 Applications of the transition operator reference.....	40
	1.12 Interpretation.....	46
CHAPTER TWO	EXCITATION ENERGIES.....	47
	2.1 Consistent ground states and the random phase approximation.....	47
	2.2 The antisymmetrized geminal power wavefunction.	51
	2.3 Density matrices and the total energy expres- sion.....	53
	2.4 Interpretations of the total energy expression.	55
	2.5 Coefficient optimization.....	56
	2.6 Orbital optimization.....	58

	Page
2.7 Results for lithium hydride.....	59
2.8 The random phase approximation of the polarization propagator.....	66
2.9 Polarization propagator calculations on lithium hydride.....	70
APPENDIX.....	73
BIBLIOGRAPHY.....	76
BIOGRAPHICAL INFORMATION.....	80

LIST OF TABLES

Table		Page
1-1	$\text{Cl}_2$ and $\text{Cl}_2^-$ CGTO Basis.....	14
1-2	Total Energies for $\text{Cl}_2$ and $\text{Cl}_2^-$ below -918.0 a.u.....	16
1-3	Hartree-Fock Total Energy Lowering for $\text{Cl}_2$ and $\text{Cl}_2^-$ .....	17
1-4	Vertical Electron Affinities for $\text{Cl}_2$ .....	18
1-5	Adiabatic Electron Affinity of $\text{Cl}_2$ .....	19
1-6	Adiabatic Electron Affinity of $\text{Cl}_2$ .....	20
1-7	Adiabatic Electron Affinity of $\text{Cl}_2$ .....	21
1-8	CN and $\text{CN}^-$ CGTO Basis.....	23
1-9	Total Hartree-Fock Energies for CN and $\text{CN}^-$ .....	25
1-10	Hartree-Fock Total Energy Lowering for CN and $\text{CN}^-$ .....	26
1-11	SCF Equilibrium Nuclear Geometries.....	27
1-12	Vertical Ionization Energy of $\text{CN}^-$ .....	28
1-13	Hydrogen CGTO Basis ( $\text{NH}_2^-$ , $\text{PH}_2^-$ ).....	30
1-14	CGTO Basis for $\text{NH}_2^-$ .....	31
1-15	Vertical Ionization Energies for $\text{NH}_2^-$ .....	33
1-16	Adiabatic Ionization Energies for $\text{NH}_2^-$ and $\text{PH}_2^-$ .....	35
1-17	CGTO Basis for $\text{PH}_2^-$ .....	37
1-18	Vertical Ionization Energies for $\text{PH}_2^-$ .....	39
1-19	26 CGTO Basis for $\text{H}_2\text{O}$ .....	41
1-20	Vertical Ionization Energies of $\text{H}_2\text{O}$ .....	42
1-21	Neon Gaussian Basis Set.....	43
1-22	Ionization Energies for Ne.....	44

Table	Page	
1-23	Vertical Ionization Energies of $\text{NH}_2^-$ and $\text{CN}^-$ Calculated with the Transition Operator Method and Self-Energy Corrections.....	45
2-1	LiH Basis.....	60
2-2	Convergence Behavior for AGP Wavefunction Optimization for LiH $1\Sigma^+$ at $R = 3.015$ bohr.....	62
2-3	AGP Geminal Coefficients and Principal Natural Orbital Occupation Numbers for LiH.....	64
2-4	LiH Total Energies and Correlation Percentages for $1\Sigma^+$ Ground State.....	67
2-5	Total Energy Differences Along the Ground State $1\Sigma^+$ Potential Curves with Respect to the Total Energy at $R = 3.015$ bohr.....	68
2-6	AGP-RPA Excitation Energies.....	71

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PROPAGATOR CALCULATIONS ON MOLECULAR  
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Renormalizations, which sum classes of diagrams to all orders in perturbation theory, are applied to the electron propagator. The separation of relaxation and correlation self-energy diagrams enables the construction of electron propagators that include relaxation contributions to all orders. Correlation self-energies are obtained in second order, third order, and in the diagonal 2p-h Tamm-Dancoff approximation, which is also a renormalization. These propagators are applied to the electron binding energies of  $\text{CN}^-$ ,  $\text{NH}_2^-$ ,  $\text{PH}_2^-$  and  $\text{Cl}_2$ . An alternative propagator renormalization through the transition operator method reference state is applied to the electron binding energies of Ne,  $\text{H}_2\text{O}$ ,  $\text{NH}_2^-$  and  $\text{CN}^-$ .

The antisymmetrized geminal power wavefunction, which is the form of the consistent ground state of the random phase approximation of the polarization propagator, is variationally optimized for the LiH ground

state potential curve. Random phase approximation polarization propagator calculations yield excitation energies.

Physical concepts suggested by these theories are discussed.

## INTRODUCTION

Modern chemical investigation inevitably revolves about the axis of molecular electronic structure theory. The quantum mechanical investigation of the structure and properties of isolated molecules lays a foundation for studies of complex chemical systems. Energy differences between states are properties of continuing importance in molecular electronic structure theory, for they provide insight into macroscopic chemical phenomena. Propagator theory is a theoretical technique that concentrates on determining energy differences and transition probabilities. The concepts that are introduced with propagator theory therefore explain the energy differences themselves without necessarily treating the total energies or wavefunctions of the states of interest.

Molecular energy differences are associated with nuclear and electronic rearrangements. The Born-Oppenheimer approximation permits a separation of electronic and nuclear motion that facilitates quantum mechanical calculations based on the time independent Schrödinger equation. With the nuclei fixed at given positions, the electronic states of the molecule are studied. A series of nuclear configurations defines an adiabatic potential energy surface, where the total electronic energy plus the internuclear repulsion energy is plotted against the nuclear positions. Ground state potential energy surfaces have typically been calculated using the variational method; propagator theory has made few contributions to this field. However, for the calculation of energy differences between potential energy surfaces, propagator theory is competitive with current variational techniques. In the chapters that

follow, propagator theory will be applied to energy differences between electronic states. The calculations will be made in a limited basis of square integrable functions and there will be no explicit treatment of the continuum.

Electron binding energies are energy differences between  $N$  electron and  $N\pm 1$  electron states, i.e., ionization energies and electron affinities. Hartree-Fock theory provides predictions of electron binding energies based on Koopmans's theorem (Koopmans, 1933) which states that orbital energies are interpretable as ionization energies or electron affinities. Unfortunately, the invariance of the Hartree-Fock wavefunction under unitary transformations of the occupied (or the unoccupied) orbitals among themselves places in doubt the validity of the orbital energy interpretation. Propagator theory justifies and delimits the simple orbital model and suggests ways to improve it. These ways include the extension of the orbital concept to quasi-particle concepts of electron binding energies and the introduction of energy-dependent correlation potentials.

Excitation energies, or energy differences between electronic states with the same number of electrons, are also amenable to propagator interpretations. Hartree-Fock theory also gives a model for excitation energies that can be extended with perturbative propagator corrections, but propagator theory also suggests models that abandon the orbital picture as a point of reference. Correlated model Hamiltonians provide physical pictures for the ground and excited states and explain the nature of the interactions present in each state.

These applications illustrate how propagators provide direct determination of energy differences and introduce concepts that are, so far, inaccessible to purely variational theories.

CHAPTER ONE  
ELECTRON BINDING ENERGIES

1.1 The electron propagator

Electron propagators efficiently determine and explain electron binding energies. The poles of the electron propagator are energy differences between the  $N$  electron ground state and the  $N\pm 1$  electron states, i.e., electron binding energies. The residues of the propagator are overlap amplitudes between the  $N$  electron and  $N\pm 1$  electron states and describe the electronic structure of the ground state. The electron propagator matrix (Linderberg and Öhrn, 1973),  $\underline{G}$ , in a spin-orbital basis has the elements

$$G_{ij}(E) = \sum_n \frac{f_n^*(i)f_n(j)}{E - E_n(N+1) + E_0(N) + i\sigma} + \sum_n \frac{g_n^*(i)g_n(j)}{E + E_n(N-1) - E_0(N) - i\sigma} \quad (1-1)$$

The total energy of the  $N$  electron ground state is  $E_0(N)$ , and  $E_n(N\pm 1)$  is the total energy of the  $n$ -th  $N\pm 1$  electron state. The poles of the propagator are real energy differences when the positive parameter  $\sigma$  approaches zero. The continuum can be treated with the electron propagator in conjunction with other techniques (Mishra, 1981). The overlap amplitudes (Purvis and Öhrn, 1975) between the ground and  $N\pm 1$  electron states are

$$f_n(i) = \langle N+1, n | a_i^\dagger | N \rangle \quad g_n(i) = \langle N-1, n | a_i | N \rangle, \quad (1-2)$$

where the field operators satisfy the relations

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = [a_i, a_j^\dagger]_+ - \delta_{ij} . \quad (1-3)$$

In this notation, the many-electron Hamiltonian is

$$H = \sum_i \sum_j h_{ij} a_i^\dagger a_j + \frac{1}{4} \sum_i \sum_j \sum_k \sum_l \langle ij || kl \rangle a_i^\dagger a_j^\dagger a_l a_k , \quad (1-4)$$

where  $\langle ij || kl \rangle = \langle i(1)j(2) | \frac{1-P_{12}}{|\vec{r}_1 - \vec{r}_2|} | k(1)l(2) \rangle$

$$h_{ij} = \langle i | -\frac{1}{2}\nabla^2 + \sum_{\alpha} \text{NUCLEI} \frac{Z_{\alpha}}{|\vec{R}_{\alpha} - \vec{r}|} | j \rangle . \quad (1-5)$$

This Hamiltonian operates in Fock space and is independent of the number of electrons in the states on which it operates.

## 1.2 An uncorrelated propagator

Consider the model Hamiltonian

$$H_0 = \sum_i \epsilon_i a_i^\dagger a_i \quad (1-6)$$

in the spin orbital basis that diagonalizes the Fock matrix,

$$F_{ij} = h_{ij} + \sum_k \sum_l \langle ik || jl \rangle \langle a_k^\dagger a_l \rangle , \quad (1-7)$$

where

$$\langle a_k^\dagger a_l \rangle = \langle \text{ground state} | a_k^\dagger a_l | \text{ground state} \rangle , \quad (1-8)$$

so that

$$F_{ij} = \epsilon_i \delta_{ij} . \quad (1-9)$$

Since the model Hamiltonian contains only one-electron terms, the electrons do not interact. The model ground state is

$$|N\rangle = \prod_{i=1}^N a_i^\dagger |\text{vac}\rangle \quad (1-10)$$

where

$$N_{\text{op}}|\text{vac}\rangle = \sum_i n_i |\text{vac}\rangle = \sum_i a_i^\dagger a_i |\text{vac}\rangle = 0 \cdot |\text{vac}\rangle . \quad (1-11)$$

The ground state total energy is

$$\langle N | H_0 | N \rangle = \sum_i \epsilon_i \langle a_i^\dagger a_i \rangle = \sum_i \epsilon_i n_i . \quad (1-12)$$

There are  $N$  orbitals where  $n_i = 1$ ; the rest of the orbitals have  $n_i = 0$ . The  $N \pm 1$  electron states differ from the ground state in the choice of occupation numbers. The poles of the model electron propagator are

$$E_{\text{POLE}} = E_0(N) - E_n(N-1) = \epsilon_n \quad (1-13)$$

which are negative ionization energies, and

$$E_{\text{POLE}} = E_n(N+1) - E_0(N) = \epsilon_n \quad (1-14)$$

which are negative electron affinities. The overlap amplitudes are

$$\begin{aligned} f_n(i) &= \langle N+1, n | a_i^\dagger | N \rangle = \delta_{in} \\ g_n(i) &= \langle N-1, n | a_i | N \rangle = \delta_{in} . \end{aligned} \quad (1-15)$$

The purpose of this exercise is to recover Koopmans's theorem (Koopmans, 1933) and the attendant orbital concept of electronic

structure. The remaining discussion considers how the electron propagator can be extended to describe correlated electron dynamics.

### 1.3 Toward correlated electron propagators

Given the notation for the propagator

$$G_{ij}(E) = \langle\langle a_i; a_j^\dagger \rangle\rangle_E, \quad (1-16)$$

the identities

$$\begin{aligned} E[E - E_n(N+1) + E_0(N)]^{-1} &= 1 + \frac{E_n(N+1) - E_0(N)}{E - E_n(N+1) + E_0(N)}, \\ \langle N | a_i | N+1, n \rangle (E_n(N+1) - E_0(N)) &= \langle N | [a_i, H] | N+1, n \rangle, \end{aligned} \quad (1-17)$$

and the corresponding relations for the N-1 electron case imply that

$$E \langle\langle a_i, a_j^\dagger \rangle\rangle_E = \langle [a_i, a_j^\dagger]_+ \rangle + \langle\langle [a_i, H]; a_j^\dagger \rangle\rangle_E. \quad (1-18)$$

This equation can be iterated to give

$$\begin{aligned} \langle\langle a_i, a_j^\dagger \rangle\rangle_E &= E^{-1} \langle [a_i, a_j^\dagger]_+ \rangle + E^{-2} \langle\langle [a_i, H], a_j^\dagger \rangle\rangle_E \\ &\quad + E^{-3} \langle\langle [[a_i, H], H], a_j^\dagger \rangle\rangle_E + \dots \end{aligned} \quad (1-19)$$

The definition of superoperators (Goscinski and Lukman, 1970),  $\hat{I}$  and  $\hat{H}$

$$\hat{I}X = X \quad \hat{H}X = [X, H], \quad (1-20)$$

which act on the set of field operators (Redmon et al., 1975)

$$X = \{a_i, a_i^\dagger a_j a_k, a_i^\dagger a_j^\dagger a_k a_l, \dots\}, \quad (1-21)$$

and the definition of a scalar product (Goscinski and Lukman, 1970)

$$(X|Y) = \langle [Y, X^\dagger]_+ \rangle \quad (1-22)$$

convert the expansion in equation 1-19 to the form

$$\langle\langle a_i; a_j^\dagger \rangle\rangle_E = (a_j | (E\hat{I} - \hat{H})^{-1} a_i) . \quad (1-23)$$

The inverse operator which occurs in the propagator matrix,

$$\underline{G}(E) = (\underline{a} | (E\hat{I} - \hat{H})^{-1} \underline{a}) , \quad (1-24)$$

can be circumvented by the inner projection technique (Löwdin, 1965):

$$\underline{G}(E) = (\underline{a} | \underline{h})(\underline{h} | (E\hat{I} - \hat{H})\underline{h})^{-1} (\underline{h} | \underline{a}) , \quad (1-25)$$

where the operator manifold is complete, i.e.,

$$\underline{h} = \{ \underline{a}, \underline{a}^\dagger \underline{a} \underline{a}, \underline{a}^\dagger \underline{a}^\dagger \underline{a} \underline{a} \underline{a}, \dots \} , \quad (1-26)$$

and where the superoperator matrix elements are evaluated with respect to the exact ground state. A partitioning (Löwdin, 1965 and 1971) of  $\underline{h}$ ,

$$\underline{h} = \{ \underline{a} | \underline{f} \} , \quad (1-27)$$

such that

$$(\underline{a} | \underline{f}) = 0 \quad (\underline{a} | \underline{a}) = (\underline{f} | \underline{f}) = \underline{1} , \quad (1-28)$$

implies that

$$\underline{G}^{-1}(E) = (\underline{a} | (E\hat{I} - \hat{H})\underline{a}) - (\underline{a} | \hat{H}\underline{f})(\underline{f} | (E\hat{I} - \hat{H})\underline{f})^{-1} (\underline{f} | \hat{H}\underline{a}) . \quad (1-29)$$

For the model uncorrelated system where

$$|N\rangle = |\text{Hartree-Fock}\rangle \quad (1-30)$$

and where the model Hamiltonian is

$$H_0 = \sum_i \epsilon_i a_i^\dagger a_i \quad (1-31)$$

the exact inverse propagator is

$$\underline{G}_0^{-1}(E) = (\underline{a} | (E\hat{I} - \hat{H}_0) \underline{a} ), \quad (1-32)$$

since the second term in the right-hand side of equation 1-29 vanishes.

Koopmans's theorem appears once again since

$$[\underline{G}_0^{-1}(E)]_{ij} = (a_i | (E\hat{I} - \hat{H}_0) a_j ) = (E - \epsilon_i) \delta_{ij} . \quad (1-33)$$

For the full Hamiltonian, approximations of the exact ground state and choices of a subspace of  $\underline{f}$  are necessary. If the ground state is written as

$$|N\rangle = |\text{Hartree-Fock}\rangle + |\text{correlation}\rangle , \quad (1-34)$$

then the propagator becomes

$$\begin{aligned} \underline{G}^{-1}(E) = & E\underline{1} - (\underline{a} | \hat{H}_a)_{\text{HF}} - (\underline{a} | \hat{H}_a)_{\text{CORR}} \\ & - (\underline{a} | \hat{H}_f) (\underline{f} | (E\hat{I} - \hat{H}) \underline{f})^{-1} (\underline{f} | \hat{H}_a) , \end{aligned} \quad (1-35)$$

where  $(\underline{a} | \hat{H}_a)_{\text{HF}}$  is  $(\underline{a} | \hat{H}_a)$  taken only with respect to the Hartree-Fock contribution to the ground state, and where the remainder of  $(\underline{a} | \hat{H}_a)$  is  $(\underline{a} | \hat{H}_a)_{\text{CORR}}$ . In other words,

$$\underline{G}^{-1}(E) = \underline{G}_0^{-1}(E) - \underline{\Sigma}' - \underline{\Sigma}'(E) . \quad (1-36)$$

The superoperator matrix element

$$(a_j | \hat{H} a_i) = h_{ji} + \sum_k \sum_l \langle jk || il \rangle \langle a_k^\dagger a_l \rangle \quad (1-37)$$

depends only on the one-electron reduced density matrix and is independent of  $E$ . Taken together, the energy dependent and energy independent corrections to the uncorrelated propagator,

$$\underline{\Sigma}' + \underline{\Sigma}'(E) = \underline{\Sigma}(E) \quad (1-38)$$

are the self-energy and appear in the Dyson equation,

$$\underline{G}^{-1}(E) = \underline{G}_0^{-1}(E) - \underline{\Sigma}(E) . \quad (1-39)$$

The self-energy contains all correlation effects.

#### 1.4 Approximations

Choices for the ground state and for a subset of  $f$  define approximate propagators. A specific physical problem or computational feasibility may motivate these choices. Redmon et al. (1975) and Nehr Korn et al. (1976) thoroughly analyzed the corrections to Hartree-Fock from single and double excitation contributions to the second order Rayleigh-Schrödinger perturbation theory wavefunction. Several authors have studied choices for the operator manifold (Pickup and Goscinski, 1973; Purvis and Öhrn, 1975; Redmon et al., 1975; Nehr Korn et al., 1976; Herman et al., 1980a and 1980b; Simons, 1977 and 1978; McCurdy et al., 1977). An example is  $f_3$ :

$$\begin{aligned} f_3 &= \{f_{klm}\} = \{(a_k^\dagger a_l a_m) + \langle n_k \rangle a_l \delta_{km} - \langle n_k \rangle a_m \delta_{lm}\} N_{klm}^{-\frac{1}{2}} , \\ N_{klm} &= \langle n_k \rangle (1 - \langle n_l \rangle - \langle n_m \rangle) + \langle n_l \rangle \langle n_m \rangle . \end{aligned} \quad (1-40)$$

The components of the self-energy also derive from diagrammatic perturbation theory (Cederbaum and Domcke, 1977). In this approach, the terms of the self-energy are classified by their order of electron interaction. Born has discussed the connections between the order by order approach and the inner projection formalism (Born, 1979). Operator product manifolds, such as  $\underline{f}_3$  or  $\underline{f}_5$ , sum classes of terms in the diagrammatic expansion to all orders in electron interaction. The infinite summations, or renormalizations, are useful when the convergence of the diagrammatic series is in doubt. For example, the choice of the Hartree-Fock ground state and the  $\underline{f}_3$  operator product manifold sums all terms in second order and also includes classes of diagrams called rings, ladders, and mixed ring-ladder diagrams to all orders. If the ground state includes double excitations from the first order RSPT wavefunction and single excitations from the second order RSPT wavefunction, then the renormalization sums all diagrams through third order, in addition to other diagrams in higher orders. The two complementary modes of analysis of the self-energy, from diagrammatic theory or from the approximation of the inner projection formula, enable verification of approximate self-energies. They are alternative terminologies which suggest improvements of the self-energy.

Yet another method of analysis of the self-energy is the identification of so-called relaxation and correlation terms by perturbation theory (Born et al., 1978). Relaxation terms are terms that occur in the difference between Hartree-Fock total energies for the  $N$  electron and  $N\pm 1$  electron states. (The  $\Delta$ SCF method is discussed in Bagus, 1965.) The perturbation is the difference between the Fock operators of each state. In general, the total energies are unrestricted Hartree-Fock total energies. The relaxation terms appear in the diagonal elements of the

propagator matrix when  $E = \epsilon_i$ , where  $\epsilon_i$  is the orbital energy pertaining to the  $N \pm 1$  electron state of interest. Perturbation theory connects the SCF total energy of the  $N \pm 1$  electron states with the orbitals and orbital energies of the  $N$  electron SCF calculation. The terms in the self-energy which are not relaxation terms are correlation terms. Since all self-energy contributions treat correlation effects with respect to the uncorrelated Hartree-Fock propagator, the use of the term correlation self-energy will refer only to contributions that do not originate from relaxation effects.

A further approximation proceeds from investigations (Schirmer et al., 1978) which demonstrate the unimportance of nondiagonal elements of the propagator matrix when the matrix is constructed in the basis of canonical Hartree-Fock orbitals. (This observation holds for outer valence and core binding energies of molecules near their equilibrium geometries.) Neglecting the nondiagonal elements sacrifices little numerical accuracy. Mixings of canonical Hartree-Fock orbitals of the same symmetry in the overlap amplitudes are obliterated when the diagonal, or quasi-particle, approximation is made. Previous studies of the non-diagonal propagator have also indicated that these mixings are small (Schirmer et al., 1978). The quasi-particle approximation causes many poles to be assigned to each canonical orbital. In the uncorrelated propagator, only one pole is assigned to each orbital.

### 1.5 Approximate propagator expressions

With the orbital energy and the relaxation terms in the self-energy included in the  $\Delta$ SCF energy difference, the renormalized quasi-particle propagators under consideration will have the form (Kurtz and Öhrn, 1978)

$$G_{ii}^{-1}(E) = E - (\Delta\text{SCF})_i - \sum \text{CORR}_{ii}(E) . \quad (1-41)$$

The quasi-particle assumption permits direct iteration of equation 1-41 with respect to  $E$ , i.e., there is no need to diagonalize with every new value of  $E$ . However, since relaxation terms are strictly defined only when  $E = \epsilon_i$ , the expression (Kurtz and Öhrn, 1978)

$$G_{ii}^{-1}(\epsilon_i) = \epsilon_i - (\Delta\text{SCF})_i - \sum \text{CORR}_{ii}(\epsilon_i) \quad (1-42)$$

will be evaluated and reported. Typically, when the quasi-particle approximation is valid,  $dG^{-1}(E)/dE$  is small. Consequently, the results of 1-41 and 1-42 closely agree (within 0.1 electron volts). Diagrammatic theory suggests the second and third order correlation self-energies.. (See the Appendix for correlation self-energy formulas.) Another approximation, which derives from the inner projection formalism with the  $f_3$  operator product manifold and a Hartree-Fock ground state, ignores off diagonal terms in the matrix (Born and Öhrn, 1978, 1979 and 1980)

$$(f_3 | (E\hat{I} - \hat{A}) f_3 )^{-1} . \quad (1-43)$$

This approximation is the so-called diagonal 2p-h Tamm-Dancoff approximation (2p-h TDA) (Cederbaum and Domcke, 1977; Schirmer and Cederbaum, 1978) and is no more difficult to compute than second order. It renormalizes certain ring, ladder and mixed ring-ladder diagrams. (For a discussion of the nondiagonal 2p-h TDA, see Mishra and Öhrn, 1980.) All of the following applications of the  $\Delta\text{SCF}$  plus correlation self-energy propagators are discussed in Ortiz and Öhrn, 1980 and 1981.

## 1.6 Vertical and adiabatic electron affinities of Cl<sub>2</sub>

A vertical electron binding energy is an energy difference between N electron and N+1 electron states at the same nuclear geometry. An adiabatic electron binding energy is an energy difference between the same states evaluated at their equilibrium nuclear geometries. For Cl<sub>2</sub>, the change in the equilibrium internuclear distance upon the addition of an electron is about 1.3 bohr. To calculate the adiabatic electron affinity of Cl<sub>2</sub> requires the difference between the energies at the internuclear distances of the neutral molecule and of the anion. Either Cl<sub>2</sub> or Cl<sub>2</sub><sup>-</sup> curves, combined with the appropriate vertical electron affinity, give the adiabatic electron affinity.

Basis sets for all the systems consist of contracted Gaussian type orbitals (CGTOs). Dunning and Hay's (1977) chlorine basis set is the simplest choice (Basis A in Table 1-1); d functions and diffuse s and p functions are subsequent augmentations. As the basis set is enlarged, numerical convergence of the results occurs. Furthermore, similarities in numerical convergence between theoretical approximations establish criteria for choosing basis sets in subsequent applications. For example, numerical convergence with respect to basis sets in the  $\Delta$ SCF approximation might be indicative of convergence in the correlation self-energy. For propagator calculations, where one basis set describes more than one state, the use of different basis sets for each state in the  $\Delta$ SCF calculations is undesirable. When convergence of SCF total energies for each state is attained with basis set augmentations, the occupied orbitals and their energies have been adequately characterized. Virtual orbitals, however, may change markedly as the basis set is improved. Diffuse basis functions have a pronounced effect on the virtual orbitals.

Table 1-1

Cl<sub>2</sub> and Cl<sub>2</sub><sup>-</sup> CGTO Basis

<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Basis</u>	<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Basis</u>
s	40850.	0.002532	A,B,C,D,E,F	p	240.8	0.014595	A,B,C,D,E,F
	6179.	0.019207			56.56	0.099047	
	1425.	0.095257			17.85	0.330562	
	409.2	0.345589			6.350	0.682874	
	135.5	0.636401					
s	135.5	0.120956		p	6.350	1.0	A,B,C,D,E,F
	50.13	0.648511	A,B,C,D,E,F	p	2.403	1.0	A,B,C,D,E,F
	20.21	0.275487		p	0.6410	1.0	A,B,C,D,E,F
s	6.283	1.0	A,B,C,D,E,F	p	0.1838	1.0	A,B,C,D,E,F
s	2.460	1.0	A,B,C,D,E,F	p	0.064	1.0	B,C,F
s	0.5271	1.0	A.B.C.D.E.F.	p	0.028	1.0	C
s	0.1884	1.0	A.B.C.D.E.F				
s	0.082	1.0	B,C,F	d	0.6	1.0	D,F
s	0.41	1.0	C	d	0.28	1.0	E

The correlation self-energy exhibits the aggregate effect of these apparent instabilities.

As the data in Tables 1-2 and 1-3 demonstrate, the augmentations may affect the SCF total energy of one state more than the other. One p and two diffuse s functions are added to basis A to form basis B. These additions cause a much greater energy lowering for  $\text{Cl}_2^-$  than for  $\text{Cl}_2$ . Further improvements of this kind lead to basis C, but the  $\Delta\text{SCF}$  electron affinities change little. The addition of d functions to the original basis (Basis D and Basis E) has an important effect on the  $\Delta\text{SCF}$  electron affinity at the equilibrium internuclear distance of  $\text{Cl}_2$ , but has a less important effect at the  $\text{Cl}_2^-$  equilibrium distance. Results for the second order relaxation contributions to the self-energy are also listed in Table 1-4. These terms change similarly to  $\Delta\text{SCF}$  with respect to basis set improvements. (See also the restricted SCF study of Gilbert and Wahl, 1971.)

Second order and diagonal 2p-h TDA correlation self-energies are constructed with the orbitals from the  $\text{Cl}_2$  SCF calculation. The improvement of the correlation description decreases the vertical electron affinity, but improved basis sets increase it.

For  $\text{Cl}_2$ , as with many molecules, experimentalists have measured only the adiabatic electron affinity (Dispert and Lacmann, 1977). Energy differences, calculated or empirical (Douglas et al., 1963), along the  $\text{Cl}_2^-$  or  $\text{Cl}_2$  potential curves are necessary. Energy differences in the SCF approximation for the  $\text{Cl}_2$  curve, as well as second order RSPT calculations for  $\text{Cl}_2$ , are in Table 1-5. Adiabatic electron affinities using various combinations of potential energy curves and vertical electron affinities are in Tables 1-5, 1-6 and 1-7. The restricted Hartree-Fock potential curve is inadequate because it separates into ions instead of

Table 1-2  
Total Energies for  $Cl_2$  and  $Cl_2^-$  below -918.0 a.u.

	R (bohr)	T.E. of $Cl_2$ (a.u.)	T.E. of $Cl_2^-$ (a.u.)
Basis A (Dunning and Hay) 42 CGTO; [6s,5p]	3.8	-.8493913	-.8601298
	4.1 $R_e(Cl_2)$	-.8611844	-.9197945
	5.0	-.8222161	-.9704808
	5.1 $R_e(Cl_2^-)$	-.8155302	-.9706475
Basis B (Basis A + 2 Diffuse s-Functions and 6 Diffuse p-Functions) 50 CGTO; [7s,6p]	3.8	-.8555922	-.8840327
	4.1 $R_e(Cl_2)$	-.8660123	-.9413989
	5.0	-.8252044	-.9918355
	5.1 $R_e(Cl_2^-)$	-.8186089	-.9921941
Basis C (Basis B + 2 Diffuse s-Functions and 6 Diffuse d-Functions) 58 CGTO; [8s,7p]	3.8	-.8578865	-.8860848
	5.0	-.8261116	-.9928280
Basis D (Basis A + 12 d-Functions with $\xi = 0.6$ ) 54 CGTO; [6s,5p,1d]	3.8	-.9013375	-.8950720
	5.0	-.8290721	-.9764388
Basis E (Basis A + 12 d-Functions with $\xi = 0.28$ ) 54 CGTO; [6s,5p,1d]	3.8	-.8883	-.8814
	5.0	-.8299	-.9753
Basis F (Basis B + 12 d-Functions with $\xi = 0.6$ ) 62 CGTO; [7s,6p,1d]	3.8 $R_e(Cl_2)$	-.9046429	-.9199628
	4.1	-.8954893	-.9970523
	5.0 $R_e(Cl_2^-)$	-.8320003	-.9970151
	5.1		

Table 1-3

Hartree-Fock Total Energy Lowering for  $\text{Cl}_2$  and  $\text{Cl}_2^-$ 

<u>Basis Change</u>	<u>R (bohr)</u>	<u><math>\text{Cl}_2[\Delta\text{RHF}]</math></u> a.u.	<u>eV</u>	<u><math>\text{Cl}_2^-[\Delta\text{UHF}]</math></u> a.u.	<u>eV</u>
A → B	3.8	-0.0062009	-0.17	-0.0239029	-0.65
	4.1	-0.0048279	-0.13	-0.0216044	-0.59
	5.0	-0.0029883	-0.08	-0.0213547	-0.58
	5.1	-0.0030787	-0.08	-0.0215466	-0.59
B → C	3.8	-0.0022943	-0.06	-0.0020521	-0.06
	5.0	-0.0009072	-0.02	-0.0009925	-0.03
A → D	3.8	-0.0519462	-1.41	-0.0349422	-0.95
	5.0	-0.0068560	-0.19	-0.0059580	-0.16
A → E	3.8	-0.0390	-1.06	-0.0213	-0.58
	5.0	-0.0077	-0.21	-0.0048	-0.13
B → F	3.8	-0.0490507	-1.33	-0.0359301	-0.98
	4.1	-0.294770	-0.80		
	5.0	-0.0067959	-0.18	-0.0052168	-0.14
	5.1			-0.0048210	-0.13

Table 1-4

Vertical Electron Affinities for Cl<sub>2</sub><sup>a</sup>

Basis	R (bohr)	$\epsilon(\text{Cl}_2^-)$ (a.u.)	$-I(\Delta\text{SCF})^b$ (a.u.)	$\epsilon(\text{Cl}_2)^b + \Sigma^{\text{R}}(2)$ (a.u.)	$-I(\Delta\text{SCF}) + \Sigma^{\text{C}}(2)$ (a.u.)	$-I(\Delta\text{SCF}) + \Sigma^{\text{p-h}} \text{TDA}$ (eV)
A	3.8	.0388	.0107	.0120	.0065	.0103
	4.1	.0865	.0586	.0594	.0362	.0304
	5.0	.1743	.1483	.1482	.1086	.0933
	5.1	.1810	.1551	.1549	.1131	.0963
B	3.8	.0632	.0284	.0249	.0185	.0163
	4.1	.1125	.0754	.0724	.0574	.0534
	5.0	.2035	.1666	.1637	.1277	.1140
	5.1	.2103	.1736	.1706	.1322	.1171
C	3.8	.0628	.0282	.0219	.0221	.0207
	5.0	.2043	.1667	.1636	.1279	.1145
D	3.8	.0281	.0042	.0063	.0015	.0009
	5.0	.1781	.1474	.1468	.1287	.1177
E	3.8	.0537	.0153	.0099	.0287	.0289
	5.0	.2059	.1651	.1618	.1469	.1375

<sup>a</sup> The listed results are the negative of the electron propagator pole given by the expression in each heading.  
(a.u.) = atomic unit of energy (Hartree).

<sup>b</sup>  $\Delta\text{RHF}$  result of Gilbert and Wahl: Vertical Electron Affinity of Cl<sub>2</sub> at 3.8 bohr = -0.03 eV.

Table 1-5

Adiabatic Electron Affinity of  $\text{Cl}_2^-$  (eV)

Basis	$R(\text{Cl}_2^-)$	$R(\text{Cl}_2^-)$	Vertical <sup>a</sup>	$V(\text{Cl}_2^-)$	$D(\text{Cl}_2^-)^b$	$D(\text{Cl}_2^-)^c$	EA(adiab) <sup>b</sup>	EA(adiab) <sup>c</sup>
A	4.1	5.1	Eq. (A-1)	3.08	1.24	0.69	1.84	2.39
			Eq. (A-2)	2.62			1.38	1.93
B	4.1	5.1	Eq. (A-1)	3.60	1.29	0.67	2.31	2.93
			Eq. (A-2)	3.19			1.90	2.52
E	3.8	5.0	Eq. (A-1)	4.00	1.98	1.22	2.02	2.78
			Eq. (A-2)	3.74			1.76	2.52

a Eq. (A-1) means that  $V(\text{Cl}_2^-)$  is calculated as  $-I + \Sigma C(2)$ . Eq. (A-2) means that  $V(\text{Cl}_2^-)$  is calculated as  $-I + \Sigma 2p-h \text{ TDA}$ .

b Calculated with RHF total energy differences.  $\Delta$ RHF adiabatic electron affinity of Gilbert and Wahl = 2.19 eV.

c Calculated with second order RSPT total energy differences.

Table 1-6

Adiabatic Electron Affinity of  $\text{Cl}_2^-$  (eV)

Basis	$R(\text{Cl}_2)$	$R(\text{Cl}_2^-)$	Vertical <sup>a</sup>	$V(\text{Cl}_2)$	+	$D(\text{Cl}_2^-)$ <sup>b</sup>	=	EA(adiab)
A	4.1	5.1	Eq. (A-1)	.99		1.38		2.37
			Eq. (A-2)	.83				2.21
B	4.1	5.1	Eq. (A-1)	1.56		1.38		2.94
			Eq. (A-2)	1.45				2.83
E	3.8	5.0	Eq. (A-1)	.78		2.10		2.88
			Eq. (A-2)	.79				2.89

<sup>a</sup> Eq. (A-1) means that  $V(\text{Cl}_2)$  is calculated as  $-I + \Sigma^2(2)$ . Eq. (A-2) means that  $V(\text{Cl}_2^-)$  is calculated as  $-I + \Sigma^{2p-h} \text{TDA}$ .

<sup>b</sup> Calculated with  $\Delta\text{UHF}$  energy differences.

Table 1-7  
Adiabatic Electron Affinity of  $\text{Cl}_2$  (eV)

<u>Basis</u>	<u>Vertical<sup>a</sup></u>	<u><math>V(\text{Cl}_2^-)</math></u>	<u>EA(adiab)</u>
A	Eq. (A-1)	3.08	1.59
	Eq. (A-2)	2.62	1.13
B	Eq. (A-1)	3.60	2.11
	Eq. (A-2)	3.19	1.70
E	Eq. (A-1)	4.00	2.51
	Eq. (A-2)	3.74	2.25 <sup>b</sup>

$D(\text{Cl}_2) = 1.49$  eV (see Douglas et al., 1963)

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a Eq. (A-1) means that  $V(\text{Cl}_2^-)$  is calculated as  $-I + \Sigma^{\text{C}(2)}$ . Eq (A-2) means that  $V(\text{Cl}_2^-)$  is calculated as  $-I + \Sigma^{2p-h}$  TDA.

b EXPERIMENT EA(adiab) =  $2.4 \pm 0.2$  eV (Dispert and Lacmann, 1977).

into neutral chlorine atoms. The second order RSPT results contain some correlation. The experimental energy difference or the second order RSPT energy difference along the  $\text{Cl}_2$  curve, combined with the vertical electron affinity at 5.0 bohr, give an adiabatic electron affinity that is within experimental error. A smaller basis set combined with a simpler treatment of correlation could have produced a prediction that was also within experimental tolerance through a fortuitous cancellation of errors.

### 1.7 The electron affinity of CN

The vertical electron affinity of CN is negligibly different from the adiabatic electron affinity since there is little change in the bond length upon addition of an electron. (See Table 1-11.) The total energies listed in Tables 1-9 and 1-10 show the small change in the SCF total energy from one equilibrium distance to the other. Therefore, vertical electron affinities are computed at only one point per basis set. (See Table 1-8.) As the total energies indicate, the d functions produce the greatest improvements. The addition of diffuse functions is not as important since basis A has already been optimized for anionic molecules (Pacansky and Liu, 1977). Griffing and Simons also studied the electron affinity of CN using the equation of motion technique (Griffing and Simons, 1976). They chose Hartree-Fock plus first order RSPT corrections for the ground state and the  $f_3$  operator product manifold. They also varied the exponents of the s and p Gaussian basis functions to minimize the  $5\sigma$  orbital energy (see the critique of Liu, 1977) and included no d functions whatsoever.

The two smallest basis sets permit third order correlation self-energy calculations (see Table 1-12). For the smallest basis set, the

Table 1-8  
CN and CN<sup>-</sup> CGTO Basis

CARBON				NITROGEN			
<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Basis</u>	<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Basis</u>
S	27736.60	0.000117	A,B,C,D,	S	40564.455	0.000108	A,B,C,D
	4143.52	0.000912			6061.2526	0.000839	
	939.514	0.004787			1374.9180	0.004406	
	264.795	0.019857			388.04177	0.018258	
	85.779	0.067684			126.21030	0.062159	
	30.677	0.182120			45.51710	0.167955	
S	11.81810	0.349353	A,B,C,D	S	17.742148	0.331020	A,B,C,D
	4.86688	0.377588			7.370599	0.384095	
	2.09088	0.146235			3.187096	0.175006	
S	0.678103	1.0	A,B,C,D	S	1.026631	1.0	A,B,C,D
S	0.262973	1.0	A,B,C,D	S	0.398715	1.0	A,B,C,D
S	0.102594	1.0	A,B,C,D	S	0.151533	1.0	A,B,C,D
S	0.053	1.0	C	S	0.072	1.0	C
S	0.033	1.0	C	S	0.041	1.0	C

p	51.72330	0.002734	A,B,C,D	p	82.771495	0.002359	A,B,C,D
	12.33970	0.018979			19.381951	0.017447	
	3.77224	0.080810			5.997132	0.074626	
	1.32487	0.227778			2.143546	0.212116	
p	0.481904	1.0	A,B,C,D	p	0.756824	1.0	A,B,C,D
p	0.163810	1.0	A,B,C,D	p	0.245241	1.0	A,B,C,D
p	0.047449	1.0	A,B,C,D	p	0.067063	1.0	A,B,C,D
p	0.022	1.0	D	p	0.028	1.0	D
p	0.013	1.0	D	p	0.015	1.0	D
d	0.63	1.0	B,C,D	d	0.95	1.0	B,C,D

Table 1-9

Total Hartree-Fock Energies for CN and CN<sup>-</sup>

	<u>R (bohr)</u>	<u>(UHF) CN (a.u.)</u>	<u>(RHF) CN<sup>-</sup> (a.u.)</u>
Basis A (Pacansky and Liu) 34 CGTO; [5s,4p]	2.213	-92.1781094	-92.2790088
Basis B (Pacansky and Liu) 34 CGTO; [5s,4p,1d]	2.183	-92.2268502	-92.3323838
Basis C (Basis B + 4 Diffuse s-Functions) 50 CGTO; [7s,4p,1d]	2.213	-92.2263183	-92.3317676
Basis C (Basis B + 4 Diffuse s-Functions) 50 CGTO; [7s,4p,1d]	2.183	-92.2272608	-92.3339783
Basis D (Basis B + 12 Diffuse p-Functions) 58 CGTO; [5s,6p,1d]	2.183	-92.2269896	-92.3330489

Table 1-10  
Hartree-Fock Total Energy Lowering for CN and CN<sup>-</sup>

<u>Basis Change</u>	<u>R (bohr)</u>	CN( $\Delta$ UHF)		CN <sup>-</sup> ( $\Delta$ RFH)	
		<u>a.u.</u>	<u>eV</u>	<u>a.u.</u>	<u>eV</u>
A $\rightarrow$ B	2.213	-0.0482089	-1.31	-0.0527588	-1.44
B $\rightarrow$ C	2.183	-0.0004106	-0.01	-0.0015945	-0.04
B $\rightarrow$ D	2.183	-0.0001394	-0.004	-0.0006651	-0.02

Table 1-11  
 SCF<sup>a</sup> Equilibrium Nuclear Geometries

<u>System</u>	<u>State</u>	<u>Basis</u>	<u>Bond Distance (bohr)</u>	<u>Bond Angle (deg)</u>
CN <sup>-</sup>	$1\Sigma^+$	C: 5s,4p N: 5s,4p	2.213	-
CN <sup>-</sup>	$1\Sigma^+$	C: 5s,4p,1d N: 5s,4p,1d	2.183	-
NH <sub>2</sub> <sup>-</sup>	$1A_1$	N: 5s,4p,1d H: 3s,1p	1.92	103.9
NH <sub>2</sub>	$2B_1$		1.92	105.4
	$2A_1$		1.88	142.3
PH <sub>2</sub> <sup>-</sup>	$1A_1$	P: 6s,5p,1d H: 3s,1p	2.70	94
	$2B_1$		2.67	94
PH <sub>2</sub>	$2A_1$		2.63	121

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<sup>a</sup> RHF calculations for anions and UHF calculations for neutral molecules.

Table 1-12

Vertical Ionization Energy of  $\text{CN}^-$  <sup>a</sup>

Basis	R (bohr)	$\epsilon$ (a.u.)	$-I(\Delta\text{SCF})$ (a.u.)	$\epsilon + \Sigma^{\text{R}}(2)$ (a.u.)	$-I(\Delta\text{SCF}) + \Sigma^{\text{C}}(2)$ (a.u.)	$-I(\Delta\text{SCF}) + \Sigma^{\text{C}}(2) + \text{p-h TDA}$ (eV)	$-I(\Delta\text{SCF}) + \Sigma^{\text{C}}(3)$ (eV)
A	2.213	.1916	.1009	.1157	.0936	2.82	3.46
B	2.213	.1915	.1056	.1132	.1142	3.43	-
B	2.183	.1903	.1055	.1112	.1154	3.44	4.20
C	2.183	.1922	.1067	.1115	.1170	3.49	-
D	2.183	.1911	.1061	.1114	.1161	3.50 <sup>b</sup>	-

<sup>a</sup> The listed results are the negative of the electron propagator pole given by the expression in each heading. (a.u.) = Hartree unit of energy.

<sup>b</sup> Experimental ionization energy =  $3.82 \pm 0.02$  eV (Berkowitz et al., 1969).

third order result is in closest agreement with experiment, but the addition of the d functions casts doubt on the balance of this approximation. If the trends of the basis set improvement continue, the third order approximation will be inferior to the diagonal 2p-h TDA result as the basis set is improved.

### 1.8 Ionization energies of $\text{NH}_2^-$

The lowest ionization energy of  $\text{NH}_2^-$  is the electron affinity of  $\text{NH}_2$ . The second ionization energy of  $\text{NH}_2^-$  yields an excited final state of  $\text{NH}_2$  and, in combination with the lowest ionization energy, an excitation energy. For the first ionization, there is little nuclear rearrangement and, as with CN, the vertical electron binding energy at one nuclear geometry is sufficient. For the second ionization, however, there is a large change in the bond angle and a small change in the bond distances. Once again, energy differences along the N electron or N±1 electron surface are necessary. Other investigators (Bender and Schaefer, 1971; Heaton and Cowdry, 1975) have calculated energy differences using SCF and CI wavefunctions. These calculations indicate that SCF calculations are reliable for the surfaces of interest. (Heaton and Cowdry calculated  $\Delta\text{SCF}$  electron binding energies of  $\text{NH}_2$  with a basis set optimized only for uncharged molecules.) The first basis consists of the nitrogen 5s, 4p, 1d basis from the  $\text{CN}^-$  study plus the 3s, 1p hydrogen basis of Table 1-13. The second basis consists of an 8s, 7p, 2d nitrogen basis (Dunning, 1970) and a 7s, 1p hydrogen basis (Huzinaga, 1965). (See Table 1-14.) The clear superiority of the second basis over the first does not manifest itself by large changes in the electron binding energies. The differences for all theoretical approximations between the basis sets are small and indicate that the first basis is adequate. [Anderson and Simons (1976)

Table 1-13  
 Hydrogen CGTO Basis ( $\text{NH}_2^-$ ,  $\text{PH}_2^-$ )<sup>a</sup>

<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>
s	68.16	0.00255	s	0.224660	0.49221
	10.2465	0.01938		0.082217	0.24260
s	2.34648	0.09280	p	1.0	1.0
	0.67332	0.29430			

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a Huzinaga, 1965.

Table 1-14  
CGTO Basis for  $\text{NH}_2^-$

NITROGEN<sup>a</sup>

Type	Exponent	Coefficient	Type	Exponent	Coefficient
s	13520.	0.000760	p	35.91	0.040319
	1999.	0.006276		8.48	0.243602
	440.	0.032847		2.706	0.805968
	120.9	0.132396			
	38.47	0.393261	p	0.9921	1.0
	13.46	0.546339			
			p	0.3727	1.0
s	13.46	0.252036			
	4.993	0.779385	p	0.1346	1.0
s	1.569	1.0	p	0.059	1.0
s	0.58	1.0	p	0.033	1.0
s	0.1923	1.0	p	0.21	1.0
s	0.088	1.0			
s	0.048	1.0	d	1.5	1.0
s	0.30	1.0	d	0.95	1.0

HYDROGEN<sup>b</sup>

s	68.16	1.0	s	0.082217	1.0
s	10.2465	1.0	s	0.03580	1.0
s	2.34648	1.0			
s	0.673320	1.0	p	1.0	1.0
s	0.22460	1.0			

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a Dunning, 1970.

b Huzinaga, 1965.

found that d functions are important in describing the ground state potential energy surface, but their effect on equation of motion calculations for the electron affinity of  $\text{NH}_2^-$  is small.] The first basis is small enough to permit a third order correlation self-energy calculation. (See Table 1-15.)

The results of the calculations indicate that the diagonal 2p-h TDA is the most reliable predictor. Although the third order results are not markedly inferior for the vertical ionization energy of  $\text{NH}_2^-$ , they give less accurate values for the adiabatic splitting of the  $\text{NH}_2$  states. (See Table 1-16.) The adiabatic electron affinity obtained with the anionic surface is slightly better than that estimated with the neutral surface. The satisfactory approximation of the electron affinity of  $\text{NH}_2^-$  and the energy splitting of the  $\text{NH}_2$  states indicate that the  $\Delta\text{SCF}$  plus diagonal 2p-h TDA correlation self-energy is a balanced treatment of electron affinities.

### 1.9 Ionization energies of $\text{PH}_2^-$

The states of  $\text{PH}_2^-$  and  $\text{PH}_2$  are similar to those of  $\text{NH}_2^-$  and  $\text{NH}_2$ . These calculations show if the approach taken for  $\text{NH}_2^-$  with regard to the basis set choice and to the treatment of correlation is valid for a molecule with a third period atom. The phosphorus basis set (McLean and Chandler, 1980) is approximately as good as the first basis set for  $\text{NH}_2^-$ . (See Table 1-17.) The phosphorus basis set has been optimized for the anionic atom as was the first nitrogen basis of the  $\text{NH}_2^-$  study. The hydrogen basis is in Table 1-13. The nuclear geometries of the neutral states and of the anionic state are optimized with this basis. The third order self-energy is certainly no better than the diagonal 2p-h TDA self-energy. The agreement with experiment for the vertical electron

Table 1-15

Vertical Ionization Energies for  $\text{NH}_2^-$  (eV)

<u>Basis</u>	<u>Bond Distance R (bohr)</u>	<u>Bond Angle <math>\theta</math> (deg.)</u>	<u>Symmetry i</u>	<u><math>-\epsilon_i</math></u>
N: 5s,4p,1d	1.92	103.9	1b <sub>1</sub>	1.28
H: 3s,1p			3a <sub>1</sub>	3.63
N: 8s,7p,2d	1.92 <sup>c</sup>	102.6 <sup>c</sup>	1b <sub>1</sub>	1.32
H: 7s,1p			3a <sub>1</sub>	3.87

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a Compare difference with the observed splitting of  ${}^2A_1$  and  ${}^2B_1$  (1.98 to

b Compare with experiment ( $0.779 \pm 0.037$  eV); Celotta et al. (1974).

c Heaton and Cowdry (1975).

Table 1-15 - Extended

$I_i(\Delta\text{SCF})$	$\frac{-(-I_i(\Delta\text{SCF}))}{+\sum C(2)_{ii}(E)}$	$\frac{-(-I_i(\Delta\text{SCF}))}{+\sum C(2p-h \text{ TDA})_{ii}(E)}$	$\frac{-(-I_i(\Delta\text{SCF}))}{+\sum C(3)_{ii}(E)}$
-1.10	0.21	0.61 <sup>b</sup>	0.52
1.03	2.22	2.50	3.56
-1.09	0.31	0.67 <sup>a,b</sup>	
1.11	2.36	2.63 <sup>a</sup>	

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2.4 eV); Dressler and Ramsay (1959).

Anderson and Simons (1976) obtain 0.42 eV.

Table 1-16

Adiabatic Ionization Energies for  $\text{NH}_2^-$ <sup>a</sup> and  $\text{PH}_2^-$  (eV)

Species	Symmetry $i$	$I_i(\Delta\text{SCF})$	$\frac{-(-I_i(\Delta\text{SCF}) + \sum_i C(2)_i(E))}{i_i(E)}$	$\frac{-(-I_i(\Delta\text{SCF}) + \sum_i C(2p-h \text{ TDA})_i(E))}{i_i(E)}$	$\frac{-(-I_i(\Delta\text{SCF}) + \sum_i C(3)_i(E))}{i_i(E)}$
$\text{NH}_2^-$	$1b_1^d$	-1.09	0.21	0.61 <sup>e</sup>	0.52
	$3a_1^b$	0.24	1.42	1.70 <sup>e</sup>	2.76
	$3a_1^c$		1.56	1.95 <sup>e</sup>	2.75
$\text{PH}_2^-$	$2b_1^d$	0.05	0.68	0.85 <sup>f</sup>	0.80
	$5a_1^b$	2.43	2.97	2.95 <sup>f</sup>	3.10
	$5a_1^c$		3.03	3.03 <sup>f</sup>	3.13

<sup>a</sup> Calculated with N: 5s,4p,1d/H: 3s,1p basis.

<sup>b</sup> Obtained with the vertical detachment energy of the anion and the total energy difference along the SCF potential surface of the neutral molecule.

<sup>c</sup> Obtained with the vertical attachment energy of the neutral molecule and the total energy difference along the SCF potential surface of the anion.

d The results identical to within 0.001 eV for the two ways (b and c) to compute the adiabatic electron affinity.

e The adiabatic splitting of the lowest  ${}^2A_1$  and  ${}^2B_1$  states of  $NH_2$ ,  $\Delta SCF$  (1.41 eV) and  $\Delta CI$  (1.67 eV); Bender and Schaefer (1971) experimental estimate 1.36 eV; see Dixon (1965).

f Experimentally estimated adiabatic splittings of the lowest  ${}^2A_1$  and  ${}^2B_1$  states of  $PH_2$  (2.27 eV); Berthon et al. (1972).

Table 1-17  
CGTO Basis for  $\text{PH}_2^-$

PHOSPHORUS<sup>a</sup>

<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>	<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>
s	77492.4	0.00781	p	384.84	0.009206
	11605.8	0.006068		90.552	0.069874
	2645.96	0.031160		29.134	0.292470
	754.98	0.123431		10.886	0.728103
	248.76	0.378209			
	91.157	0.563262	p	4.3526	0.628349
				1.7771	0.428044
s	91.157	0.160255			
	36.226	0.627647	p	0.6970	1.0
	15.211	0.263849			
			p	0.2535	1.0
s	4.7942	1.0			
			p	0.0685	1.0
s	1.8079	1.0			
			d	0.43 <sup>c</sup>	1.0
s	0.3568	1.0			
s	0.1148	1.0			

HYDROGEN<sup>b</sup>

(see Table 1-13)

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a McLean and Chandler, 1980

b Huzinaga, 1965.

c Dunning and Hay, 1977.

affinity of  $\text{PH}_2$  is not as good as with  $\text{NH}_2$  (see Table 1-18). The adiabatic splitting of the  $\text{PH}_2$  states is satisfactory in the diagonal 2p-h TDA, although the third order approximation is not so far off this time as it was with  $\text{NH}_2$ . (See Table 1-16.)

The computational experience gained in these studies indicates that  $\Delta\text{SCF}$  + diagonal 2p-h TDA self-energy is a useful tool for studying electron affinities. It is sufficiently simple to allow application to larger molecules.

#### 1.10 The transition operator method

For considering the electron binding energies corresponding to the attachment or removal of an electron in spin-orbital  $i$ , a choice of spin-orbital occupation numbers (Purvis and Öhrn, 1976),

$$n_j = \begin{cases} 0, & j \text{ unoccupied} \\ \frac{1}{2}, & j = i \\ 1, & j \text{ occupied} \end{cases} \quad (1-44)$$

defines a grand-canonical one-electron reduced density matrix (Abdulnur et al., 1972). This density matrix gives the form of a transition operator matrix with the elements

$$T_{ij} = h_{ij} + \sum_k \langle ik || jk \rangle \langle n_k \rangle \quad (1-45)$$

where the subscripts are spin-orbital indices. This matrix is set up and diagonalized iteratively in much the same manner as the Fock matrix in UHF spin-orbital optimizations. At convergence, the spin-orbitals satisfy

$$\mathbf{I} = \epsilon \text{DIAGONAL} \cdot \quad (1-46)$$

Table 1-18

Vertical Ionization Energies for  $\text{PH}_2^-$  (eV)

Bond Distance $R$ (bohr)	Bond Angle $\theta$ (deg.)	Symmetry $i$	$-\epsilon_i$	$I_i(\Delta\text{SCF})$	$-\langle I_i(\Delta\text{SCF}) \rangle$ $+\Sigma C(2) i_i(E)$	$-\langle I_i(\Delta\text{SCF}) \rangle$ $+\Sigma C(2p-h \text{ TDA}) i_i(E)$	$-\langle I_i(\Delta\text{SCF}) \rangle$ $+\Sigma C(3) i_i(E)$
2.70	94	$2b_1$	1.06	0.05	0.68	$0.85^a$	0.80
		$5a_1$	4.17	2.94	3.47	3.45	3.60

<sup>a</sup> Compare with experiment ( $1.271 \pm 0.010$  eV); Zittel and Lineberger (1976).

The  $i$ -th spin-orbital energy agrees with  $\Delta$ SCF through third order except for some correction terms (Goscinski et al., 1973; Born et al., 1978). These terms have been evaluated in a number of systems and are small. (They are less than 0.01 electron volts for all the basis sets of  $\text{CN}^-$  and  $\text{Cl}_2$ .) This method incorporates many relaxation effects into a single spin-orbital and suggests a reference state for a propagator calculation. Specifically, the transition operator method (TOM) spin-orbitals and energies are the basis of the self-energy. The ground state density is the grand-canonical density formed from the occupation numbers of equation 1-44. It is possible, then, to evaluate second order and diagonal 2p-h TDA corrections to the TOM spin-orbital energy in the quasi-particle approximation, but without excluding terms in the self-energy that correspond to relaxation when Hartree-Fock orbitals are used. Since the relaxation is itself renormalized into the orbital, there is no need to restrict the summations in the self-energy.

### 1.11 Applications of the transition operator reference

TOM spin-orbital energies and spin-orbital energies plus self-energy corrections are in Table 1-20, along with results in the same basis for  $\text{H}_2\text{O}$  (Dunning, 1970; Huzinaga, 1965). (See Table 1-19.) Among the other approximations are the  $\Delta$ SCF plus correlation self-energy results. The TOM plus diagonal 2p-h TDA self-energy results are superior to the other approximations.

For Ne, the TOM plus self-energy calculations employ a large Gaussian basis set (Table 1-21). While the 2s and 2p ionizations are satisfactorily predicted, the 1s prediction is much poorer. The diagonal 2p-h TDA result is much worse than the second order result (see Table 1-22); this effect could be due to the necessity for precisely describing certain

Table 1-19  
26 CGTO Basis for H<sub>2</sub>O

<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>
H,s	17.37	0.032828
	2.6273	0.23121
	0.58994	0.81724
H,s	0.16029	1.0
H,p	1.0	1.0
O,s	7816.5	0.002031
	1175.8	0.015436
	273.19	0.073771
	81.17	0.2476
	27.184	0.61183
	3.4136	0.2412
O,s	9.5322	1.0
O,s	0.9398	1.0
O,s	0.2846	1.0
O,p	35.183	0.01958
	7.904	0.12419
	2.3051	0.39473
	0.7171	0.6273
O,p	0.2137	1.0
O,d	1.0	1.0

---

Oxygen s and p basis from Dunning, 1970.

Hydrogen s basis from Huzinaga (1965).

Table 1-20  
Vertical Ionization Energies of H<sub>2</sub>O (eV)  
26 CGTO Basis Set

	<u>1a1</u>	<u>2a1</u>	<u>1b2</u>	<u>3a1</u>	<u>1b1</u>
TOM	540.35	33.97	17.41	13.03	10.75
TOM + 2nd order	540.51	33.36	18.56	14.13	11.84
TOM + diag. 2p-h TDA		33.56	18.94	14.61	12.38
Orbital energy	559.39	36.62	19.35	15.66	13.67
$\Delta$ SCF	540.49	33.86	17.93	13.15	10.89
$\Delta$ SCF + 2nd order	540.70	32.78	18.99	14.20	11.93
$\Delta$ SCF + diag. 2p-h TDA	540.62	31.28	19.20	14.44	12.19
Second order <sup>a</sup>		33.4	18.0	13.4	11.1
Diag. 2p-h TDA <sup>a</sup>		33.7	18.5	14.1	11.8
Second order <sup>b</sup>		32.93	17.70	13.18	10.92
Third order <sup>b</sup>		35.10	19.22	15.18	13.03
Experiment <sup>c</sup>	540.2	32.2	18.6	14.7	12.6

---

a Diagonalization of full propagator matrix (Born and Öhrn, 1979).

b Diagonalization of full propagator matrix (Cederbaum et al., 1973).

c Photoelectron spectroscopy (Siegbahn et al., 1969).

Table 1-21

Neon Gaussian Basis Set<sup>a</sup>

<u>Type</u>	<u>Exponent</u>
s	279341.011322
	43638.324426
	9155.291348
	2399.53
	744.787
	260.221
	100.115
	41.7663
	18.6344
	8.76275
	4.21282
	1.7713
	0.723060
0.285620	
p	354.616931
	82.0552
	25.6929
	9.44944
	3.82817
	0.70396
	0.30883
0.13229	
d	2.5
	2.0
	0.8

---

a The basis employs no contractions.

See van Duijneveldt (1971) for details of basis set optimization.

Table 1-22

## Ionization Energies for Ne (eV)

	<u>1s</u>	<u>2s</u>	<u>2p</u>
TOM	868.14	49.09	19.54
TOM + 2nd order	868.98	48.37	20.91
TOM + diag. 2p-h TDA	873.1	48.57	21.58
Second order <sup>b</sup>			19.86
Third order <sup>b</sup>			22.40
Valence approximation <sup>b</sup>			21.56
Experiment <sup>a</sup>	870.2	48.26	21.56

---

a Photoelectron spectroscopy (Carlson et al., 1971).

b Cederbaum and Domcke (1977).

Table 1-23

Vertical Ionization Energies of  $\text{NH}_2^-$  and  $\text{CN}^-$   
Calculated with the Transition Operator Method  
and Self-Energy Corrections (eV)

<u>System</u>	<u>Orbital</u>	<u>TOM</u>	<u>TOM + 2nd order</u>	<u>TOM + diag 2p-h TDA</u>
$\text{CN}^-$	$5\sigma$	2.80	3.57	3.86
$\text{NH}_2^-$	$3a_1$	0.78	1.93	2.51
$\text{NH}_2^-$	$1b_1$	-1.37	-0.24	0.30

---

$\text{CN}^-$ : Basis D from Table 1-8.

$\text{NH}_2^-$ : First Basis from Table 1-15.

integrals involving core orbitals which arise in the denominator shift. Such precision may be lacking when a Gaussian basis set is employed (see Cederbaum and Domcke, 1977).

In the case of the electron affinity of CN, the results using the largest basis set from the previous group of calculations are superior to all other results. (See Table 1-23.)

Finally, less satisfactory results are obtained for the  $\text{NH}_2^-$  ionizations. Since  $\Delta\text{SCF}$  calculations are worse than Koopmans's theorem predictions in this case, the relaxation renormalization may hinder the convergence of self-energy improvements.

### 1.12 Interpretation

Quasi-particle approximations are conservative methods for extending the orbital energy concept to explain electron binding energies without invoking the full apparatus of electron propagator theory. The overlap amplitudes remain proportional to simple Hartree-Fock canonical orbitals. There are many poles that correspond to each orbital, but the poles have different weights. Thus, certain so-called shakeup peaks in a photoelectron spectrum may be assigned to a simple orbital. The success of these methods implies that it may not be necessary to completely abandon the simple orbital picture to explain binding energies, particularly in the core and outer valence regions.

## CHAPTER TWO

### EXCITATION ENERGIES

#### 2.1 Consistent ground states and the random phase approximation

The previous chapter's study of the uncorrelated electron propagator and its extension to correlated electron dynamics is an example of how approximate propagators are constructed to give improved energy differences and transition probabilities. Avoiding the construction of wavefunctions for states other than the ground state is the salient difference between the propagator approach to correlation and variational theory. This characteristic is at once the strength and the enigma of propagator theory (Linderberg and Öhrn, 1977). Since improved ground state density matrices from the propagator are useful for the calculation of properties (Jorgensen, 1975; Purvis and Öhrn, 1975), it is important to know if there exists a corresponding wavefunction. This is the so-called N-representability problem (Davidson, 1976 and references therein) which also occurs in other theories that seek to circumvent the explicit use of wavefunctions, such as density matrix and density functional theories (Öhrn, 1976). The question of N-representability in propagator theory can be formulated in terms of so-called consistency requirements or in terms of sum rules, which, when satisfied, imply the existence of wavefunctions for the ground and excited states generated by the propagator (Linderberg and Öhrn, 1968).

To elucidate the points made above, the model electron propagator of the previous chapter will serve as an example of a consistent

propagator. The model electron propagator with the Hartree-Fock ground state and the operator manifold consisting of simple field operators has electron addition operators

$$|N+1\rangle = a_p^\dagger |N\rangle \quad (2-1)$$

which generate N+1 electron states and electron annihilation operators

$$|N-1\rangle = a_h |N\rangle \quad (2-2)$$

which generate N-1 electron states. The adjoints of these operators annihilate the ground state, i.e.,

$$a_p |N\rangle = a_h^\dagger |N\rangle = 0. \quad (2-3)$$

Thus, the model electron propagator provides an explicit wavefunction for the ground state and the N±1 electron states. If the model electron propagator is constructed in a basis so that its inverse matrix elements are

$$G_{ij}^{-1}(E) = E\delta_{ij} - (h_{ij} + \sum_k \sum_l \langle ik || jl \rangle \langle a_k^\dagger a_l \rangle) = (E\underline{1} - \underline{E})_{ij}, \quad (2-4)$$

(see equations 1-5 for an explanation of the symbols), then this matrix is easily related to the Fock matrix which is constructed in a Hartree-Fock self-consistent field calculation (see McWeeny and Sutcliffe, 1969). When the eigenvectors of this propagator are reinserted into the propagator, an identical self-consistent calculation ensues. The Hartree-Fock SCF procedure is a self-consistent electron propagator calculation. This self-consistent procedure is justified because it is known that the consistent ground state for the simple field operator

manifold is a determinantal wavefunction. Consistent ground states are states where the adjoints of the excitation operators (or ionization operators in the case of the electron propagator) destroy the ground state. If the operator manifold is extended beyond simple field operators, then the consistency requirements are no longer fulfilled. The Dyson equation will yield correlated binding energies and overlap amplitudes, but there will be no explicit wavefunctions for the  $N\pm 1$  electron states and no consistent ground state. The propagator can yield an improved ground state one-electron density matrix, but it is not necessarily  $N$ -representable.

A correlated consistent ground state is associated with the particle-hole or polarization propagator. This propagator produces excitation energies and overlap amplitudes between  $N$  electron states as the electron propagator produces ionization energies, electron affinities and overlap amplitudes between the ground state and  $N\pm 1$  electron states (Linderberg and Öhrn, 1973). The polarization propagator, expressed as a matrix in a basis of spin-orbitals, is given by the expression

$$P_{ijkl}(E) = \sum_n \left| \frac{\langle 0 | a_i^\dagger a_j | n \rangle \langle n | a_k^\dagger a_l | 0 \rangle}{E - E_n + E_0 + i\sigma} + \frac{\langle 0 | a_k^\dagger a_l | n \rangle \langle n | a_i^\dagger a_j | 0 \rangle}{E + E_n - E_0 - i\sigma} \right|. \quad (2-5)$$

Note that the poles

$$E = \pm(E_n - E_0) \quad (2-6)$$

and the residues

$$\langle 0 | a_i^\dagger a_j | n \rangle \langle n | a_k^\dagger a_l | 0 \rangle \quad (2-7)$$

have an interpretation for excitation processes that is completely

analogous to the interpretation of the poles and residues of the electron propagator for ionization processes. As the electron propagator was developed to give the Dyson equation from the inner projection technique, the polarization propagator can yield the Bethe-Salpeter equation with the aid of inner projection theory. The simplest operator manifold that is inspired by the inner projection technique uses the  $f_2$  operator product manifold:

$$P(E) = (\underline{a}^\dagger \underline{a} | \underline{h}) (\underline{h} | (E\hat{I} - \hat{H}) \underline{h})^{-1} (\underline{h} | \underline{a}^\dagger \underline{a}), \quad (2-8)$$

where

$$\underline{h} \cong f_2 = \{a_k^\dagger a_l, k \neq l\}. \quad (2-9)$$

Improvements can be realized by including higher operator products, such as  $f_4$  or  $f_6$ . Now the question of the ground state choice arises. The choice of the Hartree-Fock ground state produces the time-dependent Hartree-Fock approximation (Jorgensen and Linderberg, 1970). This ground state is not consistent and leads to inquiries concerning the form of the ground state that is consistent with  $f_2$  (Linderberg and Öhrn, 1977; Öhrn and Linderberg, 1979; Goscinski and Weiner, 1980; Weiner and Goscinski, 1980a and 1980b). The form of the consistent ground state is the anti-symmetrized geminal power (AGP),

$$|\text{ground state}\rangle = 0_{AS} \prod_{i=1}^{N/2} g(2i-1, 2i), \quad (2-10)$$

where  $N$  is the number of electrons and  $0_{AS} = \frac{1}{N!} \sum_P (-1)^P P$ , which suggests that a variationally optimized AGP might be an interesting ground state for a polarization propagator calculation with the  $f_2$  operator product

manifold. All polarization propagator calculations that employ the  $f_2$  operator manifold are called random phase approximation calculations. This name is also applied when a Hartree-Fock reference state is used. The name extended RPA is applied to calculations where there are improvements in the ground state or in the operator manifold (Shibuya and McKoy, 1970). Finally, the term self-consistent RPA has been applied to calculations where improved ground state densities from the polarization propagator have been calculated iteratively (Jorgensen and Oddershede, 1972). In the present calculations there is no assurance that the variationally determined AGP will be the ground state that fulfills all the consistency requirements. Therefore, the polarization propagator calculations that follow are called AGP-RPA.

The AGP has previously been studied for reasons that are unrelated to propagator theory (Kutzelnigg, 1964 and 1965; Bratoz and Durand, 1965; Bessis et al., 1967 and 1969; Coleman, 1965; Fukutome, 1977; Fukutome et al., 1977). The sparseness of its two-electron density matrix and the incorporation of correlation into a single geminal have made AGP attractive to many investigators. The following discussion treats the mathematical properties of the AGP and the interpretation of electronic structure that it provides. In addition, the AGP is used as a reference state in a polarization propagator calculation.

## 2.2 The antisymmetrized geminal power wavefunction

The AGP

$$0_{AS} \prod_{i=1}^{N/2} g(2i-1, 2i) \quad (2-11)$$

is formed from the geminal,  $g(1,2)$ , which is expressed in terms of a

spin-orbital basis as follows,

$$g(1,2) = \sum_{i=1}^M \sum_{j=1}^M c_{ij} [\phi_i(1)\phi'_j(2) - \phi'_j(1)\phi_i(2)] \quad (2-12)$$

where M is the dimension of the orbital basis. This geminal can also be written in natural form

$$g(1,2) = \sum_{i=1}^M g_i [\phi_i(1)\phi'_i(2) - \phi'_i(1)\phi_i(2)] \quad (2-13)$$

where unprimed  $\phi$  stands for a spin-orbital with alpha spin and primed  $\phi$  stands for a spin-orbital with beta spin. The Hartree-Fock wavefunction is included as a special case of the AGP by restricting M to be the number of electrons divided by two. For the case of odd-electron systems, the generalized AGP

$$O_{AS} = \prod_{i=N+1}^{N+K} \chi_i(i) \prod_{i=1}^{N/2} g(2i-1, 2i) \quad (2-14)$$

where the system has  $N + K$  electrons, is the wavefunction that fulfills the consistency requirements of the RPA. Returning to the simple AGP, a superposition of configurations is generated when M is greater than half the number of electrons. This expansion of configurations is

$$\sum_{i_1 > i_2 > \dots > i_{N/2}} g_{i_1} g_{i_2} \dots g_{i_{N/2}} \times \det\{\phi_{i_1}(1)\phi'_{i_1}(2)\phi_{i_2}(3)\phi'_{i_2}(4)\dots\phi_{i_{N/2}}(N-1)\phi'_{i_{N/2}}(N)\} \quad (2-15)$$

and includes certain double, quadruple, sextuple and higher even-fold excitations from any determinant which is chosen as the reference

configuration. In this study, the geminal will be optimized in its natural form and the further restrictions to the singlet, restricted case

$$g(1,2) = \sum_{i=1}^M g_i \phi_i(1) \phi_i(2) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \quad (2-16)$$

will be made, where  $\{\phi_i\}$  stand for spatial orbitals.

### 2.3 Density matrices and the total energy expression

The singlet, restricted geminal,

$$g(1,2) = \sum_{i=1}^M \sum_{j=1}^M C_{ij} \phi_i(1) \phi_j(2) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) , \quad (2-17)$$

may be transformed to natural form,

$$g(1,2) = \sum_{i=1}^M g_i \phi_i(1) \phi_i(2) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2)) , \quad (2-18)$$

where the natural orbitals of the geminal are  $\{\phi_i\}$  and the natural orbital occupation numbers of the geminal are  $|g_i|^2$ . The superposition of configurations derived from the AGP contains no configuration that is singly excited with respect to any other determinant when the geminal is in natural form. The elements of the one-electron density matrix of the AGP

$$N_{ij} = \langle a_i^\dagger a_j \rangle = N_{ii} \delta_{ij} \quad (2-19)$$

are zero unless the indices are equal. Therefore, the natural orbitals of the AGP are the natural orbitals of the geminal. The diagonal element  $N_{ii}$  is the sum of the squared absolute values of the coefficients of the configurations in which the orbital  $i$  appears:

$$N_{ii} = |g_i|^2 \sum_{\substack{i_1 > i_2 > \\ \neq i}} \sum_{\substack{i_2 > i_3 > \\ \neq i}} \dots \sum_{\substack{i_{N/2-1} > i_{N/2} \\ \neq i}} |g_{i_1}|^2 |g_{i_2}|^2 \dots |g_{i_{N/2-1}}|^2. \quad (2-20)$$

By introducing the symmetric function of order  $N/2$  of the squares of the coefficients,  $g_i$ , the occupation numbers of the one-electron density matrix of the geminal,

$$C\left(\frac{N}{2}\right) = \sum_{i_1 > i_2 > \dots} \sum_{i_{N/2}} |g_{i_1}|^2 |g_{i_2}|^2 \dots |g_{i_{N/2}}|^2, \quad (2-21)$$

the elements of the one-electron density matrix of the AGP can be expressed as

$$N_{ii} = \frac{1}{C\left(\frac{N}{2}\right)} g_i \frac{\partial C\left(\frac{N}{2}\right)}{\partial g_i}. \quad (2-22)$$

The elements of the two-electron density matrix that are not zero follow in a similar way according to the formulas

$$\langle a_i^\dagger a_j^\dagger a_j a_i \rangle = \frac{1}{C\left(\frac{N}{2}\right)} g_i g_j \frac{\partial^2 C\left(\frac{N}{2}\right)}{\partial g_i \partial g_j}, \quad (2-23)$$

where  $i$  and  $j$  are the spin-orbitals, and

$$\langle a_i^\dagger a_{\bar{i}}^\dagger a_{\bar{j}} a_j \rangle = \frac{1}{C\left(\frac{N}{2}\right)} \frac{\partial^2 C\left(\frac{N}{2} + 1\right)}{\partial g_i \partial g_{\bar{j}}}, \quad (2-24)$$

where  $\bar{i} = i$  with opposite spin. The total energy is

$$E = \sum_i (2h_{ii} + \langle ii|ii \rangle) N_{ii} + \sum_i \sum_j (4\langle ij|ij \rangle - 2\langle ij|ji \rangle) \langle a_i^\dagger a_j^\dagger a_j a_i \rangle \quad (2-25)$$

$$+ 2\text{Re}\left\{ \sum_i \sum_j \langle ii|jj \rangle \langle a_i^\dagger a_i^\dagger a_j a_j \rangle \right\}$$

(Linderberg, 1980), with  $i$  and  $j$  now spatial orbital indices.

#### 2.4 Interpretations of the total energy expression

The total energy expression can be interpreted with the terminology of configuration interaction. The first two summations in equation 2-25 arise from Hamiltonian matrix elements between identical configurations. Each configuration's total energy is weighted by the absolute value squared of its coefficient in the CI expansion generated by the AGP. Thus, the integrals that occur in the first two terms are one-electron, Coulomb and exchange integrals. In the third summation, the integrals cannot be classified as Coulomb or exchange integrals; they arise from matrix elements in the CI expansion between configurations that differ by two spin orbitals.

Another framework in which the total energy may be analyzed is in terms of pair-correlation theories (Meyer, 1977 and references therein) and many-body perturbation theory (MBPT), in which pair correlation energies provide corrections to the Hartree-Fock total energy (Bartlett and Shavitt, 1977; Bartlett and Purvis, 1978). These pair correlation terms are produced by matrix elements of double excitations with the closed-shell Hartree-Fock configuration. In MBPT, the contributions from the first and second summations in equation 2-25 that do not come from the reference configuration vanish according to the linked-cluster theorem (Brueckner, 1955a and 1955b; Goldstone, 1957). The contributions from the third term derive from the same type of CI matrix elements as the pair energies of the various many-body approaches.

## 2.5 Coefficient optimization

Because of the simplifications in the two-electron density matrix that obtain by considering the natural form of the geminal, both the coefficients,  $g_i$ , of the geminal and the natural orbitals of the geminal must be optimized. If the general form of the geminal had been employed (see equation 2-17), it would have been sufficient to only vary the coefficients,  $c_{ij}$ .

The coefficient variation procedure is obtained by imposing a necessary condition for the stationarity of the total energy. Let the Rayleigh-Ritz variational quotient,

$$E = \frac{\langle \text{AGP} | H | \text{AGP} \rangle}{\langle \text{AGP} | \text{AGP} \rangle}, \quad (2-26)$$

be written as

$$E = \frac{E'}{C\left(\frac{N}{2}\right)}, \quad (2-27)$$

where  $E'$  is the unnormalized AGP total energy, and  $C(N/2)$  is the normalization, or the symmetric function of order  $N/2$  of the squares of the absolute values of the coefficients of the geminal. If the first variation of the energy with respect to the coefficients is zero,

$$\frac{\partial}{\partial g_i^*} E = 0, \quad (2-28)$$

subject to the constraint that the geminal be normalized,

$$\sum_j g_j^* g_j = 1, \quad (2-29)$$

then the necessary condition

$$\frac{\partial}{\partial g^*_{i}} [E - \lambda(\sum_j g^*_j g_j - 1)] = 0 \quad (2-30)$$

is obtained, where  $\lambda$  is a Lagrange multiplier. By noticing that both the normalization of equation 2-27 and the unnormalized total energy satisfy the Euler formula for symmetric functions,

$$E' = \frac{1}{N/2} \sum_j g_i \frac{\partial E'}{\partial g_i} \quad (2-31)$$

$$C\left(\frac{N}{2}\right) = \frac{1}{N/2} \sum_j g_j \frac{\partial C\left(\frac{N}{2}\right)}{\partial g_j} \quad (2-32)$$

the necessary condition for stationarity of the total energy can be rewritten

$$\frac{\partial}{\partial g^*_{i}} = \frac{1}{C\left(\frac{N}{2}\right)} \frac{\partial E'}{\partial g^*_{i}} - \frac{E'}{[C\left(\frac{N}{2}\right)]^2} \frac{\partial C\left(\frac{N}{2}\right)}{\partial g^*_{i}} \quad (2-33)$$

$$= \frac{1}{\frac{N}{2} C\left(\frac{N}{2}\right)} \sum_j \left\{ \frac{\partial^2 E'}{\partial g^*_{i} \partial g_j} - E' \frac{\partial^2 C\left(\frac{N}{2}\right)}{\partial g^*_{i} \partial g_j} \right\} g_j \quad (2-34)$$

$$= \frac{1}{\frac{N}{2} C\left(\frac{N}{2}\right)} \sum_j H_{ij} g_j, \quad (2-35)$$

where  $H_{ij} = H^*_{ji}$ . Now with the introduction of the constraint on the normalization of the wavefunction, equation 2-30 implies that

$$\frac{1}{\frac{N}{2} C\left(\frac{N}{2}\right)} \sum_j H_{ij} g_j = \lambda g_i. \quad (2-36)$$

Equation 2-36 is a standard eigenvalue problem that is iteratively

solved. At self-consistency, the value of  $\lambda$  is zero since

$$\frac{1}{2C \binom{N}{2}} \sum_j H_{ij} g_j = \frac{\partial E}{\partial g_i^*} = 0, \quad (2-37)$$

provided that  $g_i$  is itself not zero.

## 2.6 Orbital optimization

A unitary transformation of the orbitals in the AGP may be written as

$$\tilde{a}_r^{\dagger} = e^{i\Lambda} a_r^{\dagger} e^{-i\Lambda} \quad (2-38)$$

(Dalgaard and Jorgensen, 1978), where

$$\Lambda = i \sum_k \sum_l \lambda_{kl} (a_k^{\dagger} a_l - a_l^{\dagger} a_k). \quad (2-39)$$

The resulting total energy after such a transformation on  $|0\rangle$  is

$$\begin{aligned} E(\lambda) = \langle 0 | e^{-i\Lambda} H e^{i\Lambda} | 0 \rangle &= \langle 0 | H | 0 \rangle + -i \langle 0 | [\Lambda, H] | 0 \rangle \\ &+ \frac{1}{2} \langle 0 | [\Lambda, [H, \Lambda]] | 0 \rangle \\ &+ \langle 0 | [[\Lambda, H], \Lambda] | 0 \rangle + \dots \end{aligned} \quad (2-40)$$

A stationary point occurs when  $\delta E(\lambda) = 0$ , or

$$\begin{aligned} \delta E(\lambda) &= -i \langle 0 | [\delta\Lambda, H] | 0 \rangle + \frac{1}{2} \langle 0 | [\delta\Lambda, [H, \Lambda]] | 0 \rangle + \\ &+ \langle 0 | [[\delta\Lambda, H], \Lambda] | 0 \rangle + \dots \end{aligned} \quad (2-41)$$

Let

$$W_{rs} = \langle 0 | [a_r^\dagger a_s - a_s^\dagger a_r, H] | 0 \rangle \quad (2-42)$$

and let

$$A_{rs, r's'} = \frac{1}{2} \{ \langle 0 | [a_r^\dagger a_s - a_s^\dagger a_r, [H, a_{r'}^\dagger a_{s'} - a_{s'}^\dagger a_{r'}]] | 0 \rangle \\ + \langle 0 | [[a_r^\dagger a_s - a_s^\dagger a_r, H], a_{r'}^\dagger a_{s'} - a_{s'}^\dagger a_{r'}] | 0 \rangle \} . \quad (2-43)$$

With the neglect of terms higher than second order, equation 2-41 becomes

$$\underline{\lambda} = -\underline{A}^{-1}\underline{W} . \quad (2-44)$$

The solutions,  $\lambda$ , are increment vectors and are converted to unitary orbital transformation matrices according to

$$\underline{\chi} = e^{-\underline{\Lambda}} = -\underline{U} \cosh(\underline{d}) \underline{U}^\dagger - \underline{\lambda} \underline{U} \sinh(\underline{d}) \underline{d}^{-1} \underline{U}^\dagger \quad (2-45)$$

where

$$\underline{\lambda}^2 = \underline{U} \underline{d} \underline{U}^\dagger . \quad (2-46)$$

The integrals are transformed to the new basis before the next orbital or coefficient iteration.

## 2.7 Results for lithium hydride

Calculations for AGP wavefunction optimizations are attempted with a small Gaussian basis set (see Table 2-1). The total energies from these calculations and the total energy differences along the ground state potential energy curve are compared to results from Hartree-Fock, second order MBPT, an MC-SCF wavefunction that contains the same configurations as AGP, but not the constraints on the coefficients, and to the

Table 2-1

LiH Basis13 CGTO Basis<sup>a</sup>

<u>Type</u>	<u>Exponent</u>	<u>Coefficient</u>
Li,s	642.41895	0.00214
	96.79849	0.01621
	22.09109	0.07732
	6.20107	0.24579
	1.93512	0.47019
	0.63674	0.34547
Li,s	2.19146	0.03509
	0.59613	0.19123
Li,s	0.07455	1.00000
Li,s	0.02079	0.39951
	0.00676	0.70012
Li,s	0.08948	1.00000
Li,p	2.19146	0.00894
	0.59613	0.14101
	0.07455	0.94535
Li,p	0.08948	0.15559
	0.02079	0.60768
	0.00676	0.39196
H,s	18.73110	0.00349
	2.82539	0.83473
	0.64012	0.81376
H,s	0.16128	1.00000

---

a Kurtz and Öhrn, 1978.

full CI result. The percentage of the correlation energy is also monitored.

The usual starting point for beginning the optimizations is the Hartree-Fock wavefunction in the canonical orbital basis. The choice of coefficients is zero or one according to whether the orbital in question is occupied or not in the Hartree-Fock wavefunction. (The coefficients are assumed to be real.) Coefficient optimizations are begun; usually five coefficient iterations are sufficient to begin the orbital optimization. Only one orbital optimization is made before the next round of coefficient optimizations is started (see Table 2-2). The motivation for favoring the coefficient optimizations stems from the comparatively smaller effect of the orbital optimizations on the total energy and from the necessity of performing an integral transformation after each orbital optimization. For the regions of the potential energy curve where the Hartree-Fock determinant dominates the full CI expansion, this procedure is satisfactory and converges in about 20 cycles, where each cycle is composed of five coefficient iterations and one orbital iteration. The convergence behavior for other regions of the curve grows worse as the doubly excited determinant  $\sigma_2^2 \rightarrow \sigma_3^2$  becomes more important in the CI expansion of the wavefunction. The AGP thus begun also has a tendency to converge to an excited state. For this region of the potential curve (beyond  $R = 4.0$  bohr), the natural orbitals of the full CI result were used, and the AGP calculation converged as quickly as the previous results. The full CI natural orbitals were also used to start AGP calculations in the interior of the potential curve (within  $R = 4.0$  bohr) as a check on the original results. The AGP iterations converged to the original result. A typical example of the convergence behavior is given in Table 2-2. The use of a damping factor of 0.5 in the coefficient

Table 2-2

Convergence Behavior for AGP Wavefunction  
Optimization for LiH  $1\Sigma^+$  at R = 3.015 bohr

<u>Cycle</u> <sup>a</sup>	<u>Energy (a.u.)</u>
0	-7.96216
1	-7.97133
2	-7.97416
3	-7.97512
4	-7.97514
5	-7.97515
10	-7.97515 53658
15	-7.97515 53664

---

a One cycle is five coefficient iterations followed by one orbital iteration.

optimizations has been found to assure convergence, although it is not necessary to impose a damping factor in all cases. The convergence behavior listed in the table is probably not the most rapid possible with this method. The convergence criterion for the total energy of  $10^{-10}$  is generally the first criterion to be satisfied. The sum of the squares of the orbital transformation matrix elements and the sum of the squares of the elements of the orbital gradient matrix,

$$\sum_r \sum_s |X_{rs}|^2 \quad \text{and} \quad \sum_r \sum_s |\langle 0 | [a_r^\dagger a_s, H] | 0 \rangle|^2, \quad (2-47)$$

are also employed as convergence criteria. When these tolerances are both set equal to  $10^{-12}$ , the former criterion is invariably the last to be satisfied, often requiring five iterations after the satisfaction of the total energy requirement.

Inspection of the coefficients of the geminal at each internuclear distance reveals a trend (see Table 2-3). Near the equilibrium internuclear distance, two of the coefficients dominate the geminal. This dominance is revealed by the table in which natural occupation numbers for the AGP are listed. The other terms in the geminal are quite small and have the opposite sign as the dominant coefficients. As the bond length is increased, a third coefficient becomes important. This coefficient has a negative sign and approximates the lower of the two other important coefficients. The absolute values of the second and third largest coefficients decrease as the distance between the nuclei increases. The largest coefficient attains the maximum value of one. The AGP coefficients are forcing the AGP to approximate a two configuration wavefunction where both electrons of the highest occupied sigma orbital in the Hartree-Fock wavefunction are promoted to the lowest

Table 2-3

AGP Geminal Coefficients and Principal Natural Occupation Numbers for LiH

Orbital	GEMINAL COEFFICIENTS						R = 20.0
	R(bohr) = 2.0	R = 3.015	R = 4.0	R = 6.0	R = 8.0	R = 10.0	
1	1.5209x10 <sup>-1</sup>	9.4632x10 <sup>-2</sup>	6.5115x10 <sup>-2</sup>	9.9999x10 <sup>-1</sup>	1.0000x10 <sup>0</sup>	1.0000x10 <sup>0</sup>	1.0000x10 <sup>0</sup>
2	9.8835x10 <sup>-1</sup>	9.9551x10 <sup>-1</sup>	9.9787x10 <sup>-1</sup>	3.4709x10 <sup>-3</sup>	8.5689x10 <sup>-4</sup>	2.5699x10 <sup>-4</sup>	1.0007x10 <sup>-5</sup>
3	-8.8383x10 <sup>-7</sup>	-1.0662x10 <sup>-7</sup>	-6.1721x10 <sup>-8</sup>	-6.6135x10 <sup>-5</sup>	-4.6458x10 <sup>-6</sup>	7.7295x10 <sup>-9</sup>	8.0805x10 <sup>-10</sup>
4	-9.3768x10 <sup>-7</sup>	-7.6373x10 <sup>-7</sup>	-8.8534x10 <sup>-7</sup>	3.3299x10 <sup>-7</sup>	1.8380x10 <sup>-7</sup>	-2.2853x10 <sup>-8</sup>	-2.5104x10 <sup>-10</sup>
5	-6.1496x10 <sup>-5</sup>	-2.7149x10 <sup>-5</sup>	-1.3420x10 <sup>-5</sup>	-2.2868x10 <sup>-6</sup>	-1.2918x10 <sup>-8</sup>	-3.8991x10 <sup>-7</sup>	-7.3899x10 <sup>-12</sup>
6	-2.8771x10 <sup>-4</sup>	-1.6410x10 <sup>-4</sup>	-1.0347x10 <sup>-4</sup>	-1.3873x10 <sup>-3</sup>	-6.2659x10 <sup>-4</sup>	-2.3185x10 <sup>-4</sup>	-9.9628x10 <sup>-6</sup>
7	-5.4478x10 <sup>-4</sup>	-2.2593x10 <sup>-4</sup>	-1.3458x10 <sup>-4</sup>	-8.4331x10 <sup>-6</sup>	-7.6066x10 <sup>-8</sup>	-5.7980x10 <sup>-9</sup>	-8.7239x10 <sup>-10</sup>
8	-1.9879x10 <sup>-4</sup>	-1.0894x10 <sup>-4</sup>	-5.6204x10 <sup>-5</sup>	-4.6831x10 <sup>-5</sup>	-6.2226x10 <sup>-6</sup>	-4.6549x10 <sup>-7</sup>	-4.6891x10 <sup>-10</sup>
9	-5.8514x10 <sup>-3</sup>	-3.6947x10 <sup>-3</sup>	-2.5573x10 <sup>-3</sup>	-8.3019x10 <sup>-7</sup>	-7.1168x10 <sup>-7</sup>	4.2659x10 <sup>-8</sup>	5.3099x10 <sup>-12</sup>
10	-8.2803x10 <sup>-6</sup>	-3.7418x10 <sup>-6</sup>	-2.0105x10 <sup>-6</sup>	-2.5763x10 <sup>-5</sup>	-1.1271x10 <sup>-7</sup>	8.2023x10 <sup>-9</sup>	1.6881x10 <sup>-10</sup>
11	-2.4494x10 <sup>-4</sup>	-1.2598x10 <sup>-4</sup>	-7.9917x10 <sup>-5</sup>	-9.4966x10 <sup>-7</sup>	-2.6003x10 <sup>-6</sup>	-3.2231x10 <sup>-7</sup>	-5.3093x10 <sup>-10</sup>
12	-8.2803x10 <sup>-6</sup>	-3.7418x10 <sup>-6</sup>	-2.0105x10 <sup>-6</sup>	-2.5763x10 <sup>-5</sup>	-1.1271x10 <sup>-7</sup>	8.2023x10 <sup>-9</sup>	1.6881x10 <sup>-10</sup>
13	-2.4494x10 <sup>-4</sup>	-1.2598x10 <sup>-4</sup>	-7.9917x10 <sup>-5</sup>	-9.4966x10 <sup>-7</sup>	-2.6003x10 <sup>-6</sup>	-3.2231x10 <sup>-7</sup>	-5.3093x10 <sup>-10</sup>

OCCUPATION NUMBERS ( $>10^{-6}$ )

1	1.996997	1.996928	1.996899	1.999997	1.999999	2.000000	2.000000
2	1.999929	1.999972	1.999987	1.723504	1.303106	1.102607	1.004471
3	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	0.000630	0.000038	$<10^{-6}$	$<10^{-6}$
4	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
5	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	0.000001	$<10^{-6}$	0.000003	$<10^{-6}$
6	0.000007	0.000006	0.000005	0.275355	0.696762	0.897383	0.995529
7	0.000026	0.000012	0.000009	0.000010	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
8	0.000003	0.000002	0.000001	0.000314	0.000069	0.000004	$<10^{-6}$
9	0.003026	0.003072	0.003093	$<10^{-6}$	0.000001	$<10^{-6}$	$<10^{-6}$
10	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	0.000095	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
11	0.000005	0.000004	0.000003	$<10^{-6}$	0.000012	0.000002	$<10^{-6}$
12	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$	0.000095	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
13	0.000005	0.000004	0.000003	$<10^{-6}$	0.000012	0.000002	$<10^{-6}$

unoccupied sigma orbital, i.e.,  $\sigma_1^2\sigma_2^2 \rightarrow \sigma_1^2\sigma_3^2$ . This type of excitation is included in the AGP wavefunction. The next most important configuration in the AGP is the configuration where all four electrons are assigned to the sigma orbitals that were just mentioned:  $\sigma_2^2\sigma_3^2$ . The core orbitals on lithium are not occupied in this configuration. In the limit of infinite separation of nuclei, such a configuration should have a coefficient of zero in the CI wavefunction since it corresponds to a  $\text{Li}^+$  atom and a  $\text{H}^-$  atom. The AGP reduces the importance of this unphysical configuration by making the second and third largest coefficients very small. When the ratio of the largest coefficient to the next largest coefficient approaches infinity, the AGP wavefunction approaches a generalized AGP wavefunction (Weiner and Goscinski, 1981).

The AGP at the equilibrium internuclear distance provides slightly less than half of the correlation energy (see Table 2-4). This result is similar to the results obtained by other investigators (Jensen, 1980; Bessis et al., 1967 and 1969; Linderberg, 1980; Kurtz et al., 1981). At the internuclear distance of 20.0 bohr, however, the percentage of the correlation energy rises to 92. What is of greatest importance is the treatment of total energy differences along the potential curve (see Table 2-5). The results from AGP give a curve that is similar to the full CI curve. The AGP wavefunction predicts dissociation into uncharged atoms, unlike restricted Hartree-Fock. This dissociation property makes the AGP a useful ground state for the investigation of potential energy surfaces.

## 2.8 The random phase approximation of the polarization propagator

The AGP is now used as a ground state for the determination of excitation energies with the random phase approximation of the polarization

Table 2-4

LiH Total Energies (a.u.) and Correlation Percentages for  $1\Sigma^+$  Ground State

<u>R (bohr)</u>	<u>Hartree-Fock</u>	<u>MBPT(2)</u>	<u>AGP</u>	<u>MC-SCF</u>	<u>Full-CI</u>
2.0	-7.86752 0%	-7.88950 78%	-7.88039 46%	-7.89425 95%	-7.89567 100%
3.015	-7.96216 0%	-7.98332 76%	-7.97516 47%	-7.98838 95%	-7.98985 100%
4.0	-7.95075 0%	-7.97309 71%	-7.96379 42%	-7.98050 95%	-7.98216 100%
6.0	-7.89030 0%	-7.91816 56%	-7.92596 72%	-7.93783 96%	-7.93973 100%
8.0	-7.84455 0%	-7.88184 47%	-7.91108 84%	-7.92291 98%	-7.92421 100%
10.0	-7.81544 0%	-7.86806 49%	-7.90895 88%	-7.92077 99%	-7.92216 100%
20.0	-7.76679 0%		-7.90859 92%	-7.92040 99%	-7.92163 100%

Table 2-5

Total Energy Differences along the Ground State ( $1\Sigma^+$ ) Potential Curves (a.u.)  
with Respect to the Total Energy at  $R = 3.015$  bohr

<u>R</u>	<u><math>\Delta(\text{Hartree-Fock})</math></u>	<u><math>\Delta(\text{MBPT})</math></u>	<u><math>\Delta(\text{AGP})</math></u>	<u><math>\Delta(\text{MC-SCF})</math></u>	<u><math>\Delta(\text{Full CI})</math></u>
2.0	0.09465	0.09383	0.09477	0.09413	0.09418
3.015	0	0	0	0	0
4.0	0.01142	0.01023	0.01137	0.00788	0.00769
6.0	0.07186	0.06516	0.04919	0.05055	0.05012
8.0	0.11761	0.10148	0.06408	0.06547	0.06564
10.0	0.14672	0.11526	0.06620	0.06761	0.06769
20.0	0.19537		0.06657	0.06798	0.06822

propagator. If the operator manifold is transformed so that

$$q_{ij}^\dagger = g_{j\bar{j}}^* a_i^\dagger a_j - g_{i\bar{i}}^* a_{\bar{j}}^\dagger a_{\bar{i}}, \quad (2-48)$$

$$q_{ij} = g_j a_j^\dagger a_i - g_i a_{\bar{i}}^\dagger a_{\bar{j}}, \quad (2-49)$$

where  $\bar{j} = j$  with opposite spin, then the polarization propagator will be block diagonal,

$$\underline{P}(E) = \begin{pmatrix} \langle\langle g^\dagger; g^\dagger \rangle\rangle_E & \underline{0} \\ \underline{0} & \langle\langle q; q \rangle\rangle_E \end{pmatrix} \quad (2-50)$$

for a self-consistent RPA polarization propagator (Weiner and Goscinski, 1980a and 1980b). The excitation energies are obtained from

$$\langle\langle g^\dagger; g^\dagger \rangle\rangle_E Q^\dagger = \underline{\epsilon} Q^\dagger. \quad (2-51)$$

While the AGP that has been calculated for use in this calculation has been variationally optimized, there is no guarantee that it is the AGP that is the consistent ground state of the RPA. The previously cited proofs only state that the consistent ground state is of the AGP form. Nonetheless, if the upper block of equation 2-50 is constructed and diagonalized, the eigenvectors form excitation operators and their adjoints destroy the AGP ground state. To this extent, the variationally determined AGP is a consistent ground state. Of course, the other blocks of the propagator have been neglected and are, in general, not equal to zero.

## 2.9 Polarization propagator calculations on lithium hydride

The lowest excitation energies and the corresponding excitation operators are calculated according to the previously discussed procedure (see equation 2-51). In Table 2-6, they are compared to full CI excitation energies. Near the equilibrium internuclear distance, the agreement between the AGP-RPA calculation and full CI is good. As the internuclear distance is increased, the results grow worse. This perhaps is due to the need for elements of  $f_4$  in the operator manifold since more than one configuration is important in the ground state. Specifically, near the equilibrium internuclear distance, the single determinant, molecular orbital description of electronic structure is qualitatively correct. Excitations are approximately single replacements from a reference determinant. As the internuclear distance grows, configuration interaction in the ground state becomes important. The two configuration wavefunction that is appropriate for such regions of the potential energy curve,  $\sigma_1^2 \sigma_2^2 - \sigma_1^2 \sigma_3^2$ , can be approximately written as a valence bond wavefunction,

$$\det\{\phi_{\text{Li},1s}(1)\alpha(1)\phi_{\text{Li},1s}(2)\beta(2)\phi_{\text{Li},2s}(3)\alpha(3)\phi_{\text{H},1s}(4)\beta(4)\} + \quad (2-52)$$

$$\det\{\phi_{\text{Li},1s}(1)\alpha(1)\phi_{\text{Li},1s}(2)\beta(2)\phi_{\text{H},1s}(3)\alpha(3)\phi_{\text{Li},2s}(4)\beta(4)\}$$

and the lowest excitation is easily characterized as

$$[\phi_{\text{Li},2s}\phi_{\text{H},1s} + \phi_{\text{H},1s}\phi_{\text{Li},2s}] \rightarrow \phi_{\text{H},1s}\phi_{\text{H},1s} \quad (2-53)$$

which is a single excitation from the valence bond wavefunction. In the delocalized molecular orbital treatment, the same excitation must be written as

Table 2-6

## AGP-RPA Excitation Energies (a.u.)

R	$A^1\Sigma$		$B^1\Pi$		$3^1\Sigma^+$		$3^1\Pi$	
	<u>Full CI</u>	<u>AGP</u>	<u>Full CI</u>	<u>AGP</u>	<u>AGP</u>	<u>AGP</u>	<u>AGP</u>	<u>AGP</u>
2.0	0.1322	0.1273	0.1757	0.1645	0.1568	0.1568	0.2014	0.2014
3.015	0.1244	0.1162	0.1626	0.1608	0.1511	0.1511	0.1895	0.1895
4.0	0.0978	0.0802	0.1347	0.1407	0.1267	0.1267	0.1640	0.1640
6.0	0.0550	0.0678	0.0875	0.0467	0.1208	0.1208	0.1175	0.1175
8.0	0.0535	0.0323	0.0717	0.0262	0.1142	0.1142	0.1073	0.1073
10.0	0.0614	0.0248	0.0697	0.0234	0.1014	0.1014	0.1056	0.1056
20.0	0.0691	0.0230	0.0692	0.0230	0.1054	0.1054	0.1053	0.1053

$$\sigma_1^2 \sigma_2^2 - \sigma_1^2 \sigma_3^2 \rightarrow \sigma_1^2 \sigma_2^2 + \sigma_1^2 \sigma_3^2 - \sigma_1^2 \sigma_2 \sigma_3 - \sigma_1^2 \sigma_3 \sigma_2 \quad (2-54)$$

where

$$\sigma_1 = \phi_{\text{Li},1s} \quad (2-55)$$

$$\sigma_2 = \phi_{\text{Li},2s} + \phi_{\text{H},1s} \quad (2-56)$$

$$\sigma_3 = \phi_{\text{Li},2s} - \phi_{\text{H},1s} . \quad (2-57)$$

This change in the nature of the electron distribution suggests that perhaps a transformation of the basis of excitation operators might be useful in cases where more than one configuration is dominant in the CI wavefunction.

APPENDIX  
CORRELATION SELF-ENERGIES

The following terms should be excluded from the self-energy in the calculation of electron binding energies when the  $\Delta$ SCF plus correlation self-energy formulas are used. These exclusions apply only to the diagonal elements of the self-energies. The indices refer to spin-orbitals. Indices a,b,c,... refer to occupied spin-orbitals, and indices p,q,r,... refer to unoccupied spin-orbitals.

The second order correlation self-energy is

(A-1)

$$\sum_{ii} C,2(E) = \frac{1}{2} \sum_{a \neq i} \sum_{b \neq i} \sum_p \frac{\langle ip || ab \rangle \langle ab || ip \rangle}{E + \epsilon_p - \epsilon_a - \epsilon_b} + \frac{1}{2} \sum_a \sum_{p \neq i} \sum_{q \neq i} \frac{\langle ia || pq \rangle \langle pq || ia \rangle}{E + \epsilon_a - \epsilon_p - \epsilon_q} .$$

The diagonal 2p-h TDA correlation self-energy is

(A-2)

$$\sum_{ii} C,DIAG \text{ 2p-h TDA } (E) = \frac{1}{2} \sum_{a \neq i} \sum_{b \neq i} \sum_p \frac{\langle ip || ab \rangle \langle ab || ip \rangle}{E + \epsilon_p - \epsilon_a - \epsilon_b + \frac{1}{2} \langle ab || ab \rangle - \langle pa || pa \rangle - \langle pb || pb \rangle} + \frac{1}{2} \sum_a \sum_{p \neq i} \sum_{q \neq i} \frac{\langle ia || pq \rangle \langle pq || ia \rangle}{E + \epsilon_a - \epsilon_p - \epsilon_q - \frac{1}{2} \langle pq || pq \rangle + \langle aq || aq \rangle + \langle ap || ap \rangle} .$$

The third order correlation self-energy is

(A-3)

$$\begin{aligned}
\sum_{ii}^{C,3}(\epsilon) = & \frac{1}{4} \sum_a \sum_p \sum_q \sum_r \sum_s \frac{\langle ia || pq \rangle \langle pq || rs \rangle \langle rs || ia \rangle (1 - \delta_{pr} \delta_{pi})}{(E + \epsilon_a - \epsilon_r - \epsilon_s) (E + \epsilon_a - \epsilon_p - \epsilon_q)} \\
& - \frac{1}{4} \sum_a \sum_b \sum_c \sum_d \sum_p \frac{\langle ip || ab \rangle \langle ab || cd \rangle \langle cd || ip \rangle (1 - \delta_{ac} \delta_{ia})}{(E + \epsilon_p - \epsilon_c - \epsilon_d) (E + \epsilon_p - \epsilon_a - \epsilon_b)} \\
& - \sum_a \sum_b \sum_c \sum_p \sum_r \frac{\langle ib || rq \rangle \langle ra || pb \rangle \langle pq || ia \rangle ((1 - \delta_{ab} \delta_{ia}) (1 - \delta_{pr} \delta_{ip}) + (1 - \delta_{qj}))}{(E + \epsilon_a - \epsilon_p - \epsilon_q) (E + \epsilon_b - \epsilon_q - \epsilon_r)} \\
& + \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle iq || cb \rangle \langle cp || aq \rangle \langle ab || ip \rangle ((1 - \delta_{ac} \delta_{ia}) (1 - \delta_{pq} \delta_{ip}) + (1 - \delta_{bi}))}{(E + \epsilon_p - \epsilon_a - \epsilon_b) (E + \epsilon_q - \epsilon_b - \epsilon_c)} \\
& + \frac{1}{4} \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ic || ab \rangle \langle ab || pq \rangle \langle pq || ic \rangle}{(E + \epsilon_c - \epsilon_p - \epsilon_q) (\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)} \\
& + \frac{1}{4} \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ia || pq \rangle \langle pq || bc \rangle \langle bc || ia \rangle}{(E + \epsilon_a - \epsilon_p - \epsilon_q) (\epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q)} \\
& + \frac{1}{4} \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ip || ab \rangle \langle ab || qr \rangle \langle qr || ip \rangle}{(E + \epsilon_p - \epsilon_a - \epsilon_b) (\epsilon_a + \epsilon_b - \epsilon_q - \epsilon_r)} \\
& + \frac{1}{4} \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ip || qr \rangle \langle qr || ab \rangle \langle ab || ip \rangle}{(E + \epsilon_p - \epsilon_a - \epsilon_b) (\epsilon_a + \epsilon_b - \epsilon_q - \epsilon_r)} \\
& - \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ir || aq \rangle \langle ab || pr \rangle \langle pq || ib \rangle (1 - \delta_{qi})}{(E + \epsilon_b - \epsilon_p - \epsilon_q) (\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_r)} \\
& - \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ib || pr \rangle \langle pq || ab \rangle \langle ar || iq \rangle (1 - \delta_{ri})}{(E + \epsilon_b - \epsilon_p - \epsilon_r) (\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)} \\
& - \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle iq || ac \rangle \langle ab || pq \rangle \langle pc || ib \rangle (1 - \delta_{ci})}{(E + \epsilon_q - \epsilon_a - \epsilon_c) (\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)} \\
& - \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ic || qb \rangle \langle qp || ac \rangle \langle ab || ip \rangle (1 - \delta_{bi})}{(E + \epsilon_p - \epsilon_a - \epsilon_b) (\epsilon_a + \epsilon_c - \epsilon_p - \epsilon_q)}
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ir || ip \rangle \langle ab || rq \rangle \langle pq || ab \rangle}{(\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)(\epsilon_a + \epsilon_b - \epsilon_q - \epsilon_r)} \\
& - \frac{1}{2} \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ia || ic \rangle \langle cb || pq \rangle \langle pq || ab \rangle}{(\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)(\epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q)} \\
& + \frac{1}{2} \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ip || ia \rangle \langle ab || qr \rangle \langle qr || pb \rangle}{(\epsilon_a + \epsilon_b - \epsilon_q - \epsilon_r)(\epsilon_a - \epsilon_p)} \\
& - \frac{1}{2} \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ip || ia \rangle \langle bc || pq \rangle \langle aq || bc \rangle}{(\epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q)(\epsilon_a - \epsilon_p)} \\
& + \frac{1}{2} \sum_a \sum_b \sum_p \sum_q \sum_r \frac{\langle ia || ir \rangle \langle rb || pq \rangle \langle pq || ab \rangle}{(\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)(\epsilon_a - \epsilon_r)} \\
& - \frac{1}{2} \sum_a \sum_b \sum_c \sum_p \sum_q \frac{\langle ic || ip \rangle \langle pq || ab \rangle \langle ab || cq \rangle}{(\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q)(\epsilon_c - \epsilon_p)} .
\end{aligned}$$

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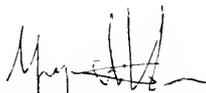
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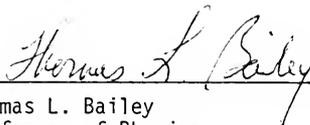
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June 1981

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