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**CORRELATED POSITRON-ELECTRON  
ORBITAL (CPEO): A NOVEL METHOD  
THAT MODELS POSITRON-ELECTRON  
CORRELATION IN VIRTUAL PS AT THE  
MEAN-FIELD LEVEL**

DISSERTATION

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AFIT-DS-ENC-J-001

**DEPARTMENT OF THE AIR FORCE  
AIR UNIVERSITY**

***AIR FORCE INSTITUTE OF TECHNOLOGY***

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AFIT-ENC-DS-J-001

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VIRTUAL PS AT THE MEAN-FIELD LEVEL

DISSERTATION

Presented to the Faculty  
Graduate School of Engineering and Management  
Air Force Institute of Technology  
Air University  
Air Education and Training Command  
in Partial Fulfillment of the Requirements for the  
Degree of Doctor of Philosophy

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March 2021

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AFIT/DS/ENC/17-21

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VIRTUAL PS AT THE MEAN-FIELD LEVEL

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## Abstract

The Correlated Positronic-Electronic Orbital (CPEO) method was developed and implemented to capture correlation effects at between the positron and electron in the modeling of systems that involve a bound positron. Methods that effectively model these systems require many hundred basis functions and use a mean field approach as the beginning step. CPEO builds an orbital for virtual Positronium (Ps) that contains a positron in a bound state along with an accompanying electron to the larger system. Assigning the virtual Ps orbital allows for the two particle variational optimization in conjunction with the other particles that compose the whole system. This novel method required the mathematical development of Fock-operators for each of the three distinct Atomic Orbitals (AO) used in the model. Thus, the CPEO method required the solution of these three coupled Fock-operators. This approach results in the successful capture of positron-electron Coulomb correlation in a mean field method.

The virtual Ps orbital theory is developed and tested on Ps as well as PsH,  $e^+Li$  and  $e^+Na$ . The results from these models suggest that strong correlation effects have been captured at a mean-field level. Previous mean-field methods lacked the correlation needed to bring the positron into close enough contact with electrons, this resulted in low annihilation rates. The CPEO model as implemented resulted in the model of an electron and the positron in perfect correlation and therefore to high of an annihilation rate.

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## List of Abbreviations

Abbreviation	Page
Ps	Positronium ..... 1
CPEO	correlated positron electron orbital ..... 1
ECG	Explicitly Correlated Gaussian ..... 3
QMC	Quantum Monte-Carlo ..... 5
CI	Configuration Interaction ..... 7
CC	Coupled-Cluster ..... 7
MP2	Møller-Plesset perturbation theory ..... 7
SVM	Stochastic Variational Method ..... 8
ECG	explicitly correlated Gaussians ..... 8
FCSVM	Fixed-core SVM ..... 8
NEO	Nuclear-Electronic Orbital ..... 10
NEO-HF	NEO Hartree-Fock ..... 10
NEO-CI	NEO-Configuration Interaction ..... 10
NEO-MCSF	NEO-MultiConfigurational Self-Consistent field ..... 10
NEO-XCHF	NEO- Explicit electron-proton Correlated Hartree-Fock ..... 10
NEO-RXCHF	NEO-Reduced Explicit electron-proton Correlated Hartree-Fock ..... 10
a.u.	atomic units ..... 12
GTG	Gaussian-type geminal ..... 21
SCF	Self-Consistent Field ..... 26
AOs	atomic orbitals ..... 29
STOs	Slater-Type Orbitals ..... 29

Abbreviation	Page
GTFs	Gaussian-Type Functions . . . . . 29
UHF	Unrestricted Hartree-Fock . . . . . 128
RHF	Restricted Hartree-Fock . . . . . 128



## List of Symbols

Symbol	Page
$e^+$	positron ..... 1
$e^-$	electron ..... 1
$E_{\text{corr}}$	electron correlation ..... 5
$E_{\text{HF}}$	Hartree-Fock energy ..... 6
$E_{\text{exact}}$	exact non-relativistic Born-Oppenheimer energy ..... 6
$a_0$	first Bohr orbit of the hydrogen atom ..... 12
$m_e$	mass of electron ..... 12
$k_e$	Coulomb constant ..... 12
$\epsilon_0$	permittivity of free space or electric constant ..... 12
$\chi$	Spin Orbitals ..... 13
$\mathbf{x}$	spin coordinate ..... 13
$\mathbf{r}$	spatial coordinate ..... 13
$\omega$	spin coordinate ..... 13
$\psi$	spatial orbital ..... 13
$\alpha(\omega)$	one of two possible spin factors ..... 13
$\beta(\omega)$	one of two possible spin factors ..... 13
$\phi$	Basis Function ..... 14
$C_\mu$	expansion coefficient for the basis function $\phi_\mu$ ..... 14
$K$	number of basis functions ..... 14
$N_N$	number of nuclei in a system ..... 14
$N_e$	number of electrons in a system ..... 14
$\mathbf{R}_A$	position vector for the $A^{\text{th}}$ nucleus ..... 14

Symbol		Page
$\mathbf{r}_i$	position vector for the $i^{\text{th}}$ electron . . . . .	14
$r_{iA}$	Distance between $i^{\text{th}}$ electron and $A^{\text{th}}$ nucleus . . . . .	14
$R_{AB}$	Distance between the $A^{\text{th}}$ nucleus and $B^{\text{th}}$ nucleus . . . . .	14
$\mathcal{H}$	Hamiltonian . . . . .	14
$M_A$	atomic mass of nucleus $A$ . . . . .	14
$Z_A$	charge of nucleus $A$ . . . . .	14
$\nabla_i^2$	Laplacian operator for the $i^{\text{th}}$ electron . . . . .	14
$\nabla_A^2$	Laplacian operator for the $A^{\text{th}}$ nucleus . . . . .	14
$\mathbf{r}_p$	position vector for the positron . . . . .	16
$r_{pi}$	distances between the positron and the $i^{\text{th}}$ electron . . . . .	16
$r_{pA}$	distances between the positron and the $A^{\text{th}}$ nucleus . . . . .	16
$\nabla_p^2$	Laplacian operator for the positron . . . . .	16
$\nabla_s^2$	Laplacian operator for the special electron . . . . .	18
$r_{ps}$	Distance between the positron and special electron . . . . .	18
$r_{si}$	Distance between the special electron and the $i^{\text{th}}$ regular electron . . . . .	18
$r_{sA}$	Distance between the special electron and the $A^{\text{th}}$ nucleus . . . . .	18
$\mathbf{x}^e$	spin coordinates for electrons . . . . .	20
$\mathbf{x}^p$	spin coordinates for positrons . . . . .	20
$\Phi^e$	Slater determinant for electrons . . . . .	20
$\chi^p$	Positron spin orbital . . . . .	20
$\hat{G}$	geminal operator for NEO-XCHF . . . . .	21
$\chi^g$	Ps orbital that is a function of both the positron and special electron . . . . .	23

Symbol		Page
$N_r$	number of regular electrons . . . . .	23
<b>F</b>	Fock matrix . . . . .	26
<b>C</b>	coefficient matrix . . . . .	26
<b>S</b>	overlap matrix . . . . .	26
$\varepsilon$	diagonal matrix of the orbital energies . . . . .	26
<b>P</b>	Density Matrix . . . . .	27
$\{\phi_\mu\}$	Set of basis functions for $\mu = 1, \dots, K$ . . . . .	27
$\psi_i^e$	spatial orbital for the $i^{\text{th}}$ regular electron . . . . .	30
$\psi^p$	spatial orbital for the positron . . . . .	30
$\psi^g$	Geminal orbital for virtual Ps . . . . .	30
$\lambda_{2\gamma}$	two-photon annihilation rate for Ps . . . . .	37

CORRELATED POSITRON-ELECTRON ORBITAL (CPEO): A NOVEL  
METHOD THAT MODELS POSITRON-ELECTRON CORRELATION IN  
VIRTUAL PS AT THE MEAN-FIELD LEVEL

## I. Introduction

The positron,  $e^+$ , is the anti-particle of the electron,  $e^-$ . Both particles have spin of  $\frac{1}{2}$  and have the same mass and magnetic moment. The electron and positron both have equal but opposite charge. Ours is an electron dominated universe which relegates the positron as the anti-particle.

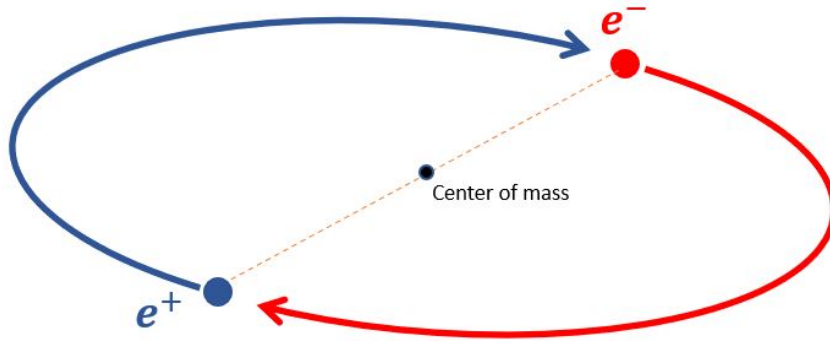
The electron and positron can under the proper conditions come together and form an atom: Positronium (Ps). In Ps, the equal mass of the  $e^+$  and the  $e^-$  orbit their mutual center of mass (see Figure 1). The theoretical study of positron interaction with matter shows how a positron can form a bond with a molecule by forming Ps with a valence electron from the molecule. Once bound, the positron has a strong point-by-point interaction with the electron in the Ps. Capturing the correlation of the positron and the electron is key to developing an effective model for a bound positron.

Many advanced methods used in modeling electronic structure use the Hartree-Fock approximation as a starting point. Hartree-Fock uses a variational approach built on single particle orbitals to create a mean field approximation to the single particle orbitals. This results in the failure to effective modeling of highly correlated systems.

The correlated positron electron orbital (CPEO) was developed to capture correlation within the Ps that forms when a positron is bound to a molecule. When

optimizing an orbital the only freedom is in the form of that orbital. To this end, CPEO uses a two particle orbital for the electron and positron in Ps. Correlation between the two particles is then maintained within the variationally optimized orbital while using a mean field approximation for the complete wavefunction.

The objective of this dissertation is to introduce a novel approach to using a mean field model of a bound positron with a molecule. This is done utilizing the CPEO ansatz. Through utilization of the variational method, optimized orbitals are realized for each orbital presented in the CPEO ansatz. The optimized orbitals create a set of non-separable partial-differential equations in three-dimensions. A solution to these equations can be found by transforming the differential equations into matrix equations using a linear expansion of the unknown function with know basis functions.



**Figure 1.** The positronium atom consist of an electron and a positron orbiting their mutual center of mass.

## II. Background

The first demonstration of an electron binding to a neutral atom came from calculations on the  $H^-$  ion by Bethe [5] and Hylleraas [37]. Today most of the periodic table has been accurately surveyed for electron binding [36]. With the electron and positron being so similar it might be easy to expect that a comparable study using a positron would have also been completed.

The answer to the question of whether a positron could attach itself to a neutral atom wasn't settled until 1997 by two independent but similar variational calculations using Explicitly Correlated Gaussian (ECG) functions. Both demonstrated that  $e^+Li$  was stable against decay into the lowest dissociation channel of  $Li^+$  and Ps by 0.00217 Hartree [71] and 0.001224 Hartree [80].

### A Brief History of Positron Chemistry

The study of positron binding to a neutral atom was for a long time an intriguing but unanswered question [19, 27, 75]. A condensed look at the study of positrons binding to neutral atoms follows [6].

- 1968, Gertler et al. disproved the existence of  $e^+He$ . [28].
- 1970, Wang and Ache [92] were unable to achieve a bound  $e^+He$  state.
- 1970, Schrader [74] produced a self-consistent field model for positron binding to closed shell electron systems which stressed the importance of treating electron-positron correlations explicitly.
- 1971, Aronson et al. proved that  $e^+H$  was unbound [4].

- 1974, Golden and Epstein [30] using adiabatic-type approximation on a model potential to conclude that He, N and Ne were all incapable of binding a positron, while, O, Ar and Kr were unlikely to bind a positron.
- 1976, Clary did large-scale configuration interaction-Hylleraas calculations on  $e^+\text{He}$ ,  $e^+\text{He}^-$  and  $e^+\text{Li}$ , and found them to be probably unstable [15].
- 1976, Drachman et al. [19] used generalized Hylleraas trial function, properly antisymmetrized in the electron coordinates, to investigate positron attachment to excited  $\text{He}(^3\text{Se})$ . They failed to find a bound state.
- 1981, Kurtz and Jordan [46] performed static exchange and static exchange with polarisation calculations for elastic positron scattering with Be, Mg and Ca.
- 1984, Karl et al. [40] used molecular spectroscopy for many atoms to define potential curves. These were then applied to the positron problem binding problems of He, Li, N, O, F, Ne, Na, Al and Ar; with appropriate reduced mass corrections. Results suggested that atoms could not bind a positron.
- 1993, Szmytkowski using calculations restricted to only include dipole polarisation potentials on a polarised orbital scattering method within a relativistic framework found the alkaline earths (Ca, Sr, Ba, Ra) unstable against  $\text{Ps-Atom}^+$  dissociation [90]. However, Be and Mg [90] as well as Zn, Cd and Hg [89, 88] were all found to bind a positron.
- In 1995, Dzuba et al.[22] used many-body perturbation theory to examine the interaction of positrons with atoms. Their calculations predicted binding due to positron-atom polarization potential and virtual positronium for  $e^+\text{Mg}$ ,  $e^+\text{Zn}$ ,  $e^+\text{Cd}$  and  $e^+\text{Hg}$ .

- 1996, Yoshida and Miyako using the Quantum Monte-Carlo (QMC) method predicted that  $e^+Li$  is probably unstable compared to Ps and  $Li^+$  [93].
- 1998, a method using polarised orbital calculations that included higher order multipoles of the polarisation potential predicted that Mg and Zn would bind a positron [49].

## Correlation in Atoms and Molecules

This section focuses on the influence of correlation between particles as it applies to atoms and molecules and how they are modeled with a mean field wavefunction technique. Due to the very low binding energies of positrons to atoms and molecules, electron-positron correlation plays a significant role in positron chemistry. As with many advanced wave function theory techniques, I start with the Hartree-Fock approximation.

### The Hartree-Fock Approximation.

The Hartree-Fock method models a many-electron structure using a single determinant composed of single-particle functions known as orbitals. This develops a picture of electrons occupying the orbitals used in constructing the determinant and provides a view of the molecule near its equilibrium geometry. In such a model the single-particle orbitals do not explicitly depend on the instantaneous motion of the other electrons resulting in the electrons being treated as if they were not correlated.

In Quantum Chemistry electron correlation,  $E_{\text{corr}}$ , has a traditional meaning. It is the correlation that the Hartree-Fock wave function fails to model [43]. Löwdin [48] defined the electron correlation energy as the difference between the Hartree-Fock



energy,  $E_{\text{HF}}$ , and the exact nonrelativistic Born-Oppenheimer energy,  $E_{\text{exact}}$ , so that

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}. \quad (1)$$

This conceptualization that collective error from relying on an independent particle model (mean field model) are summarized as a correlation problem [66].

### **Correlation.**

In a statistical sense, correlation is a measure of the degree to which two variables move in relation to each other.

### **Electron-Electron Correlation.**

There are two primary origins for the effects of electron correlation [43, 66]:

1. Since electrons are indistinguishable the wavefunction for an  $n$ -electron system must be antisymmetric with regards to a permutation of the electrons. It therefor obeys Fermi statistics. This correlation is known as Fermi correlation.
2. The Coulomb interaction between electrons result in Coulomb correlation.

Since Hartree-Fock uses a determinant form for its wavefunction the electrons are antisymmetric. Thus the  $E_{\text{corr}}$  as defined in Equation (1) is primarily a measure of Coulomb correlation.

In smaller atoms and molecules the Hartree-Fock energy is typically more than 99% of the total energy. The energy differences of interest in chemistry such as binding are often 1% or less of the total energy [34]. Inclusion of electron-electron correlation improves convergence of the model as well as the results.

## Positron-Electron Correlation.

The electron and positron experience a Coulomb force resulting in Coulomb correlation. They are however obviously distinguishable. As different particles they are not antisymmetric and have no Fermi correlation between them. Without Fermi correlation the single-particle functions that create orbitals in the Hartree-Fock method will result in very little correlation. This is due to the Hartree-Fock weakness capturing Coulomb correlation. This results in theoretical studies of positronic systems computationally demanding.

As can be seen from Table 2 the binding energy for neutral atomic systems with positron is very small. In these neutral systems the correlation energy is the bulk of the binding energy. For  $e^+\text{Li}$  it is on the order of 0.0025 Hartree or 0.068 eV. Thus to get results that showed binding, the model energy had to include more than 99.99% of the  $E_{\text{exact}}$ . This very small binding energy makes the theoretical study of positronic systems very demanding.

## Common Methods for Describing Correlation

A complete basis set expansion for the Hartree-Fock Energy would not capture the correlation energy as it was defined by Löwdin's, Equation (1). Common methods for describing the electron correlation effects are Configuration Interaction (CI), Coupled-Cluster (CC) Methods and Møller-Plesset perturbation theory (MP2). Generally speaking these methods take the Hartree-Fock results and improve on it to include correlation between the particles. These methods can be very cost-prohibitive for large systems. See Table 1 for scaling cost with N-electrons for common methods.

The inclusion of basis sets relying on inter particle distances are explicitly correlated basis sets. Inclusion of these in the calculation serve to improve the convergence of the methods from Table 1 with fewer basis elements.

Method	Cost	Description
FCI	$\mathcal{O}(N!)$	Full Configuration Interaction [87]
CISD	$\mathcal{O}(N^6)$	CI with single and double excitations
CC	$\mathcal{O}(N!)$	Couple Cluster [13, 14]
CCSD	$\mathcal{O}(N^6)$	CC with single and double excitations [17]
CCSDT	$\mathcal{O}(N^8)$	CCSD with triple excitations
CCSD(T)	$\mathcal{O}(N^7)$	CCSD with perturbatively approximated triple excitation [62, 63]
MP2	$\mathcal{O}(N^5)$	Møller-Plessant perturbation

**Table 1. Computational cost of  $N$ -electron system for common methods that account for correlation.**

## Methods that Include Positron-Electron Correlation

This section further develops the concepts of the methods that have been successfully applied to positronic systems.

### SVM and FCSVM.

Stochastic Variational Method (SVM) was first introduced for solving the few-body problem in quantum mechanics [45]. SVM expands the wavefunction in terms of a linear combination of multidimensional Gaussian functions. Among the Gaussian terms are correlation factors for inter-particle distances or explicitly correlated Gaussians (ECG). SVM relies on the optimization of the exponents in the ECGs. The basis sets are typically between 100 and 100, each with 3 - 20 nonlinear parameters to be optimized [73, 91]. Direct optimization of such a large number of parameters is difficult to do directly so a stochastic search is utilized.

Fixed-core SVM (FCSVM) is for larger atomic systems where each component of the core potential was isolated with a combination of ab initio and semi-empirical techniques[91]. The FCSVM and SCVM methods have been used to produce highly accurate results for systems of up to five quantum particles [7] The accuracy comes at a computational cost that limits the size of systems studied.

In the years following the demonstration of positron binding to lithium in 1997 [71, 80], there were a number of neutral atoms identified as able to bind a positron (see Table 2). Using the SVM method for few body systems [44, 45, 73, 82, 91] it was shown that  $e^+\text{Be}$  had a bound state with positron [73]. The FCSVM improved the existing  $e^+\text{Li}$  calculations [52, 55, 73] and  $e^+\text{Be}$  calculations [56, 73]. FCSVM calculations have demonstrated the binding of positron to sodium [55, 70, 73], magnesium [56, 69, 73], copper [52, 67], zinc [52, 54] and silver [52, 68].

System	Method	$\varepsilon$ (Hartree)
Ps	Exact	0.250
Ps <sup>-</sup>	Hylleraas[35]	0.262 005 07
$e^+\text{He}(^3s^e)$	SVM [72]	0.000592 4
$e^+\text{He}(^3s^e)$	FCSVM [72]	0.000 586 3
$e^+\text{Li}$	SVM [73]	0.002 471
$e^+\text{Li}$	QMC [51]	0.002 382
$e^+\text{Li}$	FCSVM [55]	0.002 477
$e^+\text{Be}$	SVM [73]	0.001 687
$e^+\text{Be}$	FCSVM [56]	0.003 147
$e^+\text{Be}$	CI [50]	0.003 083
$e^+\text{Na}$	FCSVM [55]	0.000 473
$e^+\text{Mg}$	FCSVM [73]	0.015 612
$e^+\text{Ca}$	CI [8]	0.016 50
$e^+\text{Sr}$	CI [8]	0.010 05
$e^+\text{Cu}$	FCSVM [67]	0.005 597
$e^+\text{Zn}$	FCSVM [54]	0.001 425
$e^+\text{Zn}$	CI [8]	0.003 731
$e^+\text{Ag}$	FCSVM [68]	0.005 832
$e^+\text{Cd}$	CI [8]	0.006 100

**Table 2.** The method and binding energy  $\varepsilon$  for a number of positron binding systems. Abbreviations for the methods that were used are Stochastic Variational Method (SVM), Fixed Core SVM (FCSVM), Configuration Interaction (CI), and Quantum Monte Carlo (QMC).

In 1999, Mitroy and Ryzhikh [53] used the CI method to verify positron binding to copper. This was followed by a relativistic CI treatment of the positronic copper and positronic silver systems by Dzuba et al. [21, 23].

## NEO Methods.

The Nuclear-Electronic Orbital (NEO) approach was developed to include nuclear quantum effects into electronic structure calculations by the treatment of specified nuclei on the same level as the electrons. Both electronic and nuclear molecular orbitals were expressed as linear combinations of Gaussian basis functions. This approach was successfully applied to proton transfer and hydrogen tunneling problems [38, 59, 60, 64, 83, 84].

The NEO suite includes NEO Hartree-Fock (NEO-HF) , NEO-Configuration Interaction (NEO-CI), and NEO-MultiConfigurational Self-Consistent field (NEO-MCSF) methods. NEO was later modified by Adamson et al.[2] and extended to positron systems for studying mixed positronic-electronic wavefunctions, replacing the mass of the proton with the mass of the positron. These methods were not adequate enough to quantitatively describe the positronic systems due to the lack of electron-positron correlation. The qualitative utility of the wavefunctions were in the description of cations or dipoles involving Coulombic binding of positrons.

Further modifications for the NEO frame work were done to include explicit electron-proton correlation using the NEO- Explicit electron-proton Correlated Hartree-Fock (NEO-XCHF) [12, 41] and NEO-Reduced Explicit electron-proton Correlated Hartree-Fock (NEO-RXCHF) [11, 76, 78, 85] by the inclusion of a correlation factor in the wavefunction ansatz. NEO-XCHF approach was extended and applied to the positronic systems PsH, LiPs, and  $e^+$ LiH [85]. However, these computationally intense methods are inefficient, limiting their application to systems having a small number of electrons.

### III. Positron-Molecule Binding

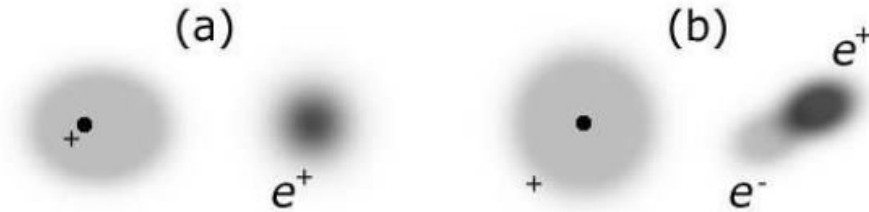
#### Mechanisms for Positron Binding

While the electron and positron are similar in every way except for having opposite charge, their interaction with atoms differs greatly from each other. “From a fundamental point of view, the interaction of a light positively charged particle free from the Pauli exclusion principle and therefore the exchange interaction characteristic of electrons, with the added richness of a positronium channel, provides new tests of our understanding of basic atomic physics.” [81] Both the electron and positron have an attractive static long range polarization potential on the electron cloud. At short range, the positron does not penetrate far inside the electron cloud due to the repulsive force with the atomic nucleus. A bound state occurs when the short range repulsion with the nucleus is overcome by the long range polarization potential [52, 81].

When the energy of the positron is below the Ps-formation threshold ( $< 0.250$  Hartree) there is an additional mechanism for binding. One of the electrons from the valence electrons can attach itself to the positron and form a Ps cluster. This Ps cluster is often also called virtual Ps. The polarization of the virtual Ps can then lead to binding with the residual positively charged ion.

The short range attractions in the bonding of the positron to an atom is similar to that of covalent molecular bonding. The system emerges as a heuristic picture of the superposition of  $e^+A$  and  $\text{Ps}A^+$  states [9, 6, 81], where  $A$  is a neutral atom and  $A^+$  is an ionized atom. A schematic from [52] shown in Figure 2 shows the two possible binding mechanisms. As a positron nears an atom the electron cloud shifts toward the positron as in (a) from Figure 2. Here the positron is bonding in the  $e^+A$  state. In (b) from Figure 2 an electron from the valence electrons has attached to the positron

to form virtual Ps. Here the positron is bonding in the  $\text{PsA}^+$  state. The  $\text{PsA}^+$  state is virtual Ps in the field of a polarized atom. The reality is that the bound positron seems to be in a superposition of these two states with one or the other being more dominant [73, 52].



**Figure 2.** The electron and positron charge clouds interaction in the vicinity of an atom. As a positron nears an atom the electron cloud shifts toward the positron as shown in (a). In (b) an electron from the valence electrons has attached to the positron to form virtual Ps. The virtual Ps is polarized in the presence of the positive residual ion [6, 52, 81].

## Kneaded Essentials

This Section puts forth the units and notation used throughout this document.

### Atomic Units.

Atomic units are chosen to reflect the properties of electrons in atoms and this document presents all formulas in atomic units (a.u.), in which  $a_0 = 1$ ,  $e = 1$ ,  $\hbar = 1$ ,  $m_e = 1$ , and  $k_e = 1$ . Conversion between atomic units and SI units are given below in Table 3. The atomic unit of length,  $a_0 = 5.2918 \times 10^{-11}\text{m}$  as previously described is the radius of the first Bohr orbit of the hydrogen atom. The atomic unit for energy (called a Hartree) is defined such that  $0.50 \text{ Hartree} = 13.6057 \text{ eV}$  (the ionization energy of the hydrogen atom with an infinite mass proton).  $\hbar$  is equal to Plank's constant divided by  $2\pi$ .  $k_e$  is the Coulomb constant which is equal to  $1/(4\pi\epsilon_0)$ , where  $\epsilon_0$  is the permittivity of free space or electric constant.

Physical Quantity	Conversion factor $X$	Value of $X$ (SI)
Length	$a_0$	$5.2918 \times 10^{-11} \text{ m}$
Mass	$m_e$	$9.1095 \times 10^{-31} \text{ kg}$
Charge	Hartree	$4.3598 \times 10^{-18} \text{ J}$
Angular Momentum	$\hbar$	$1.0546 \times 10^{-34} \text{ J s}$
Coulomb constant	$k_e$	$9.98755 \times 10^9 \text{ kg m}^3 \text{ s}^{-2} \text{ C}^{-2}$

**Table 3. Conversion of Atomic Units to SI.**

### Notation.

Spin Orbitals are denoted by the symbol  $\chi$  with appropriate superscripts and subscripts to further classify the spin orbital. The spin orbital is a function of a spin coordinate  $\mathbf{x}$  which is composed of a three-dimensional spatial coordinate  $\mathbf{r}$  and a spin coordinate  $\omega$ .

$$\chi = \chi(\mathbf{x}) = \chi(\mathbf{r}, \omega) \quad (2)$$

The spin orbital is composed of a three-dimensional spatial orbital, denoted using  $\psi$ , and one of two possible spin factors  $\alpha(\omega)$  or  $\beta(\omega)$ . Therefore,

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \psi(\mathbf{r})\beta(\omega) \end{cases} . \quad (3)$$

When expanding the orbitals in terms of some known basis functions it is basically using known spatial basis functions to expand the unknown spatial orbitals that are used to approximate the wavefunction. The work of variational optimization is done on the spin orbitals. Once derivations are complete the spin orbitals are reduced to be a properly represented with functions of spatial orbitals. The spatial orbitals are then expanded in a finite number of basis functions. Basis functions are denoted



using the Greek lower case  $\phi$ , therefore

$$\psi(\mathbf{r}) \approx \sum_{\mu=1}^K C_{\mu} \phi_{\mu}(\mathbf{r}) \quad (4)$$

where  $C_{\mu}$  is a real number used to represent the expansion coefficient for the basis function  $\phi_{\mu}$ . The capital letter  $K$  is reserved for use as the number of basis functions to be used in an expansion.

## The Hamiltonian Operator

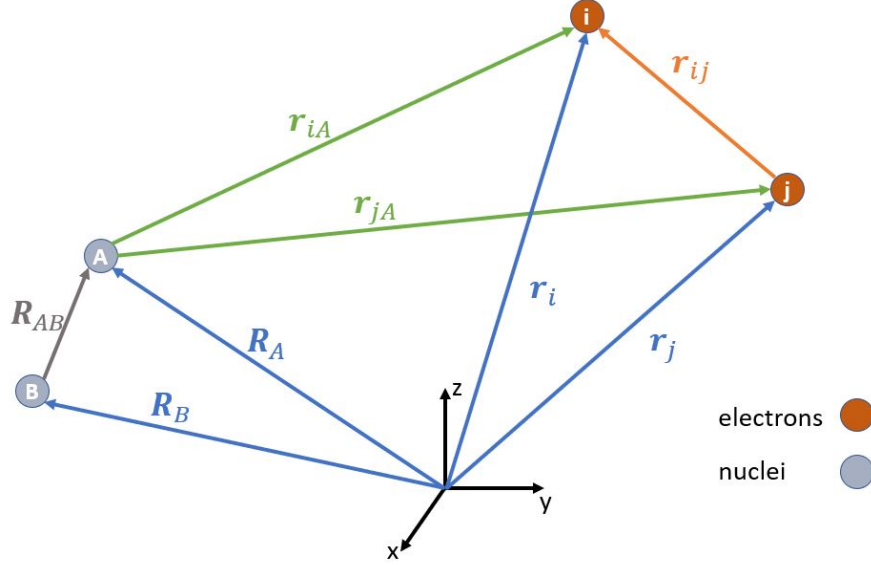
In order to begin a more formal discussion of a positron interacting with a molecule, we begin by building the electronic Hamiltonian. Then a positron is introduced to the system. At this point the Hamiltonian can be examined to illustrate the bonding shown by Figure 2.

### The Electronic Hamiltonian.

Let us consider a molecular system made of  $N_N$  nuclei and  $N_e$  electrons. A molecular coordinate system is shown in Figure 3 for this system. Let  $\mathbf{R}_A$  and  $\mathbf{r}_i$  be the position vectors for the nuclei and electrons respectively. Distances between particles are as follows:  $i^{\text{th}}$  electron and  $A^{\text{th}}$  nucleus is  $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$ ;  $i^{\text{th}}$  electron and  $j^{\text{th}}$  electron is  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ ;  $A^{\text{th}}$  nucleus and  $B^{\text{th}}$  nucleus is  $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$ . The Hamiltonian,  $\mathcal{H}$  for this system in atomic units is

$$\mathcal{H} = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_N} \frac{1}{2M_A} \nabla_A^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} + \sum_{A=1}^{N_N} \sum_{B>A}^{N_N} \frac{Z_A Z_B}{R_{AB}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}} \quad (5)$$

Where  $M_A$  and  $Z_A$  is the atomic mass and charge of nucleus  $A$ . The Laplacian operators  $\nabla_i^2$  and  $\nabla_A^2$  involve differentiation with respect to the the coordinates of the  $i^{\text{th}}$  electron and the  $A^{\text{th}}$  nucleus. The first two terms are then the kinetic energy



**Figure 3.** Molecular coordinate system:  $i, j$  = electron;  $A, B$  = nuclei.

of the electrons and the nuclei. The third term is the Coulomb repulsion between the electrons and the fourth term is the Coulomb repulsion between the nuclei. The fifth term is the Coulomb attraction between each nuclei and electron pair.

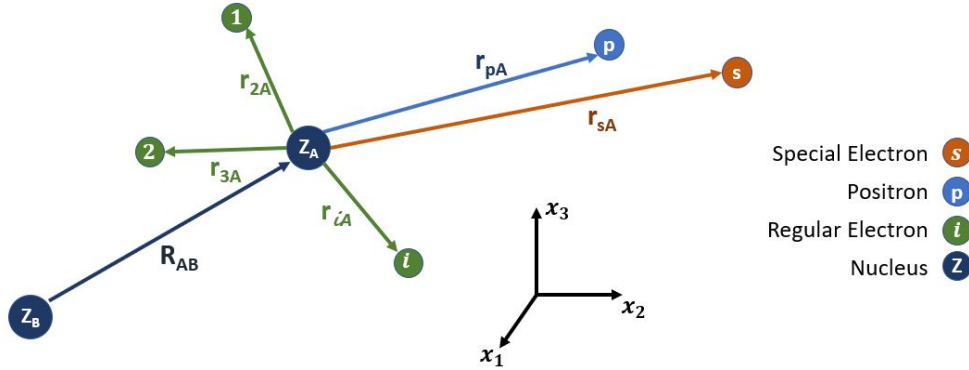
To reduce the complexity of the system described by the Hamiltonian in Equation (5) we make utilization of the Born Oppenheimer approximation. Since the nuclei are much heavier and move more slowly than electrons one can consider the electrons in a molecule to be moving in the field of fixed nuclei. Given this approximation the kinetic energy of the nuclei is neglected (reducing nuclei to fixed point charges) and the repulsion between the nuclei is considered a constant that can be added later as desired as it does not effect the Hamiltonian operator eigenfunctions. The remaining terms form Equation (5) are called the electronic Hamiltonian as they describe the motion of  $N_e$  electrons in the field of  $N_N$  point charges.

$$\mathcal{H} = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}} \quad (6)$$

### The Positronic-Electronic Hamiltonian.

Introducing a positron to the system described by the Hamiltonian in Equation (6) adds a kinetic energy term for the positron as well as Columbic repulsion and attraction with the point charges (nuclei) and electrons respectively. Letting  $\mathbf{r}_p$  be the position vector for the positron, distances between the positron and other particles are denoted by: the positron to the  $i^{\text{th}}$  electron  $r_{pi} = |\mathbf{r}_p - \mathbf{r}_i|$  and the positron to the  $A^{\text{th}}$  nucleus  $r_{pA} = |\mathbf{r}_p - \mathbf{R}_A|$ . Figure 4 shows a coordinate system for the positron interacting with the molecule. The Hamiltonian for this positronic-electronic system is now

$$\mathcal{H} = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \frac{1}{2} \nabla_p^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}} - \sum_{A=1}^{N_N} \frac{Z_A}{r_{pA}} - \sum_{i=1}^{N_e} \frac{1}{r_{pi}}. \quad (7)$$



**Figure 4.** A molecular coordinate system:  $s$  = special electron;  $p$  = positron;  $1, 2, i$  = electrons;  $A, B$  = nuclei.

Within the system described by Equation (7) there are four primary channels considered in the coming sections. Two of these are bound states (positron stays in the vicinity of the molecule) and two are not bound.

## The Unbound Positron.

If the positron is not bound to the molecular system described by Equation (6) then it will be assumed to have moved away from the system. The most obvious way for this to occur is that the positron moves away from the molecular system as a lone positron. The second channel to be discussed is that the positron interacts with the molecule and combines with a valence electron to form Ps. The Ps does not form a strong bond with the ionized molecule and the positron-electron pair move away from the ionized molecule.

1. Considering first the outcome of the positron moving away from the molecular system. As the positron moves further away, the distances  $r_{pi}$  and  $r_{pA}$ , for all  $i = 1, \dots, N_3$  and  $A = 1, \dots, N_N$ , increase causing a decrease in the columbic interaction with the molecule so that Equation (7) becomes

$$\mathcal{H}_{\text{non-interacting}}^{e^+M} = \underbrace{-\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}}}_{\text{molecule}} \underbrace{-\frac{1}{2} \nabla_p^2}_{\text{Positron}} \quad (8)$$

Here the terms that include Columbic interaction between the positron and molecule have been left out with the assumption that they have been reduced to near zero.

2. Next consider the possibility of the positron being attracted close enough to the molecule to form a bond, Ps, with one of the valence electrons in the molecule. For this consideration, the resulting Ps does not bind to the molecule but moves increasingly farther from the now ionized molecule. The outcome of this con-

sideration is a Hamiltonian of the form

$$\mathcal{H}_{\text{non-interacting}}^{PsM^+} = \underbrace{-\sum_{i=1}^{N_e-1} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e-1} \sum_{j>i}^{N_e-1} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e-1} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}}}_{\text{ionized molecule}} \underbrace{-\frac{1}{2} \nabla_s^2 - \frac{1}{2} \nabla_p^2 - \frac{1}{r_{ps}}}_{\text{Ps}} \quad (9)$$

The electron that formed Ps with the positron has been denoted by  $s$ , to identify it as separate or “special” from the other electrons. This electron will be referred to as the special electron versus the regular electrons that remain with the ionized molecule. The kinetic energy and Columbic interaction term involving the special electron have been changed to reflect the change in notation. This equation shows the two non-interacting systems: the ionized molecule and the Ps atom. The terms involving either the positron or special electron with the regular electron and the nuclei have been removed under the assumption that the distances  $r_{si}$  and  $r_{sA}$  have increased enough so as to decrease the Columbic interaction between Ps and the ionized molecule to zero.

### The Bound Positron.

There are two case to be considered here. First, the positron is bound to the molecular system. Second, the positron forms Ps with a valence electron and the Ps is then bound to the ionized molecule.

1. In the first case, valence electrons are held tightly by the molecule, but the positron is bound by the polarized molecule. This is the case depicted in Figure 2 (a) for an atom, where the electron cloud becomes polarized and then is able to create polarization potential that keeps the positron within the vicinity of

the molecule. The Hamiltonian for this bound system is

$$\mathcal{H}_{\text{bound}}^{e^+M} = \underbrace{-\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}}}_{\text{molecule}} \underbrace{-\frac{1}{2} \nabla_p^2}_{\text{positron}} \underbrace{-\sum_{i=1}^{N_e} \frac{1}{r_{pi}} + \sum_{A=1}^{N_N} \frac{Z_A}{r_{pA}}}_{\text{molecule and positron Coulombic interaction}}. \quad (10)$$

In this writing of the Hamiltonian, no terms have been modified or removed from Equation (7). Using  $e^+$  for the positron and M for nomenclature representing the molecule, this system can be seen as the binding of the system  $e^+M$ .

2. The final case to consider involves the formation of a Ps cluster with the positron and a valence electron. The Ps then is bound to the ionized molecule to form a system that can be properly represented as  $\text{PsM}^+$ . The Hamiltonian for this system can be written as

$$\mathcal{H}_{\text{bound}}^{PsM^+} = \underbrace{-\sum_{i=1}^{N_e-1} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e-1} \sum_{j>i}^{N_e-1} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e-1} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}}}_{\text{ionized molecule}} \underbrace{-\frac{1}{2} \nabla_s^2 - \frac{1}{2} \nabla_p^2 - \frac{1}{r_{ps}}}_{\text{virtual Ps}} + \underbrace{\sum_{i=1}^{N_e-1} \left( \frac{1}{r_{si}} - \frac{1}{r_{pi}} \right) - \sum_{A=1}^{N_N} \left( \frac{Z_A}{r_{pA}} - \frac{Z_A}{r_{sA}} \right)}_{\text{ionized molecule and Ps Coulombic interaction}}. \quad (11)$$

Here the utilization of  $s$ , for the special electron has again been utilized to denote that a single electron has joined the positron to form the Ps cluster. This is the same Hamiltonian as given in Equation (7), the terms have merely been rearranged to emphasis the formation of a virtual Ps. Virtual Ps forms as a result of an electron tunneling or hopping between the molecule and the positron[22, 31] The formation of Ps where a molecular electron has (at least temporarily) joined the positron creates a covalent like bonding [3, 20, 22, 24].

The bound nature of a positron with a molecule has emerged as a mix or superposition of the two cases for which a positron can be bound to a molecule. In positronic beryllium the dominant configuration is to see the positron orbiting the polarized electron. Here beryllium has two electrons in its outer shell. Li on the other hand has only a single electron in its outer shell and will bond with a positron by predominantly forming virtual Ps. All positron bound systems though demonstrate a significant amount of Ps clustering, even those in which valence electrons are held tightly and the positron tends to orbit at a large radius [6, 39].

## NEO-Suite of Methods for Modeling Positron Systems

In this section, the underlying equations for NEO-HF, NEO-XCHF and NEO-RXCHF are briefly reviewed. This is beneficial since even though the CPEO approach is fundamentally different it has its origins with the techniques developed within NEO. Each of these methods are based off the Hamiltonian in Equation (7).

### NEO-HF.

In the NEO-HF method the wavefunction is the product of an electronic determinant and a positronic orbital [1, 2, 86].

$$\Psi^{\text{NEO-HF}}(\mathbf{x}_1^e, \dots, \mathbf{x}_N^E, \mathbf{x}^p) = \Phi^e(\mathbf{x}_1^e \dots \mathbf{x}_N^E) \chi(\mathbf{x}^p) \quad (12)$$

where  $\mathbf{x}^e$  and  $\mathbf{x}^p$  denote spin coordinates for the electrons and positron respectively,  $\Phi^e$  is a Slater determinant and  $\chi^p$  is the positron orbital. Due to the lack of electron-positron correlation in the NEO-HF method it was not adequate for describing positronic systems.

## NEO-XCHF.

In the NEO-XCHF approach a mixed positron-electron ansatz for the wavefunction is developed that includes explicit dependence on positron-electron distances using Gaussian-type geminal (GTG) functions. The ansatz for the positron-electronic wavefunction is [12]

$$\Psi^{\text{NEO-XCHF}}(\mathbf{x}_1^e, \dots, \mathbf{x}_N^E, \mathbf{x}^p) = \Phi^e(\mathbf{x}_1^e \dots \mathbf{x}_N^E) \chi(\mathbf{x}^p) (1 + \hat{G}) \quad (13)$$

where  $\hat{G}$  is the geminal operator composed of the following GTG function

$$\hat{G} = \sum_i^{N_e} g(i) \quad (14)$$

where

$$g(i) = \sum_k^{N_{\text{gem}}} b_k e^{-\gamma_k |\mathbf{r}_i^e - \mathbf{r}^p|^2} \quad (15)$$

with values for  $b_k$  and  $\gamma_k$  as parameters that remain fixed during the variational procedure. Explicit correlation between the electron and positron is done via the GTG by incorporating an electron-positron distance dependence into the wavefunction. Therefore, the total wavefunction for NEO-XCHF method is antisymmetric with respect to the interchange of any two electrons and will include some Coulomb correlation between the electron and positron into the mean field approximation for optimization of the wavefunction.

## NEO-RXCHF.

In the NEO-XCHF approach each of the electronic orbitals were correlated with the positronic orbital. In a reduced version of this approach, NEO-RXCHF only a



subset of the electronic orbitals are explicitly correlated with the positron orbital [77, 78]

$$\Psi^{\text{RXCHF-fe}}(\mathbf{x}_1^e, \dots, \mathbf{x}_N^E, \mathbf{x}^p) = \frac{\chi^p(\mathbf{x}^p)}{\sqrt{(N_e)!}} \begin{vmatrix} \chi_1^e(\mathbf{x}_1^e)g(\mathbf{r}_1^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_1^e) & \dots & \chi_{N_e}^e(\mathbf{x}_1^e) \\ \chi_1^e(\mathbf{x}_2^e)g(\mathbf{r}_2^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_2^e) & \dots & \chi_{N_e}^e(\mathbf{x}_2^e) \\ \vdots & \ddots & \ddots & \vdots \\ \chi_1^e(\mathbf{x}_{N_e}^e)g(\mathbf{r}^e, \mathbf{r}^p) & \chi_2^e(\mathbf{x}_{N_e}^e) & \dots & \chi_{N_e}^e(\mathbf{x}_{N_e}^e) \end{vmatrix}. \quad (16)$$

In this ansatz, only one electronic spin orbital is geminal-coupled to the positron spin orbital. This ansatz is denoted RXCHF-fe to emphasize that this approach contains full exchange with the electrons as the wavefunction is fully antisymmetric.

An approximation to the RXCHF-fe ansatz is given by

$$\Psi^{\text{RXCHF-ne}}(\mathbf{x}_1^e, \dots, \mathbf{x}_N^E, \mathbf{x}^p) = \frac{\chi^p(\mathbf{x}^p)\chi_1^e(\mathbf{x}_1^e)g(\mathbf{r}_1^e, \mathbf{r}^p)}{\sqrt{(N_e - 1)!}} \begin{vmatrix} \chi_2^e(\mathbf{x}_2^e) & \dots & \chi_{N_e}^e(\mathbf{x}_1^e) \\ \vdots & \ddots & \vdots \\ \chi_2^e(\mathbf{x}_N^e) & \dots & \chi_N^e(\mathbf{x}_N^e) \end{vmatrix}. \quad (17)$$

(18)

Here the positron orbital is geminal-coupled to a single electron spin orbital as in RXCHF-fe, however, with the distinguishing of one electron from the others the wavefunction is no longer fully antisymmetric. This results in a loss of Fermi correlation amongst the electronic wavefunction optimization but considerable reduction in computational costs as the number of electrons is increased. It should be emphasized that the other  $N_e - 1$  electrons maintain Fermi-correlation and are antisymmetric with respect to interchange of any two of these electrons.

## A Mean-Field Model for Virtual Ps - CPEO

In this section, the ansatz that is used for the CPEO method is introduced. As with the NEO-suite of methods this technique utilizes the Hamiltonian from Equation (7).

$$\mathcal{H} = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \frac{1}{2} \nabla_p^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}} - \sum_{A=1}^{N_N} \frac{Z_A}{r_{pA}} - \sum_{i=1}^{N_e} \frac{1}{r_{pi}} \quad (19)$$

The motivation for the CPEO method was to capture the effects of the formation of virtual Ps in the vicinity of a molecule when there is a bound positron. In order to do this a Ps orbital,  $\chi^g(\mathbf{x}^p, \mathbf{x}_s^e)$  is introduced that is a function of both electron and positron coordinates. The ansatz for the CPEO method is given by

$$\Psi^{\text{CPEO}}(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e, \mathbf{x}^p, \mathbf{x}_s^e) = \frac{\chi^p(\mathbf{x}^p) \chi^g(\mathbf{x}^p, \mathbf{x}_s^e)}{\sqrt{(N_r)!}} \begin{vmatrix} \chi_1^e(\mathbf{x}_1^e) & \dots & \chi_{N_e}^e(\mathbf{x}_1^e) \\ \vdots & \ddots & \vdots \\ \chi_1^e(\mathbf{x}_{N_r}^e) & \dots & \chi_N^e(\mathbf{x}_{N_r}^e) \end{vmatrix} \quad (20)$$

$$= \chi^p(\mathbf{x}^p) \chi^g(\mathbf{x}^p, \mathbf{x}_s^e) \Phi^e(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e) \quad (21)$$

$$= \chi^p \chi^g \Phi^e \quad (22)$$

Here the subscript  $s$  has been adopted to designate a single or “special” electron that can be considered as bound to the positron in the formation of virtual Ps; there are  $N_r$  regular electrons designated by numerical subscripts where  $N_r = N_e - 1$ ,  $\chi^p \equiv \chi^p(\mathbf{x}^p)$ ,  $\chi^g \equiv \chi^g(\mathbf{x}^p, \mathbf{x}_s^e)$  and  $\Phi^e \equiv \Phi^e(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e)$ ; and  $\Phi^e$  is a fully antisymmetric single determinant wavefunction. Just as with RXCHF-ne there is an electron that is not antisymmetric with the regular electrons. This approach could aptly be referred to as CPEO-ne.

The qualitative cost of the singling out an electron as the special electron is the loss

of Fermi correlation with the other electrons. Even with a complete basis set this loss in correlation can not be recovered. To proceed without breaking the antisymmetry of the electronic system in a reduced-exchange setting, the Fock operators for the all the regular electrons would not be identical leading to nonstandard density matrices being introduced to solve the HF equation separately. [78]

What is gained with this ansatz is explicit correlation between the positron and a special electron that can be variationally optimized in a mean field approach to solving the Schrödinger equation with the Hamiltonian in Equation (19). The CPEO Ansatz has computational tractability that is on par with the RXCHF method.

The division of the wavefunction according to the CPEO ansatz in Equation (22) can be effectively viewed as breaking it into an electronic part for the regular electrons,  $\Phi^e$ ; a virtual Ps piece for the positron and the special electron,  $\chi^g$ ; and a translational motion of the virtual Ps relative to the fixed nuclei of the ionized molecule within the regular electron cloud. As will be derived, each part of the wavefunction will have a mean field single orbital representation of the Hamiltonian. The resulting three coupled Hamiltonians will be used to minimize the energy for the system. Each step in the optimization utilizes the mean values produced in the previous iteration by each of the single orbital Hamiltonians.

## IV. More Preliminary Concepts

### The Self Consistent Field (SCF) Process

The Hartree-Fock equations are obtained by minimizing the energy expression for a single determinant using functional variation. The development of the Hartree-Fock equations using functional variation follows closely the process laid out in Szabo [87] for the electronic system. This is done in Chapter VI for the CPEO method. This section is an overview of the approximation method to the differential Hartree-Fock equations using a linear expansion in a basis set.

Upon derivation of the Fock operator  $f$  for a system of  $N$  electrons approximated by a single determinant, the Hartree-Fock equation has the form

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \varepsilon_i\chi_i(\mathbf{x}_1) \quad (23)$$

The  $N$  electron system leads to this single one-electron equation for which each orbital in the determinant is a solution. The orbitals are now expanded in  $K$  spatial basis functions.

$$\chi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu} \quad i = 1, 2, \dots, K \quad (24)$$

This transforms the Hartree-Fock equations into the Roothan equations.

$$f(\mathbf{x}_1) \sum_{\nu} C_{\nu i} \phi_{\nu}(\mathbf{x}_1) = \varepsilon_i \sum_{\nu} C_{\nu i} \phi_{\nu}(\mathbf{x}_1) \quad (25)$$

Then left multiplying by  $\chi_{\mu}^*(\mathbf{x}_1)$  and integrating yields a matrix equation

$$\sum_{\nu} C_{\nu i} \int \phi_{\mu}^*(\mathbf{x}_1) f(\mathbf{x}_1) \phi_{\nu}(\mathbf{x}_1) = \varepsilon_i \sum_{\nu} C_{\nu i} \int \phi_{\mu}^*(\mathbf{x}_1) \phi_{\nu}(\mathbf{x}_1) \quad (26)$$

This can be simplified by be simplified by introducing the matrix element notation

$$S_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{x}_1) \phi_{\nu}(\mathbf{x}_1) \quad (27)$$

$$F_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{x}_1) f(\mathbf{x}_1) \phi_{\nu}(\mathbf{x}_1). \quad (28)$$

Now the Hartree-Fock Roothan equations can be written in matrix form as

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad (29)$$

or even more simply as matrices

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon \quad (30)$$

where  $\varepsilon$  is a diagonal matrix of the orbital energies  $\varepsilon_i$ . In solving this equation a unitary transformation is done to an orthogonal basis to make  $\mathbf{S}$  go to unity. In the transformed basis the solution comes by the diagonalization of  $\mathbf{F}$ . Since  $\mathbf{F}$  depends on its own solution, the process must be done iteratively. The iterative process on the Hartree-Fock Roothan equations is often called the Self-Consistent Field (SCF) procedure.

## The Density Matrix

Given a wavefunction  $\psi(\mathbf{r})$ , the total charge density for the  $N$  particles in the system is given by

$$\rho(\mathbf{r}) = \sum_{a=1}^N |\chi_a|^2 \quad (31)$$

This equation gives the total charge density as a sum of the charge densities for each of the electrons. Using the orbital expansions from equation (24) the charge density can be approximated using the basis functions.

$$\begin{aligned}
\rho(\mathbf{r}) &= \sum_a^N \chi_a^*(\mathbf{r}) \chi_a(\mathbf{r}) \\
&= \sum_a^N \sum_\nu^K C_{\nu a}^* \phi_{\nu a}^*(\mathbf{r}) \sum_\mu^K C_{\mu a} \phi_\mu(\mathbf{r}) \\
&= \sum_{\mu\nu} \left[ \sum_a^N C_{\nu a}^* C_{\mu a} \right] \phi_\mu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) \\
&= \sum_{\mu\nu} P_{\mu\nu} \phi_\mu^*(\mathbf{r}) \phi_\mu(\mathbf{r}) \tag{32}
\end{aligned}$$

The entries in the density matrix is defined as

$$P_{\mu\nu} = \sum_a^N C_{\nu a}^* C_{\mu a}. \tag{33}$$

In the case of Restricted Hartree Fock (RHF) where all orbitals are doubly occupied the density matrix has the form

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\nu a}^* C_{\mu a}. \tag{34}$$

The density matrix,  $\mathbf{P}$  is completely specifies the charge density given the set of basis functions  $\{\phi_\mu\}$ .

## Linear Expansion of Spatial Orbitals

In Chapters V and VI the Hartree-Fock theory and equations are derived for the modeling of Ps and virtual Ps. Involved in these equations are the requirement for the computation of various energy integrals. In order to facilitate the computation of

these integrals a finite-basis expansion is used. This chapter is focused on the type of basis functions that are used for the evaluation of the integrals.

The usage of the term “orbital” in quantum chemistry has both a strict meaning and a common use meaning. “Strictly speaking: An orbital is any solution of a one-particle Shrödinger equation. But usage is much more diffuse and ‘orbital’ has come to mean: An Orbital is any normalisable function of three-dimensional space.” [16] To this end this research will endeavor to refer to basis functions as the normalisable function of three-dimensional space that are used for the derivation of the required integrals. The targeted orbital is the solution of the electrons/positron in the spatial coordinates of the spatial orbital. This would be the full solution found if the basis functions were complete. Listed here are some constraints to selecting adequate basis functions [16, 58, 87].

1. The basis functions should be the same type of variables as the targeted orbitals;
2. The basis functions should be functions of three-dimensional vectors in space.
3. Basis function boundary conditions should be the same as the targeted orbitals. Asymptotic behavior of the basis functions should match the asymptotic behavior of the targeted orbitals.
4. Basis functions must be sufficiently smooth so as to be at least twice differentiable almost everywhere (that is excluding only a countable number of points).
5. Basis functions should have some known completeness properties. Since mathematical completeness of the basis function is impractical the basis functions need approach spanning the space of the targeted orbital.

Given that we have a solution to the Shrödinger equation for Hydrogen atom, an intuitive approach is to use these solutions as the basis set for larger systems. This approach clearly meets the conditions enumerated above.

### The Basis Functions of convenience.

Here we make the assumption that hydrogenic atomic orbitals (AOs) are at least qualitatively similar to the orbitals of more complex structures and proceed to develop a basis set. The AOs of the hydrogen atom have the form

$$\chi(r, \theta, \phi) = (\text{polynomial in } r) \times \text{function of } (\theta, \phi) \times \exp(-\alpha r) \quad (35)$$

in polar coordinates  $(r, \theta, \phi)$  centered on the origin. In Cartesian coordinates the hydrogen AO can be written

$$\chi(x, y, z) = (\text{polynomial in } x, y, z) \times \exp(-\alpha r). \quad (36)$$

Basis functions that have this form are “capable of giving a good description of the electron distribution and energies of atoms.”[16] These functions are universally known as Slater-Type Orbitals (STOs). STOs have a natural attractiveness as STOs match the natural shape of the AO.

The natural attractiveness of STOs is quickly countered by the difficulties associated with computing the various integrals required in atomic and molecular calculations. To counter this we turn to the solution of Schrödinger equation solution to the simple harmonic oscillator, Gaussian-Type Functions (GTFs). GTFs in Cartesian coordinates, centered on the origin, have the form

$$\chi(x, y, z) = (\text{polynomial in } x, y, z) \times \exp(-\alpha r^2) \quad (37)$$

GTFs meet the following conditions to be efficient basis functions

1. Integrals can be evaluated analytically in terms of standard functions after separation into products of integrals of single variables.



2. Similar to STOs they can be chosen to be centered on each atom.
3. GTFs have the correct asymptotic behavior for large  $r$ .

A good way to sum up the penalty paid for these benefits was done by Cook in his “Handbook of Computational Quantum Chemistry:” [16]

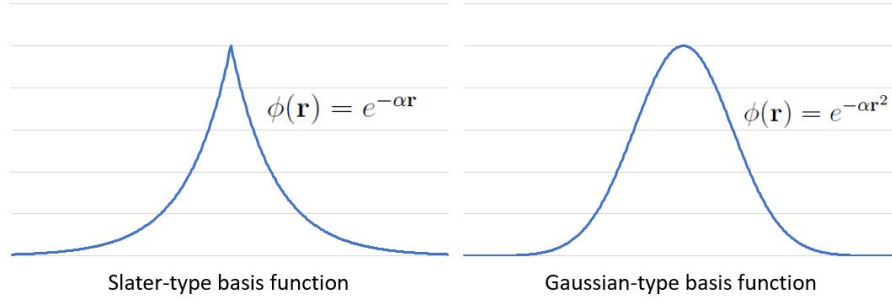
Electrons and nuclei interact with each other via Coulomb’s law not via Hooke’s law and so the expansion of a function dominated by electrostatic interaction in terms of functions well adapted to the description of particles connected together by springs might well be a lengthy one.

True to his quote, the result is that a larger number of GTFs is necessary to create similar accuracy in the solution.

The GTF general form is identical to the form for the STO. The difference is in the exponential factor. Some of the artifacts of this can be seen in Figure 5, where the shape of the STO has a sharp cusp, but for the GTF shape is flat near where the GTF is centered. In addition to this, the GTF vanishes to zero to quickly as  $r$  increases. To compensate for this what is known as primitive Gaussians (a single GTF) can be grouped together in linear combinations to create a more STO-like AO. The linear combination of primitive Gaussian functions is called a contracted Gaussian function. Although more functions and more integrals now are part of the calculation, the integrals involving Gaussian functions are quicker to compute than those involving exponentials.

### **Basis Function Selection.**

In the research presented here there are three types of orbitals that will be represented using basis functions. These these orbitals are  $\psi_i^e$ ,  $\psi^p$  and  $\psi^g$ . Here  $\psi_i^e$  is the orbital for the  $i^{\text{th}}$  regular electron.  $\psi^p$  is the orbital for the positron.  $\psi^g$  is the geminal orbital for the Ps (positron and special electron).



**Figure 5. Radial dependence on Slater and Gaussian basis functions.**

The standard primitive Gaussians are used to form the basis functions for  $\psi_i^e$  and  $\psi^p$ . These have the Cartesian form

$$\phi_i(x, y, z) = x_A^{\ell_i} y_A^{m_i} z_A^{n_i} e^{-\alpha r_A^2} \quad (38)$$

$$= (x_A^{\ell_i} e^{-\alpha x_A^2}) (y_A^{m_i} e^{-\alpha y_A^2}) (z_A^{n_i} e^{-\alpha z_A^2}) \quad (39)$$

where the GTF is centered on a nucleus located at  $A$  so that

$$x_A = x - A_x \quad (40)$$

$$y_A = y - A_y \quad (41)$$

$$z_A = z - A_z \quad (42)$$

This type of primitive as given in Equation (39) is given by the total angular momentum quantum number

$$t = \ell_i + m_i + n_i \quad (43)$$

where

- $t = 0$  provides an s-type Gaussian or zeroth-order Gaussian.
- $t = 1$  provides a p-type Gaussian or first-order Gaussian.

- $t = 2$  provides an d-type Gaussian or second-order Gaussian.
- $t = 3$  provides an f-type Gaussian or third-order Gaussian.

In implementation  $\psi^p$  only uses Gaussian primitives as basis functions, but  $\psi_i^e$  for the electrons have the added benefit of allowing contracted Gaussian primitives as basis sets.

The geminal orbital for Ps,  $\psi^g$ , is a primitive Gaussian of S-type orbitals where  $\ell_i$ ,  $m_i$  and  $n_i$  are all set equal to zero. An additional key difference is that the geminal Gaussian function is centered between the special electron and the positron.

$$\phi_i(x, y, z) = e^{-\alpha(r_s^e - r^p)^2_A} \quad (44)$$

$$= (e^{-\alpha(x_s^e - x^p)^2})(e^{-\alpha(y_s^e - y^p)^2})(e^{-\alpha(z_s^e - z^p)^2}) \quad (45)$$

Where superscript  $e$  and  $p$  are for the electron and positron respectively and the subscript  $s$  designates the special electron described in Chapter III as interacting with the positron to form Ps.

## Annihilation

With the formation of virtual Ps in the binding of a positron to a molecule it becomes important to study and understand the properties of Ps. First among these is the annihilation rate of the matter anti-matter molecule. While on an atomic scale the lifetime of Ps is long enough to allow for Ps to interact with the ionized molecule it is of interest to understand how long the Ps will exist. To properly understand annihilation rate this section looks at the wavefunction of Ps and its spin. This is one of the few sections where other than atomic units are used since annihilation is measured and given in SI units.

### Ps: Total Spin.

The wave function for non-relativistic Ps spatial wavefunction is given in Appendix A Equation (365) and is repeated here.

$$\Psi_{n,\ell,m_\ell}(r, \theta, \phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta, \phi) \quad (46)$$

Where the definitions for  $R_{n,\ell}(r)$  and  $Y_\ell^{m_\ell}(\theta, \phi)$  are provided in Equations (369) and (370). The inputs  $r$ ,  $\theta$ , and  $\phi$  come from the Cartesian coordinate transformation of the vector  $\mathbf{r}$  to spherical coordinates.  $\mathbf{r}$  is the vector from the positron to the electron as defined in equation (342) and shown in Figure 15 The full wavefunction for Ps with spin can be written as

$$\Psi_{n,\ell,m_\ell}^{Ps}(\mathbf{r})\chi_{S,M_S}(\sigma) \quad (47)$$

where  $S$  and  $M_S$  are the Ps spin numbers.  $S$  being the total spin and  $M_S$  the projection onto the  $z$ -axis.

$S$  and  $M_S$  come from the individual spins of the electron and positron. Here the spin (both electron and positron) is either up ( $|\uparrow\rangle$ , or  $m_s = \frac{1}{2}$ ) or down ( $|\downarrow\rangle$ , or  $m_s = -\frac{1}{2}$ ). The possible states for Ps spin then are

$$\chi_{0,0} = \frac{1}{\sqrt{2}} \left( |\uparrow_e\rangle |\downarrow_p\rangle - |\downarrow_e\rangle |\uparrow_p\rangle \right) \quad (48)$$

$$\chi_{1,0} = \frac{1}{\sqrt{2}} \left( |\uparrow_e\rangle |\downarrow_p\rangle + |\downarrow_e\rangle |\uparrow_p\rangle \right) \quad (49)$$

$$\chi_{1,1} = |\uparrow_e\rangle |\uparrow_p\rangle \quad (50)$$

$$\chi_{1,-1} = |\downarrow_e\rangle |\downarrow_p\rangle \quad (51)$$

The coupling of the two spin vectors for the electron and positron is done by adding

such that commutator relationships are kept for angular momentum. This process is shown in [25] or can be read from a table of Clebsh-Gordon coefficients.

From Equations (48) through (51) there are three states where the total spin  $S = 1$ ,  $\chi_{1,0}$ ,  $\chi_{1,1}$  and  $\chi_{1,-1}$ . The total spin of 1 is the triplet state called ortho-Ps. There is one state where the total spin is 0,  $\chi_{0,0}$ . This is therefore the singlet state and is called as para-Ps.

The ground state of Ps can be in either ortho-Ps or para-Ps. In para-Ps the spins are anti-parallel whilst in ortho-Ps the spins are parallel. Due to the selection rules of annihilation the ortho-Ps or anti-parallel state is prevented from the usual two-quanta ( $\gamma$ -ray) annihilation. [18, 47] The lower order annihilation of the parallel state or para-Ps is the two  $\gamma$ -ray annihilation which is a lower order process than the three  $\gamma$ -ray annihilation of ortho-Ps. [18]. The difference in the lifetime of ortho-Ps and para-Ps is that ortho-Ps is almost 1000 times longer (see Table 4). Given the difference in lifetimes the annihilation of Ps is dominated by the faster annihilation of the para-Ps.

	para-Ps	ortho-Ps
Dominant Decay Mode	2 $\gamma$ -rays	3 $\gamma$ -rays
Lifetime	0.125 ns	142 ns
Annihilation Rate	$8.0325 \times 10^{-9}$ sec	$138.67 \times 10^{-9}$ sec

**Table 4. Ground state properties of para-Ps and othro-Ps.**

### **Para-Ps Annihilation Rate.**

The main process which determines the lifetime of Ps is the two- $\gamma$  annihilation which as shown comes from para-Ps. Letting  $\lambda_0$  be the para-Ps decay probability (annihilation rate with total spin 0). where the annihilation rate is given by [18, 29,

47, 79]

$$\lambda_0 = 4 \left| \Psi_{gs}^{Ps}(r^p, r^e) \delta(r^e, r^p) \right|^2 (v \bar{\sigma}_{2\gamma})_{v \rightarrow 0}. \quad (52)$$

Where  $\Psi_{gs}$  is the wave function, normalized to unity, of the ground state of Ps.  $v$  is the ratio of the positron velocity to electron velocity and  $\bar{\sigma}_{2\gamma}$  is the cross section of a free electron-positron pair averaged over the spin directions of both particles and is given by

$$\bar{\sigma}_{2\gamma} = \pi r_0^2 \frac{c}{v}. \quad (53)$$

Where  $r_0 = e^2/m_e c^2$  is the classical radius of the electron with  $e$ -the elementary charge,  $m_e$ - the mass of the electron and  $c$ -the speed of light. The wave function in Equation (52) is evaluated for  $\mathbf{r}^p = \mathbf{r}^e$ , meaning that the electron and positron are at the same location. The annihilation rate from the combination of Equation (52) and (53) is

$$\lambda_0 = 4\pi r_0^2 c \left| \Psi_{gs}^{Ps}(r^p, r^e) \delta(r^e, r^p) \right|^2 \quad (54)$$

This is done for Ps by using Equation (46), see also Equation (380).

$$\Psi_{gs}^{Ps}(\mathbf{r}) = \Psi_{100}^{Ps}(\mathbf{r}) = \frac{1}{\sqrt{8\pi a^3}} e^{-r/a}, \quad a = \text{Bohr radius}. \quad (55)$$

Setting  $\mathbf{r} = 0$  ( $\mathbf{r} = \mathbf{r}^p - \mathbf{r}^e$ ) then

$$\Psi_{100}^{Ps}(0) = \frac{1}{\sqrt{8\pi a^3}}. \quad (56)$$

Putting this together the annihilation rate for para-Ps is given by

$$\lambda_0 = 4\pi r_0^2 c \frac{1}{8\pi a^3} \quad (57)$$

$$= \frac{r_0^2 c}{2a^3} \quad (58)$$

$$= 8.0325 \times 10^9 \text{ sec}^{-1} \quad (59)$$

The parameters in this equation are in SI units and not atomic units.

### General 2-Photon Annihilation Rate.

The general form for the annihilation rate for a ground state wave function,  $\Psi_0$ , consisting of  $N_e$  electrons and one positron follows the same form as Equation (54). This is given by [31, 85]

$$\lambda_0 = 4\pi r_0^2 c \frac{\left\langle \Psi_0 \left| \sum_{i=1}^{N_e} \delta(\mathbf{r}_i^e - \mathbf{r}^p) \hat{\mathbf{O}}_{i,p}^S \right| \Psi_0 \right\rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (60)$$

Where the integration of the brackets is over all electrons and the positron; and

$$\hat{\mathbf{O}}_{i,p}^s = \left( 1 - \frac{1}{2} S_{i,p}^2 \right). \quad (61)$$

Here  $S$  is the total spin of the  $i^{\text{th}}$  electron and positron. The spin addition works in the same manner described for Ps in Equations (48) through (51). The total spin for the two photon annihilation is zero so Equation (60) reduces to

$$\lambda_{2\gamma} = 4\pi r_0^2 c \frac{\left\langle \Psi_0 \left| \sum_{i=1}^{N_e} \delta(\mathbf{r}_i^e - \mathbf{r}^p) \right| \Psi_0 \right\rangle}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (62)$$

Here  $\lambda_0$  has been replaced with the  $\lambda_{2\gamma}$  to emphasize that the lowest energy annihilation occurs with the release of two photons.



## V. Modeling Ps with an explicitly Correlated Orbital

In this chapter a Hartree-Fock like model for Ps is developed. The Hamiltonian for Ps is developed from the Hamiltonian posed for CPEO in Equation (19). Then removing all of the electrons except one and removing all the nuclear centers. What remain is the Hamiltonian for PS.

$$\mathcal{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{2}\nabla_p^2 - \frac{1}{\mathbf{r}_{ep}} \quad (63)$$

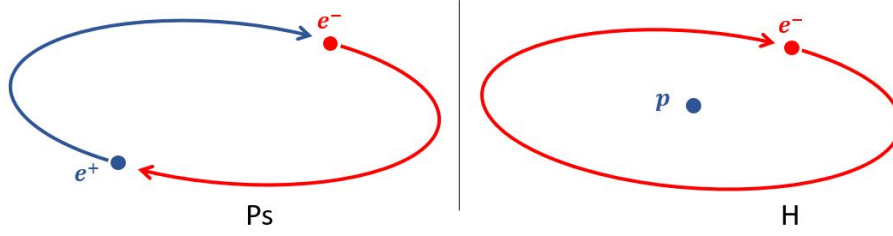
Capturing the electron-positron correlation in Ps will work very similarly as in a model for virtual Ps as discussed in Chapter III. To do this the translational motion and intrinsic motion of the Ps need to be maintained. Since the Ps will not be influenced by any outside forces it is expected that the translational motion that minimizes the energy will be in the most diffuse state allowed by the basis functions provided. This is anomalous to the free particle described by a plane wave in introductory quantum textbooks.

Equation (63) can be slightly modified to include the possibility of modeling Hydrogen as well as Ps by allowing the mass of the positively charged particle to be other than 1 as follows

$$\mathcal{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{2m_p}\nabla_p^2 - \frac{1}{\mathbf{r}_{ep}}. \quad (64)$$

Here if  $m_p = 1$  the system is Ps, if  $m_p = 1837$  the system is H. As previously discussed, the Ps atom consists of an electron and a positron of equal mass orbiting their mutual center of mass, while the Hydrogen atom has an electron that orbits a nearly stationary proton as shown in Figure 6. Both atoms are neutral systems with

the single electron of charge  $-e$  and the positron or proton with a charge of  $+e$ .



**Figure 6.** The positronium atom on the left consists of an electron and a positron orbiting their mutual center of mass. A Hydrogen atom has an electron that orbits the center of mass for the system which is located very near the proton. While the picture depicts the motion of particles in a plane, the motion being considered is in three dimensions.

The two particle system, like H or Ps, are the only atomic system for which an exact solution to the time-independent Schrödinger equation exists. The solution is obtained by a transformation to an equivalent one body problem. The two particle system solution to the time independent Schrödinger equation can be found in Appendix A. The modeling results from this chapter are compared to the exact non-relativistic solutions obtained in Appendix A.

## Formalisms

This section is focused on developing approximate solutions of the non-relativistic time-independent Schrödinger equation

$$\mathcal{H} |\Phi\rangle = \mathcal{E} |\Phi\rangle \quad (65)$$

where  $\mathcal{H}$  is the Hamiltonian operator for the two-particle system given by Equation (64). The eigenfunction  $|\Phi\rangle$  is often called the wave function and the eigenvalue  $\mathcal{E}$  is the energy for the system. Figure 7 provides a coordinate system schematic for this two particle system.

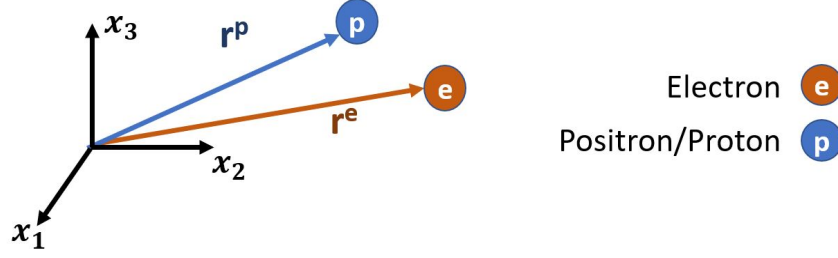


Figure 7. Coordinate System for the two particle atoms, hydrogen or positronium:  $\mathbf{r}^p$  and  $\mathbf{r}^e$  are the position vectors for the positron/proton and the electron respectively.

### Ansatz.

Traditionally an orbital is defined as a wave function for a single particle [87]. In doing this our wave function for the system described in Figure 7 would be a standard Hartree product. It is not necessary to use a Slater determinant here since the antisymmetry principle does not apply as there are no duplicate particles in this system.

$$\Psi^{\text{HP}}(\mathbf{x}^e, \mathbf{x}^p) = \chi^e(\mathbf{x}^e)\chi^p(\mathbf{x}^p) \quad (66)$$

$\chi^e$  and  $\chi^p$  are the spin orbitals for the spin coordinates  $\mathbf{x}^e$  and  $\mathbf{x}^p$  respectively. In this equation and for those that follow,  $\mathbf{x}^e$  and  $\mathbf{x}^p$  denote spin coordinates for the electron and positron/proton respectively. For more on the difference between spin coordinates ( $\mathbf{x}^e$  and  $\mathbf{x}^p$ ) and spatial coordinates ( $\mathbf{r}^e$  and  $\mathbf{r}^p$ ) see the section on notation in Chapter III. The Hartree Product though does not facilitate correlation between the two particles in the mean field approximation. To capture effects of correlation on the system a broader class of functions is needed to describe the motion. Consider the following ansatz.

$$\Psi^{\text{Ps}}(\mathbf{x}^e, \mathbf{x}^p) = \chi^p(\mathbf{x}^p)\chi^g(\mathbf{x}^p, \mathbf{x}^e) \quad (67)$$

Here,  $\chi^p$  is a traditional spin orbital of the positron, but  $\chi^g(\mathbf{x}^p, \mathbf{x}^e)$  is not a traditional orbital since it is a wavefunction for more than a single particle.  $\chi^g(\mathbf{x}^p, \mathbf{x}^e)$  can be thought of as the wave function for the Ps atom, that is the interaction/correlation of the positron and electron is captured in  $\chi^g$ .

Using the ansatz as described in Equation (67) has restricted the form for possible solutions that will be allowed. It is worth noting that the space of possible wavefuctions that compose  $\Psi^{\text{HP}}$  is a subspace of those spanned by  $\Psi^{\text{Ps}}$ . that is

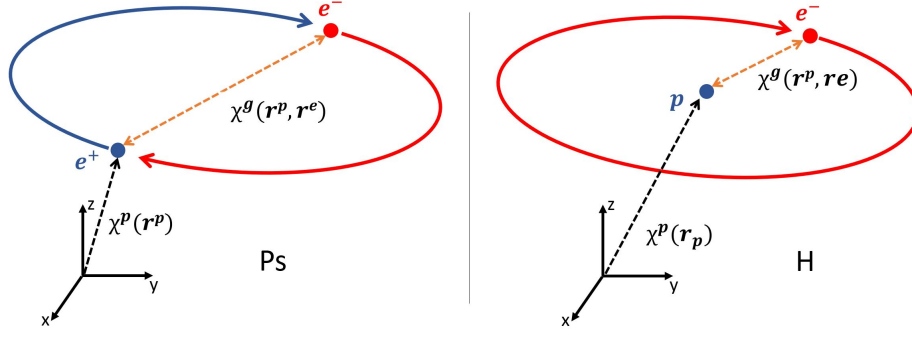
$$\{\chi^g(\mathbf{x}^e)\}_{\text{span}} \subset \{\chi^g(\mathbf{x}^p, \mathbf{x}^e)\}_{\text{span}} \quad (68)$$

In choosing to model this system according to the ansatz in Equation (67), the form of the solution has taken to a natural separation between the motion of the system and the intrinsic motion within the system. The motion of the two-particle system uses the positron as a reference particle using the spin orbital  $\chi^p$ . While the intrinsic motion of the system is captured using  $\chi^g$ . The relative nature of this representation for the two systems under consideration is shown in Figure 8. As is standard with representing wavefuctions using an orbital representation, it is assumed that  $\chi^p(\mathbf{x}^p)$  and  $\chi^g(\mathbf{x}^e, \mathbf{x}^p)$  are normalized so that

$$\langle \chi^p | \chi^p \rangle = 1 \quad (69)$$

$$\langle \chi^g | \chi^g \rangle = 1 \quad (70)$$

where  $\chi^p \equiv \chi^p(\mathbf{x}^p)$  and  $\chi^g \equiv \chi^g(\mathbf{x}^p, \mathbf{x}^e)$ .



**Figure 8.** Shows the relative nature of the basis functions used to represent the system.  $\chi^p(\mathbf{r}^p)$  provides an atomic orbital for the reference particle (the positron) for locating the 2-particle basis functions  $\chi^g(\mathbf{r}^p, \mathbf{r}^e)$ . The interaction of the two particles with each other is with in  $\chi^g(\mathbf{r}^p, \mathbf{r}^e)$ .

### Energy of the System.

Using  $\Psi^{\text{Ps}}$  as the space for possible solutions, the eigenvalue problem of Equation (65) is now

$$\mathcal{H} |\Psi^{\text{Ps}}\rangle = \mathcal{E} |\Psi^{\text{Ps}}\rangle. \quad (71)$$

The energies associated with the wavefunction in Equation (71) are defined as the expectation values of the Hamiltonian operator given in Equation (64) so that

$$\mathcal{E} = \frac{\langle \Psi^{\text{Ps}} | \mathcal{H} | \Psi^{\text{Ps}} \rangle}{\langle \Psi^{\text{Ps}} | \Psi^{\text{Ps}} \rangle} = \frac{1}{S^{\text{Ps}}} \langle \Psi^{\text{Ps}} | \mathcal{H} | \Psi^{\text{Ps}} \rangle \quad (72)$$

where  $S^{\text{Ps}}$  is the overlap integral and arises from the non-separable nature of the orbitals in  $\Psi^{\text{Ps}}$ .  $S^{\text{Ps}}$  is evaluated as

$$S^{\text{Ps}} \equiv \langle \Psi^{\text{Ps}} | \Psi^{\text{Ps}} \rangle \equiv \langle \chi^p \chi^g | \chi^p \chi^g \rangle \quad (73)$$

The energy contributions associated with the various parts of the Hamiltonian can also be expressed using the the orbitals  $\chi^p$  and  $\chi^g$ .

$$T_e = \frac{1}{S^{\text{Ps}}} \langle \chi^p \chi^g | -\frac{1}{2} \nabla_e^2 | \chi^p \chi^g \rangle \quad (74)$$

$$T_p = \frac{1}{S^{\text{Ps}}} \langle \chi^p \chi^g | -\frac{1}{2m_p} \nabla_p^2 | \chi^p \chi^g \rangle \quad (75)$$

$$V_{ep} = \frac{1}{S^{\text{Ps}}} \langle \chi^p \chi^g | -\frac{1}{\mathbf{r}_{ep}} | \chi^p \chi^g \rangle \quad (76)$$

so that

$$\mathcal{E} = T_e + T_p + V_{ep}. \quad (77)$$

## The Variation Principle

The goal is to find the solution to Equation (71) that minimizes the energy from Equation (72). This is done following the SCF process as outlined in Chapter IV. This minimum energy level is called the ground state and will be denoted  $\mathcal{E}_0$ . The eigenfunctions associated with  $\mathcal{E}_0$  are designated  $|\Psi_0^{\text{Ps}}\rangle$ . This section sets up the Lagrangian and takes the first variation of the Lagrangian with respect to each of the orbitals. According to the variational principle this leads us to the orbitals which will minimize the energy. The result is an integro-differential equation of the orbitals that minimize the energy. This equation is known as the Hartree-Fock equation. Since variation with respect to  $\chi^p$  is not equivalent to variation with respect to  $\chi^g$ ; the solution  $|\Psi_0^{\text{Ps}}\rangle$  requires a method that involves two coupled equations:

### The Lagrangian.

To derive the Fock operators used in finding  $|\Psi_0^{\text{Ps}}\rangle$ , the functional  $E_0[\chi^p, \chi^g]$  needs to be minimized with respect to each  $\chi^p$  and  $\chi^g$  subject to the constraint that the

spin orbitals remain normal,

$$\langle \chi^p | \chi^p \rangle = 1 \quad (78)$$

$$\langle \chi^g | \chi^g \rangle = 1 \quad (79)$$

Since there is only a single orbital for the positron,  $\chi^p$  is trivially orthogonal. The same applies to  $\chi^g$ . Therefore the Lagrangian to be considered is

$$\mathcal{L}[\chi^p, \chi^g] = E_0[\chi^p, \chi^g] - \varepsilon_p (\langle \chi^p | \chi^p \rangle - 1) - \varepsilon_g (\langle \chi^g | \chi^g \rangle - 1) \quad (80)$$

where  $E_0$  is the expectation value for  $|\Psi_0^{\text{Ps}}\rangle$

$$E_0[\chi^p, \chi^g] = \frac{1}{S^{\text{Ps}}} \langle \chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle \quad (81)$$

with  $S^{\text{Ps}}$  defined by Equation (73) and  $\varepsilon_p$  and  $\varepsilon_g$  are the Lagrange multipliers. Note that since energy is a physical property (an observable) of the Hamiltonian the Lagrange multipliers are real and

$$\varepsilon_p = \varepsilon_p^* \quad (82)$$

$$\varepsilon_g = \varepsilon_g^* \quad (83)$$

that is the Lagrange multipliers are Real valued numbers.

### **First Variation With Respect to $\chi^p$ While Holding $\chi^g$ Constant.**

The first step in obtaining the Fock operator for  $\chi_p$  is to take the first variation of  $\mathcal{L}$  with respect to  $\chi^p$  and set it equal to zero. To take the first variation with respect

to  $\chi^p$ , the  $\chi^p$  orbital is varied an arbitrary infinitesimal amount:

$$\chi^p \rightarrow \chi^p + \delta\chi^p \quad (84)$$

so that

$$\begin{aligned} \delta\mathcal{L} &= \delta E_0 - \delta\varepsilon_p (\langle \chi^p | \chi^p \rangle - 1) - \delta\varepsilon_g (\langle \chi^g | \chi^g \rangle - 1) \\ &= \delta \frac{1}{S^{\text{Ps}}} \langle \chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle - \delta\varepsilon_p \langle \chi^p | \chi^p \rangle \\ &= \frac{S^{\text{Ps}} \langle \delta\chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle - \langle \delta\chi^p \chi^g | \chi^p \chi^g \rangle \langle \chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle}{(S^{\text{Ps}})^2} - \varepsilon_p \langle \delta\chi^p | \chi^p \rangle \\ &\quad + \text{complex conjugate} \\ &= \frac{1}{S^{\text{Ps}}} \langle \delta\chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle - \frac{E_0}{S^{\text{Ps}}} \langle \delta\chi^p \chi^g | \chi^p \chi^g \rangle - \varepsilon_p \langle \delta\chi^p | \chi^p \rangle \\ &\quad + \text{complex conjugate} \\ &= \frac{1}{S^{\text{Ps}}} \int \int (\delta\chi^p)^* \chi^{g*} \mathcal{H} \chi^g \chi^p d\mathbf{x}^p d\mathbf{x}^e - \frac{E_0}{S^{\text{Ps}}} \int \int (\delta\chi^p)^* \chi^{g*} \chi^g \chi^p d\mathbf{x}^p d\mathbf{x}^e \\ &\quad - \varepsilon_p \int (\delta\chi^p)^* \chi^p d\mathbf{x}^p + \text{complex conjugate} \\ &= \int (\delta\chi^p)^* \left[ \frac{1}{S^{\text{Ps}}} \int \chi^{g*} \mathcal{H} \chi^g \chi^p d\mathbf{x}^e - \frac{E_0}{S^{\text{Ps}}} \int \chi^{g*} \chi^g \chi^p d\mathbf{x}^e - \varepsilon_p \chi^p \right] d\mathbf{x}^p \\ &\quad + \text{complex conjugate} \\ &= 0 \end{aligned} \quad (86)$$

The integrals  $\int f(\mathbf{x}^p) d\mathbf{x}^p$  and  $\int f(\mathbf{x}^e) d\mathbf{x}^e$  are integrals in  $\mathbb{R}^3$  and a spin dimension. The vanishing of  $\delta\mathcal{L}$  for an arbitrary variation on  $\delta\chi^p$  and  $(\delta\chi^p)^*$  is satisfied by the condition that the quantity in the square brackets in Equation (86) is equal to zero. Remembering that  $\chi^p$  is a function of only  $\mathbf{x}^p$  so that

$$\frac{1}{S^{\text{Ps}}} \int \chi^{g*} \mathcal{H} \chi^g d\mathbf{x}^e \chi^p - \frac{E_0}{S^{\text{Ps}}} \int \chi^{g*} \chi^g d\mathbf{x}^e \chi^p = \varepsilon_p \chi^p \quad (87)$$



Written as an eigenfunction Equation (87) is the integro-differential equation known as the Hartree-Fock equation.

$$f^p |\chi^p\rangle = \varepsilon_p |\chi^p\rangle \quad (88)$$

where

$$f^p = \frac{1}{S^{\text{Ps}}} \left[ \int \chi^{g*} \mathcal{H} \chi^g d\mathbf{x}^e - \mathcal{E}_0 \int \chi^{g*} \chi^g d\mathbf{x}^e \right] \quad (89)$$

is the Fock operator for the positron orbital  $\chi^p$ .

**First Variation With Respect to  $\chi^g$  while holding  $\chi^p$  constant.**

In similar fashion, the first variation with respect to  $\chi^g$  of  $\mathcal{L}$  is done by varying  $\chi^g$  by an arbitrary infinitesimal amount. That is,

$$\chi^g \rightarrow \chi^g + \delta\chi^g \quad (90)$$

so that

$$\begin{aligned}
\delta\mathcal{L} &= \delta E_0 - \varepsilon_g \delta \langle \chi^g | \chi^g \rangle \\
&= \frac{S^{\text{Ps}} \langle \chi^p \delta \chi^g | \mathcal{H} | \chi^p \chi^g \rangle - \langle \chi^p \delta \chi^g | \chi^p \chi^g \rangle \langle \chi^p \chi^g | \mathcal{H} | \chi^p \chi^g \rangle}{(S^{\text{Ps}})^2} - \varepsilon_g \langle \delta \chi^g | \chi^g \rangle \\
&\quad + \text{ complex conjugate} \\
&= \frac{1}{S^{\text{Ps}}} \langle \chi^p \delta \chi^g | \mathcal{H} | \chi^p \chi^g \rangle - \frac{E_0}{S^{\text{Ps}}} \langle \chi^p \delta \chi^g | \chi^p \chi^g \rangle - \varepsilon_g \langle \delta \chi^g | \chi^g \rangle \\
&\quad + \text{ complex conjugate} \\
&= \frac{1}{S^{\text{Ps}}} \int \int (\delta \chi^g)^* \chi^{p*} \mathcal{H} \chi^p \chi^g d\mathbf{x}^e d\mathbf{x}^p - \frac{E_0}{S^{\text{Ps}}} \int \int (\delta \chi^g)^* \chi^{p*} \mathcal{H} \chi^p \chi^g d\mathbf{x}^e d\mathbf{x}^p \\
&\quad - \varepsilon_g \int \int (\delta \chi^g)^* \chi^g d\mathbf{x}^e d\mathbf{x}^p + \text{ complex conjugate} \\
&= \frac{1}{S^{\text{Ps}}} \int (\delta \chi^g)^* \left[ \chi^{p*} \mathcal{H} \chi^p \chi^g - E_0 \chi^{p*} \chi^p \chi^g - \varepsilon_g \chi^g \right] d\mathbf{x}^e d\mathbf{x}^p \\
&\quad + \text{ complex conjugate} \\
&= 0
\end{aligned} \tag{91}$$

The vanishing of  $\delta\mathcal{L}$  for an arbitrary variation on  $\delta\chi^g$  and  $(\delta\chi^g)^*$  is satisfied by the condition that the quantity in the square brackets in Equation (91) is equal to zero.

That is

$$\frac{1}{S^{\text{Ps}}} \chi^{p*} \mathcal{H} \chi^p \chi^g - \frac{E_0}{S^{\text{Ps}}} \chi^{p*} \chi^p \chi^g = \varepsilon_g \chi^g. \tag{92}$$

Written as an eigenfunction Equation (92) becomes

$$f^g | \chi^g \rangle = \varepsilon_g | \chi^g \rangle \tag{93}$$

where

$$f^g = \frac{1}{S^{\text{Ps}}} [\chi^{p*} \mathcal{H} \chi^p - \mathcal{E}_0 \chi^{p*} \chi^p] \quad (94)$$

is the Fock operator for the positron-electron correlated orbital  $\chi^g$ .

### Spatial Orbitals.

In the previous section, the two coupled integro-differential equations are

$$f^p | \chi^p(\mathbf{x}^p) \rangle = \varepsilon_p | \chi^p(\mathbf{x}^p) \rangle \quad (95)$$

$$f^g | \chi^g(\mathbf{x}^e, \mathbf{x}^p) \rangle = \varepsilon_g | \chi^g(\mathbf{x}^e, \mathbf{x}^p) \rangle \quad (96)$$

These are both equations of spin orbitals. Spatial orbitals differ from spin orbitals when more than one identical orbital can occupy the same space (that is one with spin up and one with spin down). Since this does not occur in hydrogen or positronium the spatial Fock-operators have the same form as the spin operators. With spatial Hartree-Fock equations

$$f^p | \psi^p(\mathbf{r}^p) \rangle = \varepsilon_p | \psi^p(\mathbf{r}^p) \rangle \quad (97)$$

$$f^g | \psi^g(\mathbf{r}^e, \mathbf{r}^p) \rangle = \varepsilon_g | \psi^g(\mathbf{r}^e, \mathbf{r}^p) \rangle \quad (98)$$

where  $\varepsilon_p$  and  $\varepsilon_g$  are the energy of the spatial orbital which are identical to the energy associated with the spin orbitals of Equations (95) and (96).  $\psi^p$  and  $\psi^g$  are the spatial orbitals associated with  $\chi^p$  and  $\chi^g$  respectively.

$$f^p = \frac{1}{S^{\text{Ps}}} \left[ \int \psi^{g*} \mathcal{H} \psi^g d\mathbf{x}^e - \mathcal{E}_0 \int \psi^{g*} \psi^g d\mathbf{x}^e \right] \quad (99)$$

$$f^g = \frac{1}{S^{\text{Ps}}} [\psi^{p*} \mathcal{H} \psi^p - \mathcal{E}_0 \psi^{p*} \psi^p] \quad (100)$$

## The Roothan Equations

### Basis Sets for $\psi^p$ and $\psi^g$ .

By introducing basis sets for the spatial orbitals in the spatial integro-differential equations, Equations (97) and (98), can be converted to a set of algebraic equations and solved using standard matrix element techniques. To this end, the basis sets  $\{\phi_{\mu'}^p\}_{\mu'=1}^{K_p}$  and  $\{\phi_k^g\}_{k=1}^{K_g}$  are introduced and  $\psi^p$  and  $\psi^g$  become

$$\psi^p(\mathbf{r}^p) = \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p(\mathbf{r}^p) \quad (101)$$

$$\psi^g(\mathbf{r}^p, \mathbf{r}^e) = \sum_{k=1}^{K_g} C_k^g \phi_k^g(\mathbf{r}^p, \mathbf{r}^e) \quad (102)$$

and  $C_{\mu'}^p$  and  $C_k^g$  are (Real or Complex) constants. If the sets  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$  were complete then this would be an exact expansion of the spatial orbitals  $\psi^p$  and  $\psi^g$ . For practical computation reason, finite sets of  $K_p$  and  $K_g$  basis functions are used. If  $K_p$  and  $K_g$  were increased to make the sets  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$  larger then the expansions in Equations (101) and (102) would lead to an increasingly accurate representation of the spatial orbitals. Therefore the finite basis sets used in Equations (101) and (102) will not be the true eigenfunctions of the Fock operators, but will be exact in the spaces spanned by  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$ .

### Hartree-Fock Equations.

The problem of calculating the basis function coefficients  $C_{\mu'}^p$  and  $C_k^g$  that provide the minimal energy is now a matter of substituting the linear expansion of the orbitals,

Equation (101) and (102), into the Hartree-Fock equations, Equations (97) and (98),

$$f^p(\mathbf{r}^p) \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p(\mathbf{r}^p) = \varepsilon_p \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p(\mathbf{r}^p) \quad (103)$$

$$f^g(\mathbf{r}^p, \mathbf{r}^e) \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g(\mathbf{r}^p, \mathbf{r}^e) = \varepsilon_g \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g(\mathbf{r}^p, \mathbf{r}^e) \quad (104)$$

Multiplying Equation (103) on the left by  $\phi_k^{p*}(\mathbf{r}^p)$  and integrating over the  $\mathbf{r}^p$  the integro-differential equations is turned into a matrix equation.

$$\sum_{\nu'=1}^{K_p} C_{\nu'}^p \underbrace{\int (\phi_{\mu'}^p)^* f^p \phi_{\nu'}^p d\mathbf{r}^p}_{F_{\mu'\nu'}^p} = \varepsilon_p \sum_{\nu'=1}^{K_p} C_{\nu'}^p \underbrace{\int (\phi_{\mu'}^p)^* \phi_{\nu'}^p d\mathbf{r}^p}_{S_{\mu'\nu'}^p} \quad (105)$$

In the above equations the elements of the overlap matrix  $\mathbf{S}^p$  and the Fock matrix  $\mathbf{F}^p$  are introduced. These matrices are defined as follows.

1. The overlap matrix for the basis set  $\{\phi_{\mu'}^p\}$  is  $\mathbf{S}^p$  and has matrix elements

$$S_{\mu'\nu'}^p = \int (\phi_{\mu'}^p)^* \phi_{\nu'}^p d\mathbf{r}^p \quad (106)$$

$$= \langle \phi_{\mu'}^p | \phi_{\nu'}^p \rangle \quad (107)$$

$\mathbf{S}^p$  is a  $K_p \times K_p$  Hermitian matrix. The basis functions  $\{\phi_{\mu'}^p\}$  have been assumed to be normalized and linearly independent, but are in general are not orthogonal to each other which gives rise to the overlap matrix.

2. The Fock matrix  $\mathbf{F}^p$  has matrix elements

$$F_{\mu'\nu'}^p = \int (\phi_{\mu'}^p)^* f^p \phi_{\nu'}^p d\mathbf{r}^p \quad (108)$$

$$= \langle \phi_{\mu'}^p | f^p | \phi_{\nu'}^p \rangle \quad (109)$$

$\mathbf{F}^p$  is also a  $K_p \times K_p$  Hermitian matrix.  $\mathbf{F}^p$  is a matrix representation of the Fock operator  $f^p$  within the basis functions  $\{\phi_{\mu'}^p\}$ . Equation (109) only shows integration over the positron spatial coordinate, however, the Fock operator  $f^p$  involves integration over the electron spatial coordinates  $\mathbf{r}^e$  as well.

Similarly, multiplying Equation (104) by  $\phi_k^{g*}(\mathbf{r}^p, \mathbf{r}^e)$  on the left and then integrating over both spatial coordinates  $\mathbf{r}^p$  and  $\mathbf{r}^e$  the integro-differential equation is turned into a matrix equation.

$$\sum_{\ell=1}^{K_g} C_{\ell}^g \underbrace{\int (\phi_k^g)^* f^g \phi_{\ell}^g d\mathbf{r}^p d\mathbf{r}^e}_{F_{k\ell}^g} = \varepsilon_g \sum_{\ell=1}^{K_g} C_{\ell}^g \underbrace{\int (\phi_k^g)^* \phi_{\ell}^g d\mathbf{r}^p d\mathbf{r}^e}_{S_{k\ell}^g} \quad (110)$$

Here the elements of the overlap matrix  $\mathbf{S}^g$  and the Fock matrix  $\mathbf{F}^g$  are introduced. These matrices are defined as follows.

1. The overlap matrix for the basis set  $\{\phi_k^g\}$  is  $\mathbf{S}^g$  and has matrix elements

$$S_{k\ell}^g = \int (\phi_k^g)^* \phi_{\ell}^g d\mathbf{r}^p d\mathbf{r}^e \quad (111)$$

$$= \langle \phi_k^g | \phi_{\ell}^g \rangle \quad (112)$$

$\mathbf{S}^g$  is an  $K_g \times K_g$  Hermitian matrix. The basis functions  $\{\phi_k^g\}$  have been assumed to be normalized and linearly independent, but are in general are not orthogonal to each other giving rise to the overlap matrix.

2. The Fock matrix  $\mathbf{F}^g$  has matrix elements

$$F_{k\ell}^g = \int (\phi_k^g)^* f^g \phi_{\ell}^g d\mathbf{r}^p d\mathbf{r}^e \quad (113)$$

$$= \langle \phi_k^g | f^g | \phi_{\ell}^g \rangle \quad (114)$$

$\mathbf{F}^g$  is an  $K_g \times K_g$  Hermitian matrix.  $\mathbf{F}^g$  is a matrix representation of the Fock operator  $f^g$  within the basis functions  $\{\phi_k^g\}$ .  $\mathbf{F}^g$  directly depends on both spatial coordinates  $\mathbf{r}^p$  and  $\mathbf{r}^e$  as the correlation between these coordinates is contained in the basis functions  $\{\phi_k^g\}$ .

With these definitions for  $\mathbf{F}^p$ ,  $\mathbf{S}^p$ ,  $\mathbf{F}^g$  and  $\mathbf{S}^g$ ; the integrated Hartree-Fock equations (105) and (110) can be written as

$$\sum_{\nu} \mathbf{F}^p \mathbf{C}_{\nu j}^p = \varepsilon_{pj} \sum_{\nu} \mathbf{S}^p \mathbf{C}_{\nu j}^p \quad j = 1, 2, \dots, K_g \quad (115)$$

$$\sum_{\ell} \mathbf{F}^g \mathbf{C}_{\ell i}^g = \varepsilon_{gi} \sum_{\ell} \mathbf{S}^g \mathbf{C}_{\ell i}^g \quad i = 1, 2, \dots, K_p. \quad (116)$$

These equations are the Roothan equations and can be written more succinctly as two coupled matrix questions

$$\mathbf{F}^p \mathbf{C}^p = \mathbf{S}^p \mathbf{C}^p \boldsymbol{\varepsilon}_p \quad (117)$$

$$\mathbf{F}^g \mathbf{C}^g = \mathbf{S}^g \mathbf{C}^g \boldsymbol{\varepsilon}_g. \quad (118)$$

Where  $\mathbf{C}^p$  is a  $K_p \times K_p$  matrix of the expansion coefficients  $C_{\nu' i}^p$

$$\mathbf{C}^p = \begin{pmatrix} C_{11}^p & C_{12}^p & \dots & C_{1K_p}^p \\ C_{21}^p & C_{22}^p & \dots & C_{2K_p}^p \\ \vdots & \vdots & & \vdots \\ C_{K_p 1}^p & C_{K_p 2}^p & \dots & C_{K_p K_p}^p \end{pmatrix} \quad (119)$$

and  $\boldsymbol{\varepsilon}_p$  is a diagonal matrix of the orbital energies  $\varepsilon_{pi}$ ,

$$\boldsymbol{\epsilon}_p = \begin{pmatrix} \epsilon_{p1} & & & \\ & \epsilon_{p2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_{pK_p} \end{pmatrix}. \quad (120)$$

In similar fashion,  $\mathbf{C}^g$  is a  $K_g \times K_g$  matrix of the expansion coefficients  $C_{\ell j}$

$$\mathbf{C}^g = \begin{pmatrix} C_{11}^g & C_{12}^g & \cdots & C_{1K_g}^g \\ C_{21}^g & C_{22}^g & \cdots & C_{2K_g}^g \\ \vdots & \vdots & & \vdots \\ C_{K_g1}^g & C_{K_g2}^g & \cdots & C_{K_gK_g}^g \end{pmatrix} \quad (121)$$

and  $\boldsymbol{\epsilon}_g$  is a diagonal matrix of the orbital energies  $\epsilon_{gj}$ ,

$$\boldsymbol{\epsilon}_g = \begin{pmatrix} \epsilon_{g1} & & & \\ & \epsilon_{g2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_{gK_g} \end{pmatrix}. \quad (122)$$

The next subsections will further expand on the development of the elements of each Fock matrix. For general details on the orthogonalization of the basis sets (page 148) and the SCF procedure (page 151) see Appendix B. The next primary section in this chapter will discuss the specif algorithm as implemented in FORTRAN to solve to find wave function for this system.



### Density Matrices $\mathbf{P}^g$ and $\mathbf{P}^p$ .

Given that both  $\psi^g$  and  $\psi^p$  both have a single filled orbital, Equation (33) is used for determining the density matrix with  $N = 1$  for both expansions so that

$$P_{\mu'\nu'}^p = C_{\mu'1}^p C_{\nu'1}^p \quad (123)$$

$$P_{k,\ell}^g = C_{k1}^g C_{\ell1}^g \quad (124)$$

$\mathbf{P}^g$  and  $\mathbf{P}^p$  are the matrices formed and provide the thorough description of the best eigenfunctions for minimizing the energy at each step of the SCF procedure within the the space spanned by  $\{\phi_{\mu'}\}$  and  $\{\phi_k\}$  from Equations (101) and (102).

### Expression for the Fock Matrix.

The Fock matrix  $F^p$  is the matrix representation of the Fock Operator

$$f^p \equiv \frac{1}{S^{\text{Ps}}} [(\chi^g)^* \mathcal{H} \chi^g - \mathcal{E}_0 (\chi^g)^* \chi^g] \quad (125)$$

in the basis  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$  . That is ,

$$F_{\mu'\nu'}^p = \int d\mathbf{r}^p d\mathbf{r}^p (\phi_{\mu'}^p)^* f^p \phi_{\nu'}^p \quad (126)$$

$$= \langle \phi_{\mu'}^p | f^p | \phi_{\nu'}^p \rangle \quad (127)$$

$$= \frac{1}{S^{\text{Ps}}} \left[ \langle \phi_{\mu'}^p | \sum_{k=1}^{K_g} C_k^g \phi_k^g | \mathcal{H} | \phi_{\nu'}^p | \sum_{k=1}^{K_g} C_k^g \phi_k^g \rangle - \mathcal{E}_0 \langle \phi_{\mu'}^p | \sum_{k=1}^{K_g} C_k^g \phi_k^g | \phi_{\nu'}^p | \sum_{k=1}^{K_g} C_k^g \phi_k^g \rangle \right] \quad (128)$$

$$= \frac{1}{S^{\text{Ps}}} \left[ \sum_{k,\ell} P_{k\ell}^g \langle \phi_{\mu'}^p | \phi_k^g | \mathcal{H} | \phi_{\nu'}^p | \phi_{\ell}^g \rangle - \mathcal{E}_0 \sum_{k,\ell} P_{k\ell}^g \langle \phi_{\mu'}^p | \phi_k^g | \phi_{\nu'}^p | \phi_{\ell}^g \rangle \right] \quad (129)$$

The Fock matrix  $F^g$  is the matrix representation of the Fock Operator

$$f^g \equiv \frac{1}{S^{\text{Ps}}} [(\chi^p)^* \mathcal{H} \chi^p - \mathcal{E}_0 (\chi^p)^* \chi^p] \quad (130)$$

in the basis  $\{\phi_{\mu'}^g\}$  and  $\{\phi_k^g\}$ . That is ,

$$F_{k\ell}^g = \int d\mathbf{r}^p d\mathbf{r}^p (\phi_k^g)^* f^p \phi_\ell^g \quad (131)$$

$$= \langle \phi_k^g | f^g | \phi_\ell^g \rangle \quad (132)$$

$$= \frac{1}{S^{\text{Ps}}} \left[ \langle \phi_k^g | \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p | \mathcal{H} | \phi_\ell^g | \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \rangle \right. \\ \left. - \mathcal{E}_0 \langle \phi_k^g | \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p | \phi_\ell^g | \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \rangle \right] \quad (133)$$

$$= \frac{1}{S^{\text{Ps}}} \left[ \sum_{\mu', \nu'} P_{\mu' \nu'}^p \langle \phi_{\mu'}^p \phi_k^g | \mathcal{H} | \phi_{\nu'}^p \phi_\ell^g \rangle - \mathcal{E}_0 \sum_{\mu', \nu'} P_{\mu' \nu'}^p \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_\ell^g \rangle \right] \quad (134)$$

In the computation of the elements of these two matrix Fock operators there are only two integrals that need to be computed.

$$\Gamma_H(\mu', \nu'; k, \ell) = \langle \phi_{\mu'}^p \phi_k^g | \mathcal{H} | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (135)$$

$$\Gamma_S(\mu', \nu'; k, \ell) = \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (136)$$

The two quantities  $S^{\text{Ps}}$  and  $\mathcal{E}_0$  can also be expressed in terms of these two integrals.

$$S^{\text{Ps}} = \sum_{k\ell} \sum_{\mu' \nu'} P_{k,\ell}^g P_{\mu' \nu'}^p \Gamma_S(\mu', \nu'; k, \ell) \quad (137)$$

$$\mathcal{E}_0 = \frac{1}{S^{\text{Ps}}} \sum_{k\ell} \sum_{\mu' \nu'} P_{k,\ell}^g P_{\mu' \nu'}^p \Gamma_H(\mu', \nu'; k, \ell) \quad (138)$$

This allows for the Fock operator matrix elements to be written in their final form.

$$F_{\mu'\nu'}^p = \frac{1}{S^{\text{Ps}}} \left[ \sum_{k,\ell} P_{k\ell}^g \Gamma_H(\mu', \nu'; k, \ell) - \mathcal{E}_0 \sum_{k,\ell} P_{k\ell}^g \Gamma_S(\mu', \nu'; k, \ell) \right] \quad (139)$$

$$F_{k\ell}^g = \frac{1}{S^{\text{Ps}}} \left[ \sum_{\mu',\nu'} P_{\mu'\nu'}^p \Gamma_H(\mu', \nu'; k, \ell) - \mathcal{E}_0 \sum_{\mu',\nu'} P_{\mu'\nu'}^p \Gamma_S(\mu', \nu'; k, \ell) \right] \quad (140)$$

## Basis Functions

One of the most significant limits on the quality of the solution is in choice and number of basis functions. The specific basis functions to be used in the SCF procedure are the GTFs described in Chapter IV by Equations (39) and (45), repeated here.

$$\phi_{\mu'}^p = x_A^{\ell_i} y_A^{m_i} z_A^{n_i} e^{-\alpha_{\mu'}(r_A^p)^2} \quad (141)$$

$$= (x_A^{\ell_i} e^{-\alpha_{\mu'}(x_A^p)^2})(y_A^{m_i} e^{-\alpha_{\mu'}(y_A^p)^2})(z_A^{n_i} e^{-\alpha_{\mu'}(z_A^p)^2}) \quad (142)$$

and

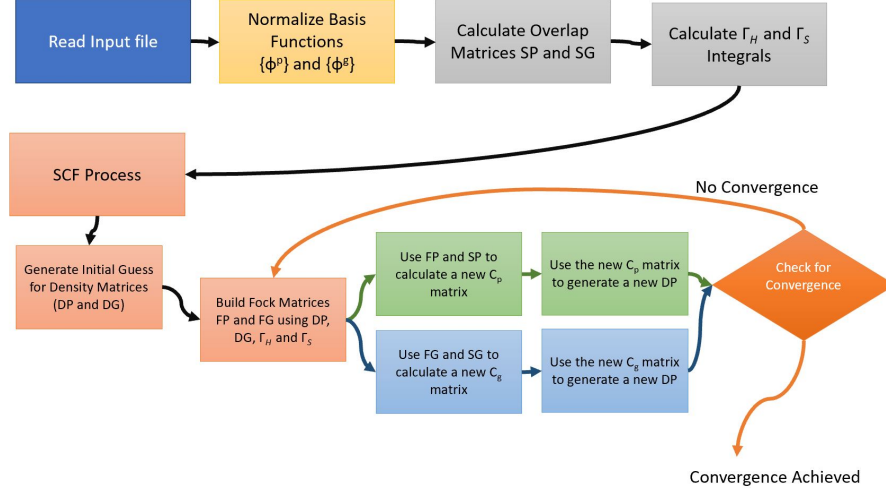
$$\phi_{\ell}^g = e^{-\alpha_{\ell}(r_s^e - r^p)^2_A} \quad (143)$$

$$= (e^{-\alpha_{\ell}(x_s^e - x^p)^2})(e^{-\alpha_{\ell}(y_s^e - y^p)^2})(e^{-\alpha_{\ell}(z_s^e - z^p)^2}). \quad (144)$$

## The Self Consistent Field Procedure

With the integrals defined and the various matrices built from the integrals established, it is time to present the computational process used in computing the energy. Figure 9 presents an overview of programming and SCF procedure that will be explained in this section.

1. Read input



**Figure 9.** The SCF procedure for calculating the minimum energy for a Ps/H system as setup in this Chapter.

2. Find the norm for each basis function in  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$ .
3. Calculate the overlap each of the integrals in  $\langle \phi_{\mu'}^p | \phi_{\nu'}^p \rangle$  for all  $\mu'$  and  $\nu'$  in  $K_p$  and  $\langle \phi_k^g | \phi_\ell^g \rangle$  for all  $k$  and  $\ell$  in  $K_g$ . The number of each of these integrals that need be calculated are  $(K_g^2)$  and  $(K_p)^2$ . The results from these integrals are used to form the overlap matrices  $\mathbf{S}^P$  and  $\mathbf{S}^G$  where

$$\mathbf{S}_{\mu'\nu'}^p = \langle \phi_{\mu'}^p | \phi_{\nu'}^p \rangle \quad (145)$$

$$\mathbf{S}_{k\ell}^g = \langle \phi_k^g | \phi_\ell^g \rangle. \quad (146)$$

4. Calculate the overlap integral  $\Gamma_S$  from Equation (136) and store the results for use in building the Fock Matrices and energy calculations. The number of integrals to be calculated in this step are  $(K_p)^2(K_g)^2$ .
5. Calculate the Hamiltonian integral  $\Gamma_H$  from Equation (135) and store them for use in building the Fock Matrices and energy calculations. The number of integrals to be calculated in this step are  $3(K_p)^2(K_g)^2$ .

6. Begin the SCF procedure:

- (a) Generate initial Density Matrices for  $\mathbf{P}^p$  and  $\mathbf{P}^g$ . The initial guess for each of these is generated using the overlap matrices  $\mathbf{S}^p$  and  $\mathbf{S}^g$ .
- (b) Build the two Fock matrices  $\mathbf{F}^p$  and  $\mathbf{F}^g$  as shown in Equations (139) and (140) using the saved integrals and the density matrices  $\mathbf{P}^p$  and  $\mathbf{P}^g$ .
- (c) Solve the Roothan Equation (117) using  $\mathbf{F}^p$  and  $\mathbf{S}^p$  to get a new  $\mathbf{C}^p$ . For additional details on the solving of these equations see Appendix B on page 148.
- (d) Solve the Roothan Equation (118) using  $\mathbf{F}^g$  and  $\mathbf{S}^g$  to get a new  $\mathbf{C}^g$ .
- (e) Use  $\mathbf{C}^p$  and  $\mathbf{C}^g$  to calculate new density matrices  $\mathbf{P}^p$  and  $\mathbf{P}^g$  respectively.
- (f) Check for convergence.
- (g) If convergence is not achieved then go to (b) using the new density matrices generated in (e).
- (h) If convergence is achieved then the density matrices can be used to calculate expectation values.

### Annihilation Rate

The Density matrices  $\mathbf{P}^p$  and  $\mathbf{P}^g$  from the SCF procedure can now be used to derive different expectation values. The expectation value for the energy and each term of the Hamiltonian is already available from completion of the SCF procedure. (see Equations (74), (75) and (76)). Using the results of the SCF procedure the electron-positron annihilation rate for Ps can be calculated.

The annihilation rate given by Equation (62) and a single electron positron system

is

$$\lambda_{2\gamma} = 4\pi r_0^2 c \frac{\left\langle \Psi_0^{\text{Ps}}(\mathbf{x}^e, \mathbf{x}^p) \left| \sum_{i=1}^{N_e} \delta(\mathbf{r}_i^e - \mathbf{r}^p) \right| \Psi_0^{\text{Ps}}(\mathbf{x}^e, \mathbf{x}^p) \right\rangle}{\langle \Psi_0^{\text{Ps}}(\mathbf{x}^e, \mathbf{x}^p) | \Psi_0^{\text{Ps}}(\mathbf{x}^e, \mathbf{x}^p) \rangle} \quad (147)$$

The Ps atom has only a single electron, so substituting the spatial orbital form of the ansatz from Equation (67) into Equation (147) gives the spatial orbital annihilation rate.

$$\lambda_{2\gamma} = 4\pi r_0^2 c \frac{\left\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \left| \delta(\mathbf{r}^e - \mathbf{r}^p) \right| \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \right\rangle}{\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) | \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \rangle} \quad (148)$$

$$= \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \left\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \left| \delta(\mathbf{r}^e - \mathbf{r}^p) \right| \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \right\rangle \quad (149)$$

$$= \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \int_{\mathbb{R}^6} \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^p, \mathbf{r}^s) \left[ \delta(\mathbf{r}^e - \mathbf{r}^p) \right] \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^p, \mathbf{r}^s) d\mathbf{r}^p d\mathbf{r}^s \quad (150)$$

$$= \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \int_{\mathbb{R}^3} \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^p, \mathbf{r}^p) \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^p, \mathbf{r}^p) d\mathbf{r}^p \quad (151)$$

Equation (151) is a single particle integral of the overlap  $\psi^p \psi^g$ . Letting  $\lambda_{bf}$  be the  $\lambda_0$  in the basis function representation for  $\psi^p$  and  $\psi^g$  gives

$$\lambda_{bf} = \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \int_{\mathbb{R}^3} \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p(\mathbf{r}^p) \sum_{k=1}^{K_g} C_k^g \phi_k^g(\mathbf{r}^p, \mathbf{r}^p) \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p(\mathbf{r}^p) \sum_{\ell=1}^{K_g} C_\ell^g \phi_\ell^g(\mathbf{r}^p, \mathbf{r}^p) d\mathbf{r}^p \quad (152)$$

$$= \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \sum_{k,\ell}^{K_g} P_{k\ell}^g \sum_{\mu',\nu'}^{K_p} P_{\mu'\nu'}^p \int_{\mathbb{R}^3} \phi_{\mu'}^p(\mathbf{r}^p) \phi_{\nu'}^p(\mathbf{r}^p) d\mathbf{r}^p \quad (153)$$

$$= \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \sum_{k,\ell}^{K_g} P_{k\ell}^g. \quad (154)$$

Where  $\phi_k^g(\mathbf{r}^p, \mathbf{r}^p) = 1$  as evaluated in the basis functions as given by Equation (45)

and that

$$\sum_{\mu', \nu'}^{K_p} P_{\mu' \nu'}^p \int_{\mathbb{R}^3} d\mathbf{r}^p \phi_{\mu'}^p(\mathbf{r}^p) \phi_{\nu'}^p(\mathbf{r}^p) = 1 \quad (155)$$

given that this is the probability of finding the positron anywhere in the three dimensional space.

Therefore the annihilation rate for  $\Psi_0^{\text{Ps}}$  as calculated in the basis functions for  $\psi^p$  and  $\psi^g$  is

$$\lambda_{bf} = \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \sum_{k, \ell}^{K_g} P_{k\ell}^g. \quad (156)$$

## Results

This section goes over the modeling of H and Ps using the explicitly correlated orbitals developed in this chapter. The exponents used in for  $\{\phi_{\mu'}^p\}$  basis set had minimal effect on the final results given that the two particle interaction in both H and Ps is captured in the  $\chi^g$  orbital using the  $\{\phi_k^g\}$  basis set.

The basis set  $\{\phi_k^g\}$  used to approximate the spatial part of  $\chi^g(\mathbf{x}^p, \mathbf{x}^e)$  consisted of 10 s-functions. The exponent values used for this basis set are provided in Table 5. Table 5 also provides the optimized weights for  $C_k^g$  for  $k = 1, 2, \dots, 10$ . The Hydrogen molecule prefers exponents  $\gamma_5$  and  $\gamma_6$  while Ps is  $\gamma_4$  and  $\gamma_5$ . As expected, Ps weighs to the smaller exponent giving it a greater distance between the two particles.

### Discussion of Energy.

Figures 10 shows the the energy level converging to the actual energy of the system as the number of basis sets are increased. Table 6 provides the energy levels for the kinetic, potential and total energy for increasing number of basis functions used to

$k$	$\gamma_k$	H - $C_k^g$	Ps - $C_k^g$
1	0.001901970	-0.000690	0.001226
2	0.007117000	0.002153	-0.001982
3	0.026631173	-0.003438	0.066258
4	0.099651454	0.063042	0.073214
5	0.372886773	0.076357	0.021614
6	1.395308746	0.023486	0.004846
7	5.221119751	0.005252	0.000927
8	19.53696021	0.001032	0.000190
9	73.10554677	0.000189	0.000032
10	273.5543765	0.000052	0.000009

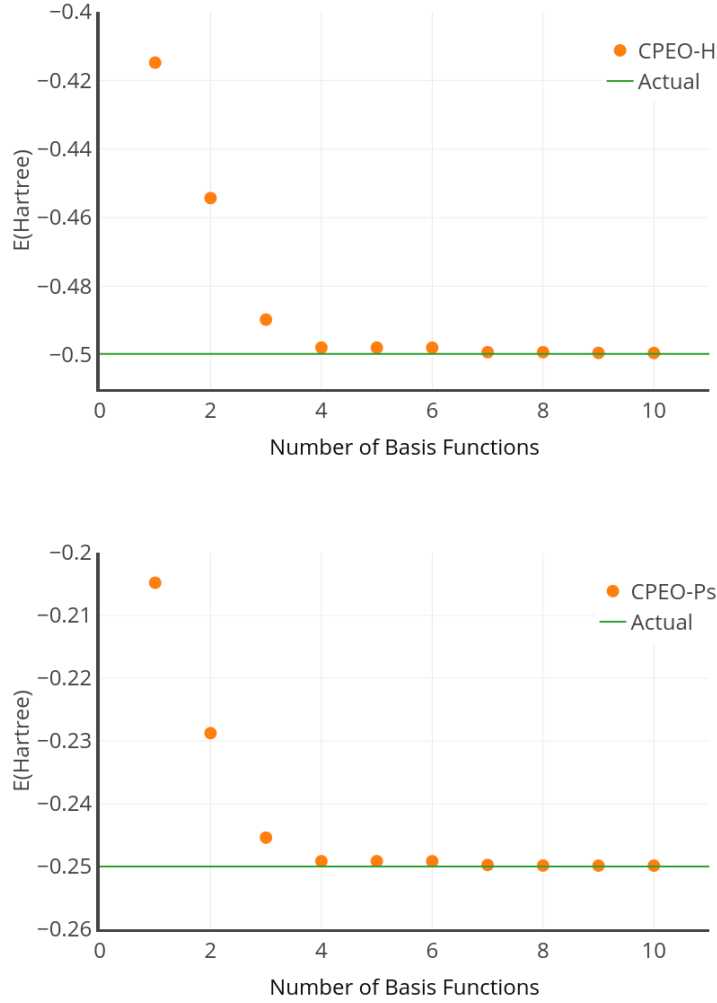
**Table 5.**  $\gamma_k$  provides the exponents for the Gaussian basis set used for the spatial part of  $\chi^g$ . The second and third column provide the optimized weights for the corresponding exponent for Hydrogen and Ps respectively.

approximate the spatial part of  $\chi^g$ . These energy levels are converging to the actual energy as their number increases.

	Number of Basis Functions	$\langle T \rangle_{1s}$	$\langle V \rangle_{1s}$	$E_{1s}$
Hydrogen:				
	3	0.46434	-0.95408	-0.48973
	7	0.49870	-0.99793	-0.49922
	10	0.49946	-0.99903	-0.49946
	Actual	0.49972	-0.99945	-0.49972
Positronium:				
	3	0.23355	-0.47895	-0.24539
	7	0.24947	-0.4992	-0.24975
	10	0.24986	-0.49973	-0.24986
	Actual	0.250	-0.50	-0.250

**Table 6.** Comparison of expectation values for total kinetic energy,  $\langle T \rangle$ ; potential energy between  $e^+$  and  $e^-$ ,  $\langle V \rangle$ , and the total energy for Hydrogen and Positronium. All units are in atomic units as provided in Table 3.





**Figure 10.** As the number of basis functions increased the ground state energy for the the model converges toward the actual energy for both the H and Ps ground state.

### Discussion on Annihilation.

The annihilation rate from Equation (156) was used with the results of modeling on Ps. The annihilation rate calculate here was for para-Ps. These results are provided in Table 7. The contact density and therefore the annihilation rate are both more than 10 times to large from the actual. The too high contact density is thought to be a result of behavior that is purely correlated between the positron and the electron in the s-function approximations for the spatial part of  $\chi^g$ .

This suggests that not only was correlation between the positron and the electron achieved using a mean field approach, but that there is too much correlation. This was surprising though due to the accuracy of the energy levels for modeling Ps. Possible fixes for the rigid nature of the way the model was employed in approximating the spatial part of  $\chi^g$  is discussed in Chapter VII.

Number of Basis Functions	$\lambda_{2\gamma}$	$\langle\delta_{ep}\rangle$
3	91.521	0.45334
7	93.756	0.46441
10	93.849	0.46489
Actual	8.0325	1.812

**Table 7.** Comparison of para-Ps annihilation rates,  $\lambda_{2\gamma}$ ; and average contact density for the electron and the positron,  $\langle\delta_{ep}\rangle$ .

## VI. Modeling Virtual Ps an Explicitly Correlated Orbital

In this chapter the mean-field model for CPEO is developed. The virtual Ps in this model will be treated just as the Ps from the previous chapter. We begin by using the Hamiltonian as given in Equation (19)

$$\mathcal{H} = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 - \frac{1}{2} \nabla_p^2 + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \sum_{A=1}^{N_N} \frac{Z_A}{r_{iA}} - \sum_{A=1}^{N_N} \frac{Z_A}{r_{pA}} - \sum_{i=1}^{N_e} \frac{1}{r_{pi}} \quad (157)$$

and the ansatz for CPEO as presented in Equation (22) where  $N_r = N_e - 1$  is the number of regular electron.

$$\Psi^{\text{CPEO}}(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e, \mathbf{x}^p, \mathbf{x}_s^e) = \frac{\chi^p(\mathbf{x}^p) \chi^g(\mathbf{x}^p, \mathbf{x}_s^e)}{\sqrt{(N_r)!}} \begin{vmatrix} \chi_1^e(\mathbf{x}_1^e) & \dots & \chi_{N_r}^e(\mathbf{x}_1^e) \\ \vdots & \ddots & \vdots \\ \chi_1^e(\mathbf{x}_{N_r}^e) & \dots & \chi_{N_r}^e(\mathbf{x}_{N_r}^e) \end{vmatrix} \quad (158)$$

$$= \chi^p(\mathbf{x}^p) \chi^g(\mathbf{x}^p, \mathbf{x}_s^e) \Phi^e(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e) \quad (159)$$

$$= \chi^p \chi^g \Phi^e. \quad (160)$$

This ansatz is for a bound positron system that is dominated by the formation of virtual Ps. To model this system we derive three Fock-Operators. Generally a Fock-Operator is accepted as a single particle approximation of the Hamiltonian. The single particle approximation for the Fock-Operator “sees” the other particles only in an average way. The orbital structure used in this ansatz has a two particle orbital that works to maintain correlation between the positron and special electron that would otherwise be lost in the single particle Hamiltonian approximation. The three Fock-operators that will be derived and used for modeling are

1.  $f^e$  for the regular electrons. Regular electrons have an orbital structure that mirrors that of standard electronic Hartree-Fock Theory.

2.  $f^p$  for the positron. The positron is given its own orbital in the same manner as the regular electrons. This orbital is correlated with the Ps using geminal coupled Ps-orbital between the positron and special electron.
3.  $f^g$  for the virtual Ps. The virtual Ps is a Correlated Positron-Electron Orbital (CPEO).

## Formalisms

### Hamiltonian.

Like the previous chapter, this chapter is also focused on developing an approximate solutions of the non-relativistic time-independent Shrödinger equation

$$\mathcal{H} |\Phi\rangle = \mathcal{E} |\Phi\rangle. \quad (161)$$

Keeping with the molecular coordinate system introduced in Chapter III and repeated here in Figure11. The Hamiltonian from Equation (157) is written in the following form.

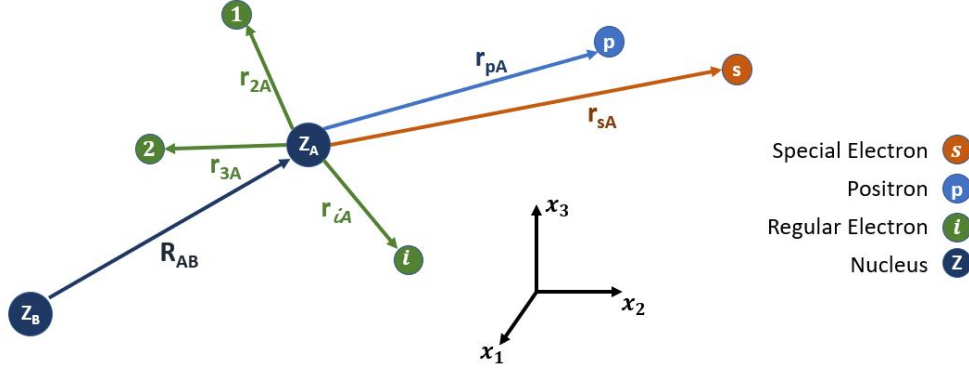
$$\mathcal{H} = \sum_{i=1}^{N_r} h^e(i) + h^s(1) + h^p(1) + \sum_{i=1}^{N_r} \sum_{j>i}^{N_r} \frac{1}{\mathbf{r}_{ij}} - \sum_{i=1}^{N_r} \left( \frac{1}{\mathbf{r}_{pi}} - \frac{1}{\mathbf{r}_{s1}} \right) - \frac{1}{\mathbf{r}_{ps}}. \quad (162)$$

Where  $N_r = N_e - 1$  is the number of regular electrons and

$$h^e(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{N_A} \frac{Z_A}{\mathbf{r}_{iA}} \quad (163)$$

$$h^s(1) = -\frac{1}{2} \nabla_s^2 - \sum_{A=1}^{N_A} \frac{Z_A}{\mathbf{r}_{sA}} \quad (164)$$

$$h^p(1) = -\frac{1}{2} \nabla_p^2 + \sum_{A=1}^{N_A} \frac{Z_A}{\mathbf{r}_{pA}} \quad (165)$$



**Figure 11.** A molecular coordinate System:  $s$  = special electron;  $p$  = positron;  $1, 2, i$  = electrons;  $A, B$  = nuclei.

It is beneficial to re-write the Hamiltonian using four operators to organize the development of the Fock operators.

$$\mathcal{H} = H^{\text{e-core}}(1, \dots, N_r) + H^{\text{ee}}(1, \dots, N_r) + \Omega_1(p, s) + \sum_{a=1}^{N_e} \Omega_2(p, 1, a) \quad (166)$$

where these four operators are defined as:

$$H^{\text{e-core}}(1, \dots, N_r) = \sum_{i=1}^{N_r} h^e(i) \quad (167)$$

$$H^{\text{ee}}(1, \dots, N_r) = \sum_{i=1}^{N_r} \sum_{j>i}^{N_r} \frac{1}{\mathbf{r}_{ij}} \quad (168)$$

$$\Omega_1(s, p) = h^s(1) + h^p(1) - \frac{1}{\mathbf{r}_{ps}} \quad (169)$$

$$\Omega_2(p, s, 1) = \frac{1}{\mathbf{r}_{p1}} - \frac{1}{\mathbf{r}_{s1}} \quad (170)$$

$H^{\text{e-core}}(1, \dots, N_e)$  is the core operator for all the regular electrons.  $H^{\text{ee}}(1, \dots, N_e)$  is the electron-electron interaction of the regular electrons.  $\Omega_1(s, p)$  combines the core operators for the special electron and the positron along with the columbic interaction between the special electron and the positron; finally  $\Omega_2(p, s, 1)$  operator has the columbic interaction of the regular electrons with both the special electron

and the positron.

### Energy of the System.

Using the ansatz for  $\Psi^{\text{CPEO}}$  the eigenvalue problem of Equation (161) is now

$$\mathcal{H}|\Psi^{\text{CPEO}}\rangle = \mathcal{E}|\Psi^{\text{CPEO}}\rangle. \quad (171)$$

The energies associated with the wavefunction in Equation (171) are defined as the expectation values of the Hamiltonian operator given in Equation (166) so that

$$\mathcal{E} = \frac{\langle \Psi^{\text{CPEO}} | \mathcal{H} | \Psi^{\text{CPEO}} \rangle}{\langle \Psi^{\text{CPEO}} | \Psi^{\text{CPEO}} \rangle} = \frac{1}{S^{\text{CPEO}}} \langle \Psi^{\text{CPEO}} | \mathcal{H} | \Psi^{\text{CPEO}} \rangle \quad (172)$$

where  $S^{\text{CPEO}}$  is the overlap integral and arises from the non-separable nature of the orbitals in  $\Psi^{\text{CPEO}}$ .  $S^{\text{CPEO}}$  is evaluated as

$$S^{\text{CPEO}} \equiv \langle \Psi^{\text{CPEO}} | \Psi^{\text{CPEO}} \rangle \quad (173)$$

$$\equiv \langle \Phi^e | \Phi^e \rangle \langle \chi^p \chi^g | \chi^p \chi^g \rangle \quad (174)$$

$$\equiv \langle \chi^p \chi^g | \chi^p \chi^g \rangle. \quad (175)$$

The energy contributions associated with the expectation value of the Hamiltonian can be expressed as

$$\mathcal{E} = E_{\text{core}} + E_{\text{ee}} + E_{\text{G1}} + E_{\text{G2}} \quad (176)$$

where

$$E_{\text{core}} = \sum_{a=1}^{N_r} \langle \chi_a^e | h^e(1) | \chi_a^e \rangle \quad (177)$$

$$E_{\text{ee}} = \frac{1}{2} \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \left[ \langle \chi_a^e \chi_b^e | \frac{1}{r_{12}} | \chi_a^e \chi_b^e \rangle - \langle \chi_a^e \chi_b^e | \frac{1}{r_{12}} | \chi_b^e \chi_a^e \rangle \right] \quad (178)$$

$$E_{\text{G1}} = \frac{1}{S_{\text{CPEO}}} \langle \chi^p \chi^g | \Omega_1(p, s) | \chi^p \chi^g \rangle \quad (179)$$

$$E_{\text{G2}} = \frac{1}{S_{\text{CPEO}}} \sum_{a=2}^{N_r} \langle \chi^p \chi^g \chi_a^e | \Omega_2(p, s, 1) | \chi^p \chi^g \chi_a^e \rangle \quad (180)$$

Here each of these energy contributions are arranged with hindsight for ease in derivation and calculation organization. Each contribution though has a physical significance:  $E_{\text{core}}$  is the kinetic energy of the regular electrons and the potential energies of the regular electrons with each nuclei;  $E_{\text{ee}}$  is the energy from the electron-electron interaction for the regular electrons;  $E_{\text{G1}}$  is the kinetic energy for virtual Ps in the presence of the nuclei (that is kinetic energy for the positron and the special electron, interaction between the special electron and the positron, and energy contribution between the positron and special electron with the nuclei);  $E_{\text{G2}}$  is the energy contribution from the interaction between the regular electrons with the positron and the special electron.

$E_{\text{G1}}$  and  $E_{\text{G2}}$  can be expressed using the following shorthand integral notation.

$$E_{\text{G1}} = \frac{\Gamma_1}{S_{\text{CPEO}}} \quad (181)$$

$$E_{\text{G2}} = \frac{1}{S_{\text{CPEO}}} \sum_{a=1}^{N_r} \Gamma_{2a} \quad (182)$$

with the integrals defined as

$$\Gamma_1 \equiv \Gamma_1(p, s) \equiv \langle \chi^p \chi^g | \Omega_1(p, s) | \chi^p \chi^g \rangle \quad (183)$$

$$\Gamma_{2a} \equiv \Gamma_{2a}(p, s, 1) \equiv \langle \chi^p \chi^g \chi_a^e | \Omega_2(p, s, 1) | \chi^p \chi^g \chi_a^e \rangle \quad (184)$$

## The Variation Principle

In this section we derive the Hartree-Fock equations in their general spin form. That is we obtain the eigenvalue equation by minimizing the energy expression for Equation (172). As in the previous chapter, the variational principal is used to find integro-differential equations that minimize the energy. As before, the ground state energy will be denoted  $\mathcal{E}_0$ . The eigenfunctions associated with  $\mathcal{E}_0$  are designated  $|\Psi_0^{\text{CPEO}}\rangle$ . This variational procedure produces three Fock operators that form a coupled system of equations that can be solved iteratively.

### The Lagrangian.

To derive the Fock operators used in finding  $|\Psi_0^{\text{CPEO}}\rangle$ , the functional  $E_0[\{\chi_a^e\}, \chi^p, \chi^g]$  needs to be minimized with respect to each spin orbital subject to the constraint that these spin orbitals remain orthonormal,

$$\langle \chi^p | \chi^p \rangle = 1 \quad (185)$$

$$\langle \chi^g | \chi^g \rangle = 1 \quad (186)$$

$$\langle \chi_a^e | \chi_b^e \rangle = \delta_{ab}, \quad \forall a, b \in 1, \dots, N_r \quad (187)$$

Note that  $\chi^p$  and  $\chi^g$  are trivially orthogonal.



Therefore the Lagrangian to be considered is the functional

$$\begin{aligned} \mathcal{L}[\{\chi_a^e\}, \chi^p, \chi^g] &= E_0[\{\chi_a^e\}, \chi^p, \chi^g] - \varepsilon_p(\langle \chi^p | \chi^p \rangle - 1) - \varepsilon_g(\langle \chi^g | \chi^g \rangle - 1) \\ &\quad - \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \varepsilon_{ab} (\langle \chi_a^e | \chi_b^e \rangle - \delta_{ab}) \end{aligned} \quad (188)$$

$$\begin{aligned} &= E_{\text{core}}[\{\chi_a^e\}] + E_{\text{ee}}[\{\chi_a^e\}] + E_{\text{G1}}[\chi^p, \chi^g] + E_{\text{G2}}[\chi^p, \chi^g, \{\chi_a^e\}] \\ &\quad - \varepsilon_p(\langle \chi^p | \chi^p \rangle - 1) - \varepsilon_g(\langle \chi^g | \chi^g \rangle - 1) \\ &\quad - \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \varepsilon_{ab} (\langle \chi_a^e | \chi_b^e \rangle - \delta_{ab}) \end{aligned} \quad (189)$$

where  $E_0$  is the expectation value for the wavefunction  $|\Psi_0^{\text{CPEO}}\rangle$

$$E_0[\{\chi_a^e\}, \chi^p, \chi^g] = \frac{1}{S_{\text{CPEO}}} \langle \Psi_0^e \chi^p \chi^g | \mathcal{H} | \Psi_0^e \chi^p \chi^g \rangle \quad (190)$$

This expectation of the Hamiltonian gives rise to the expectation values of each  $E_{\text{core}}[\{\chi_a^e\}]$ ,  $E_{\text{ee}}[\{\chi_a^e\}]$ ,  $E_{\text{G1}}[\chi^p, \chi^g]$  and  $E_{\text{G2}}[\{\chi_a^e\}, \chi^p, \chi^g]$ ; these functionals are defined in Equations (177) through (180).  $\varepsilon_p$  and  $\varepsilon_g$  and  $\{\varepsilon_{ab}\}$  are the Lagrange multipliers. Also, since energy is a physical property (an observable) of the Hamiltonian the Lagrange multipliers are real and

$$\varepsilon_p = \varepsilon_p^*. \quad (191)$$

$$\varepsilon_g = \varepsilon_g^*. \quad (192)$$

$$\varepsilon_{ab} = \varepsilon_{ab}^* \quad (193)$$

That is the Lagrange multipliers are Real valued numbers.

**First Variation With Respect to  $\chi_a^e$  while holding  $\chi^p$  and  $\chi^g$  constant.**

The first variation with respect to the spin orbitals  $\{\chi_a^e\}$  is done by the varying the spin orbitals an arbitrary infinitesimal amount

$$\chi_a^e \rightarrow \chi_a^e + \delta\chi_a^e \quad (194)$$

so that

$$\begin{aligned} \delta\mathcal{L} &= \delta E_{\text{core}} + \delta E_{\text{ee}} + \delta E_{\text{G2}} + \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \varepsilon_{ab} \delta \langle \chi_a^e | \chi_b^e \rangle \\ &= \sum_{a=2}^{N_r} \langle \delta\chi_a^e | h^e(\mathbf{x}_1^e) | \chi_a^e \rangle + \frac{1}{2} \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \left[ \langle \delta\chi_a^e \chi_b^e | \frac{1}{\mathbf{r}_{12}} | \chi_a^e \chi_b^e \rangle - \langle \delta\chi_a^e \chi_b^e | \frac{1}{\mathbf{r}_{12}} | \chi_b^e \chi_a^e \rangle \right] \\ &\quad + \sum_{a=1}^{N_r} \frac{1}{S_{\text{CPEO}}} \langle \chi^p \chi^g \delta\chi_a^e | \Omega_2 | \chi^p \chi^g \chi_a^e \rangle - \sum_{a=1}^{N_r} \sum_{b=1}^{N_r} \varepsilon_{ab} \langle \delta\chi_a^e | \chi_b^e \rangle \\ &\quad + \text{complex conjugate} \\ &= 0. \end{aligned} \quad (195)$$

It is worth noting that  $E_{\text{core}}$  and  $E_{\text{ee}}$  are functionals of only  $\{\chi_a^e\}$  and therefore the first variation on these orbitals is the standard electronic structure theory reviewed in Appendix B (specifically pages 135 through 139). With this, Equation (195) becomes

$$\begin{aligned} 0 &= \sum_{a=1}^{N_r} \int (\delta\chi_a^e)^* \\ &\quad \times \left[ \left( h^e(\mathbf{x}_1^e) + \sum_{b=1}^{N_r} \left[ J_b(\mathbf{x}_1^e) - K_b(\mathbf{x}_1^e) \right] + \frac{1}{S_{\text{CPEO}}} \int \chi^{p*} \chi^{g*} \Omega_2 \chi^p \chi^g d\mathbf{x}^p d\mathbf{x}_s^e \right) \chi_a^e \right. \\ &\quad \left. - \sum_{b=1}^{N_r} \varepsilon_{ab} \chi_b^e \right] d\mathbf{x}_a^e \\ &\quad + \text{complex conjugate} \end{aligned} \quad (196)$$

where the operator  $h^e(1)$  is given by Equation (163) and the operators  $J_b(1)$  and  $K_b(1)$  are the standard coulomb and exchange operators as defined in Appendix B Equations (444) and (446). Since  $(\delta\chi_a^e)^*$  in Equation (196) is arbitrary, it must be that the quantity in square brackets is zero for all  $a$ . Therefore,

$$\begin{aligned} \left( h^e(\mathbf{x}_1^e) + \sum_{b=1}^{N_r} \left[ J_b(\mathbf{x}_1^e) - K_b(\mathbf{x}_1^e) \right] + \frac{1}{S_{\text{CPEO}}} \int \chi^{p*} \chi^{g*} \Omega_2 \chi^p \chi^g d\mathbf{x}^p d\mathbf{x}_s^e \right) \chi_a^e(1) \\ = \sum_{b=2}^{N_r} \varepsilon_{ab} \chi_b^e(1) \quad a = 1, \dots, N_r. \end{aligned} \quad (197)$$

Written as an eigenfunction Equation (197) becomes

$$f^e |\chi_a^e\rangle = \sum_{b=2}^{N_r} \varepsilon_{ab} |\chi_b^e\rangle \quad (198)$$

where

$$f^e = h^e(\mathbf{x}_1^e) + \sum_{b=1}^{N_r} \left[ J_b(\mathbf{x}_1^e) - K_b(\mathbf{x}_1^e) \right] + \frac{1}{S_{\text{CPEO}}} \int \chi^{p*} \chi^{g*} \Omega_2 \chi^p \chi^g d\mathbf{x}^p d\mathbf{x}_s^e. \quad (199)$$

Equation (198) is the non-canonical form of the Hartree-Fock equations for the regular electrons. As shown in Appendix B in the section on Canonical Spin Orbitals (see page 139 ) there exist a unitary transformation to a unique set of spin orbitals  $\{\chi'_a{}^e\}$  for which the matrix of Lagrange multipliers is diagonal.

$$f^e |\chi'_a{}^e\rangle = \varepsilon'_a |\chi'_a{}^e\rangle \quad (200)$$

This unique set of spin orbitals  $\{\chi'_a{}^e\}$  is called the canonical spin orbitals. The primes are henceforth dropped and the Hartree-Fock equations for the regular electronic spin

orbitals  $\{\chi_a^e\}$  are written as

$$f^e |\chi_a^e\rangle = \varepsilon_a |\chi_a^e\rangle \quad (201)$$

with  $f^e$  defined by Equation (199).

**First Variation With Respect to  $\chi^p$  while holding  $\chi_a^e$  and  $\chi^g$  constant.**

The first step in obtaining the Fock operator for  $\chi_p$  is to take the first variation of  $\mathcal{L}$  with respect to  $\chi^p$  and set it equal to zero. To take the first variation with respect to  $\chi^p$ , the  $\chi^p$  orbital is varied an arbitrary infinitesimal amount:

$$\chi^p \rightarrow \chi^p + \delta\chi^p \quad (202)$$

so that

$$\begin{aligned} \delta\mathcal{L} &= \delta E_{G1} + \delta E_{G2} - \varepsilon_p \delta \langle \chi^p | \chi^p \rangle \\ &= \delta \frac{\Gamma_1}{S^{\text{CPEO}}} + \sum_{a=2}^{N_r} \delta \frac{\Gamma_{2a}}{S^{\text{CPEO}}} - \varepsilon_p \delta \langle \chi^p | \chi^p \rangle \\ &= \frac{S^{\text{CPEO}} \Gamma_1^{\delta p} - \Gamma_1 S^{\text{CPEO}-\delta_p}}{(\Gamma_S)^2} + \sum_{a=1}^{N_r} \left[ \frac{S^{\text{CPEO}} \Gamma_{2a}^{\delta p} - \Gamma_{2a} S^{\text{CPEO}-\delta_p}}{(\Gamma_S)^2} \right] - \varepsilon_p \langle \delta\chi^p | \chi^p \rangle \\ &\quad + \text{complex conjugate} \\ &= 0 \end{aligned} \quad (203)$$

Here the shorthand notation for  $\Gamma_1^{\delta p}$ ,  $\Gamma_{2a}^{\delta p}$  and  $S^{\text{CPEO}-\delta_p}$  is defined as follows:

$$\Gamma_1^{\delta p} \equiv \langle \delta \chi^p \chi^g | \Omega_1 | \chi^p \chi^g \rangle \quad (204)$$

$$\Gamma_{2a}^{\delta p} \equiv \langle \delta \chi^p \chi^g \chi_a^e | \Omega_2 | \chi^p \chi^g, \chi_a^e \rangle \quad (205)$$

$$S^{\text{CPEO}-\delta_p} \equiv \langle \delta \chi^p \chi^g | \chi^p \chi^g \rangle \quad (206)$$

Equation (203) further reduces to

$$0 = \frac{1}{S^{\text{CPEO}}} \left[ \Gamma_1^{\delta p} - E_{G1} S^{\text{CPEO}-\delta_p} + \sum_{a=1}^{N_r} \Gamma_{2a}^{\delta p} - E_{G2} S^{\text{CPEO}-\delta_p} \right] - \varepsilon_p \langle \delta \chi^p | \chi^p \rangle + \text{complex conjugate} \quad (207)$$

$$= \int (\delta \chi^p)^* \left[ \frac{1}{S^{\text{CPEO}}} \left( \int \chi^{g*} \Omega_1 \chi^g d\mathbf{x}_s^e + \sum_{a=1}^{N_r} \int \chi^{g*} \chi_a^{e*} \Omega_2 \chi^g \chi_a^e d\mathbf{x}_1^e d\mathbf{x}_s^e - E_G \int \chi^{g*} \chi^g d\mathbf{x}_s^e \right) \chi^p - \varepsilon_p \chi^p \right] d\mathbf{x}^p + \text{complex conjugate} \quad (208)$$

with

$$E_G \equiv E_{G1} + E_{G2} \quad (209)$$

The vanishing of  $\delta \mathcal{L}$  for an arbitrary variation on  $\delta \chi^p$  and  $(\delta \chi^p)^*$  is satisfied by the condition that the quantity in the square brackets in Equation (208) is equal to zero. That is

$$\frac{1}{S^{\text{CPEO}}} \left( \int \chi^{g*} \Omega_1 \chi^g d\mathbf{x}_s^e + \sum_{a=1}^{N_r} \int \chi^{g*} \chi_a^{e*} \Omega_2 \chi^g \chi_a^e d\mathbf{x}_1^e d\mathbf{x}_s^e - E_G \int \chi^{g*} \chi^g d\mathbf{x}_s^e \right) \chi^p = \varepsilon_p \chi^p \quad (210)$$

Written as an eigenfunction equation, Equation (210) is the integro-differential equation

tion or Hartree-Fock equation:

$$f^p |\chi^p\rangle = \varepsilon_p |\chi^p\rangle \quad (211)$$

where

$$f^p = \frac{1}{S^{\text{CPEO}}} \left( \int \chi^{g*} \Omega_1 \chi^g d\mathbf{x}_s^e + \sum_{a=1}^{N_r} \int \chi^{g*} \chi_a^{e*} \Omega_2 \chi^g \chi_a^e d\mathbf{x}_1^e d\mathbf{x}_s^e - E_G \int \chi^{g*} \chi^g d\mathbf{x}_s^e \right) \quad (212)$$

is Fock operator for the positron orbital  $\chi^p$ .

**First Variation With Respect to  $\chi^g$  while holding  $\chi_a^e$  and  $\chi^p$  constant.**

In similar fashion , the first variation with respect to  $\chi^g$  of  $\mathcal{L}$  is done by the varying  $\chi^g$  an arbitrary infinitesimal amount:

$$\chi^g \rightarrow \chi^g + \delta\chi^g \quad (213)$$

so that

$$\begin{aligned} \delta\mathcal{L} &= \delta E_{G1} + \delta E_{G2} + \varepsilon_p \delta \langle \chi^g | \chi^g \rangle \\ &= \delta \frac{\Gamma_1}{S^{\text{CPEO}}} + \sum_{a=2}^{N_r} \delta \frac{\Gamma_{2a}}{S^{\text{CPEO}}} + \varepsilon_g \delta \langle \chi^g | \chi^g \rangle \\ &= \frac{S^{\text{CPEO}} \Gamma_1^{\delta g} - \Gamma_1 S^{\text{CPEO}-\delta g}}{(S^{\text{CPEO}})^2} + \sum_{a=1}^{N_r} \left[ \frac{S^{\text{CPEO}} \Gamma_{2a}^{\delta g} - \Gamma_{2a} S^{\text{CPEO}-\delta g}}{(S^{\text{CPEO}})^2} \right] + \varepsilon_g \langle \delta\chi^g | \chi^g \rangle \\ &\quad + \text{complex conjugate} \\ &= 0 \end{aligned} \quad (214)$$

Here the shorthand notation for  $\Gamma_1^{\delta g}$  and  $\Gamma_{2a}^{\delta g}$  and  $S^{\text{CPEO}-\delta g}$  is defined as follows:

$$\Gamma_1^{\delta g} \equiv \langle \chi^p \delta \chi^g | \Omega_1 | \chi^p \chi^g \rangle \quad (215)$$

$$\Gamma_{2a}^{\delta g} \equiv \langle \chi^p \delta \chi^g \chi_a^e | \Omega_2 | \chi^p \chi^g, \chi_a^e \rangle \quad (216)$$

$$S^{\text{CPEO}-\delta g} \equiv \langle \chi^p \delta \chi^g | \chi^p \chi^g \rangle \quad (217)$$

Equation (214) further reduces to

$$0 = \frac{1}{S^{\text{CPEO}}} \left[ \Gamma_1^{\delta g} - E_{G1} S^{\text{CPEO}-\delta g} + \sum_{a=1}^{N_r} \Gamma_{2a}^{\delta g} - E_{G2} S^{\text{CPEO}-\delta g} \right] + \varepsilon_g \langle \delta \chi^g | \chi^g \rangle$$

+ complex conjugate (218)

$$= \int (\delta \chi^g)^* \left[ \frac{1}{\Gamma_S} \left( \chi^{p*} \Omega_1 \chi^p \right. \right. \\ \left. \left. + \sum_{a=1}^{N_r} \int \chi^{p*} \chi_a^{e*} \Omega_2 \chi^p \chi_a^e d\mathbf{x}_1^e - E_G \chi^{p*} \chi^p \right) \chi^g + \varepsilon_g \chi^g \right] d\mathbf{x}^p d\mathbf{x}_s^e$$

+ complex conjugate (219)

The vanishing of  $\delta \mathcal{L}$  for an arbitrary variation on  $\delta \chi^g$  and  $(\delta \chi^g)^*$  is satisfied by the condition that the quantity in the square brackets in Equation (219) is equal to zero. That is

$$\frac{1}{S^{\text{CPEO}}} \left( \chi^{p*} \Omega_1 \chi^p + \sum_{a=1}^{N_r} \int \chi^{p*} \chi_a^{e*} \Omega_2 \chi^p \chi_a^e d\mathbf{x}_1^e - E_G \chi^{p*} \chi^p \right) \chi^g = \varepsilon_g \chi^g \quad (220)$$

Written as an eigenfunction Equation (93) becomes

$$f^g |\chi^g\rangle = \varepsilon_g |\chi^g\rangle \quad (221)$$

where

$$f^g = \frac{1}{S^{\text{CPEO}}} \left( \chi^{p*} \Omega_1 \chi^p + \sum_{a=1}^{N_r} \int \chi^{p*} \chi_a^{e*} \Omega_2 \chi^p \chi_a^e d\mathbf{x}_1^e - E_G \chi^{p*} \chi^p \right) \quad (222)$$

is the Fock operator for the positron-electron correlated orbital  $\chi^p$ .

### **Closed Shell Hartree-Fock: Restricted Spin Orbitals.**

In the previous section three coupled integro-differential equations were derived. These Hartree-Fock equations used generalized spin orbitals  $\{\chi_a^e\}$ ,  $\chi^p$  and  $\chi^g$ . To proceed in preparing the equations for calculations of Hartree-Fock wavefunctions we begin to be more specific about the form of the orbitals. This section considers the closed shell Hartree-Fock: restricted spin Orbitals. The molecular states are thus allowed to have only an even number of  $N_r$  regular electrons, with all regular electrons paired in doubly occupied spatial orbitals.

The orbitals  $\chi^p$  and  $\chi^g$  are for the special electron and positron. The spin for these orbitals does not alter the wavefunction since the positron and special electron are each considered to be unique particles in our system. Thus as for the Ps system of the previous chapters integrating out the spin on these orbitals does not change the wavefunction. Now the spatial orbital for the positron is  $\psi^p$  while the spatial orbital for the special electron is  $\psi_s^e$ .

The regular electrons will doubly occupy orbitals with orthogonal spin. The only term in the Hartree-Fock equations effected by this is the regular electron-electron interaction. This is worked out in detail in Appendix B in the section on Restricted Spin Orbitals, page 140.



The resulting spatial Hartree-Fock equations are

$$f^e(\mathbf{r}_1^e) |\psi_a^e(\mathbf{r}_1^e)\rangle = \varepsilon_a |\psi_a^e(\mathbf{r}_1^e)\rangle \quad (223)$$

$$f^p(\mathbf{r}^p) |\psi^p(\mathbf{r}^p)\rangle = \varepsilon_p |\psi^p(\mathbf{r}^p)\rangle \quad (224)$$

$$f^g(\mathbf{r}^p, \mathbf{r}_s^e) |\psi^g(\mathbf{r}^p, \mathbf{r}_s^e)\rangle = \varepsilon_g |\psi^g(\mathbf{r}^p, \mathbf{r}_s^e)\rangle \quad (225)$$

where  $\varepsilon_p$ ,  $\varepsilon_g$  and  $\varepsilon_a$  are the energy of the spatial orbital and is identical to the energy associated with the spin orbitals under the restricted spin Orbital assumptions. The closed shell Fock operators are

$$f^e(\mathbf{r}_1^e) = h^e(\mathbf{r}_1^e) + \sum_{a=1}^{N_r/2} \left[ 2J_b(\mathbf{r}_1^e) - K_b(\mathbf{r}_1^e) \right] + \frac{1}{\Gamma_S} \int \psi^{p*} \psi^{g*} \Omega_2 \psi^p \psi^g d\mathbf{r}^p d\mathbf{r}_s^e \quad (226)$$

$$f^p(\mathbf{r}^p) = \frac{1}{\Gamma_S} \left( \int \psi^{g*} \Omega_1 \psi^g d\mathbf{r}_s^e + 2 \sum_{a=1}^{N_r/2} \int \psi^{g*} \psi_a^{e*} \Omega_2 \psi^g \psi_a^e d\mathbf{r}_1^e d\mathbf{r}_s^e - E_G \int \psi^{g*} \psi^g d\mathbf{r}_s^e \right) \quad (227)$$

$$f^g(\mathbf{r}^p, \mathbf{r}_s^e) = \frac{1}{\Gamma_S} \left( \psi^{p*} \Omega_1 \psi^p + 2 \sum_{a=1}^{N_r/2} \int \psi^{p*} \psi_a^{e*} \Omega_2 \psi^p \psi_a^e d\mathbf{r}_1^e - E_G \psi^{p*} \psi^p \right) \quad (228)$$

## The Roothan Equations

Following again the procedure laid out by Roothan [65] where spatial basis functions are introduced allowing the integro-differential equations to be converted to algebraic equations that can be solved using an iterative approach of standard matrix techniques. We therefore introduce the following known basis functions and expand

the unknown orbitals in their respective linear expansion

$$\psi_i^e(\mathbf{r}_1^e) = \sum_{\mu_i}^{K_e} C_{\mu_i}^e \phi_{\mu}^e(\mathbf{r}_1^e) \quad i = 1, \dots, N_r \quad (229)$$

$$\psi^p(\mathbf{r}^p) = \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p(\mathbf{r}^p) \quad (230)$$

$$\psi^g(\mathbf{r}^p, \mathbf{r}^e) = \sum_{k=1}^{K_g} C_k^g \phi_k^g(\mathbf{r}^p, \mathbf{r}^e) \quad (231)$$

As before, each of these expansions are not exact due to the limitations of a finite basis set for computational reasons. If the sets  $\{\phi_{\mu}^e\}$ ,  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$  were complete then this would be an exact expansion of the spatial orbitals. Because of the finite basis sets used in Equations (229) through (231), the true eigenfunctions of the Fock operators can only be approximated within the spaces spanned by  $\{\phi_{\mu}^e\}$ ,  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$ .

### Hartree-Fock Equations.

The problem of calculating the basis function coefficients that provide the minimal energy is now a matter of substituting the linear expansion of the orbitals, Equation (229) through (231), into the Hartree-Fock equations, Equations (226) through (228).

$$f^e(\mathbf{r}_1^e) \sum_{\mu_i}^{K_e} C_{\mu_i}^e \phi_{\mu}^e(\mathbf{r}_1^e) = \varepsilon_{ei} \sum_{\mu_i}^{K_e} C_{\mu_i}^e \phi_{\mu}^e(\mathbf{r}_1^e), \quad i \in \{1, \dots, N_r\} \quad (232)$$

$$f^p(\mathbf{r}^p) \sum_{\ell=1}^{K_g} C_{\ell}^p \phi_{\ell}^p(\mathbf{r}^p) = \varepsilon_p \sum_{\ell=1}^{K_g} C_{\ell}^p \phi_{\ell}^p(\mathbf{r}^p) \quad (233)$$

$$f^g(\mathbf{r}^p, \mathbf{r}_s^e) \sum_{\nu'=1}^{K_p} C_{\nu'}^g \phi_{\nu'}^g(\mathbf{r}^p, \mathbf{r}_s^e) = \varepsilon_g \sum_{\nu'=1}^{K_p} C_{\nu'}^g \phi_{\nu'}^g(\mathbf{r}^p, \mathbf{r}_s^e) \quad (234)$$

Three coupled matrix equations can now be derived. The first is the matrix equation for the regular electron. This is done by multiplying Equation (232) on

the left by  $\phi_\mu^{e*}$  and integrating over the regular electron coordinates  $\mathbf{r}_1^e$ .

$$\sum_{\nu=1}^{K_e} C_{\nu i}^e \underbrace{\int \phi_\mu^{e*} f^e \phi_\nu^e d\mathbf{r}_1^e}_{F_{\mu\nu}^e} = \varepsilon_{ei} \sum_{\nu=1}^{K_e} C_{\nu i}^e \underbrace{\int \phi_\mu^{e*} \phi_\nu^e d\mathbf{r}_1^e}_{S_{\mu\nu}^e} \quad (235)$$

Next the positron matrix equation is derived by multiplying Equation (233) on the left by  $\phi_{\mu'}^{p*}$  and integrating over the positron coordinates  $\mathbf{r}^p$ .

$$\sum_{\nu'=1}^{K_p} C_{\nu'}^p \underbrace{\int \phi_{\mu'}^{p*} f^p \phi_{\nu'}^p d\mathbf{r}^p}_{F_{\mu'\nu'}^p} = \varepsilon_p \sum_{\nu'=1}^{K_p} C_{\nu'}^p \underbrace{\int \phi_{\mu'}^{p*} \phi_{\nu'}^p d\mathbf{r}^p}_{S_{\mu'\nu'}^p} \quad (236)$$

And finally, the matrix equation for  $f^g$  is derived by multiplying Equation (234) on the left by  $\phi_k^{g*}$  and integrating over the positron and regular electron coordinates,  $\mathbf{r}^p$  and  $\mathbf{r}_s^e$ .

$$\sum_{\ell=1}^{K_g} C_\ell^g \underbrace{\int \phi_k^{g*} f^g \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e}_{F_{k\ell}^g} = \varepsilon_g \sum_{\ell=1}^{K_g} C_\ell^g \underbrace{\int \phi_k^{g*} \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e}_{S_{k\ell}^g} \quad (237)$$

In these three equations there were elements for three overlap matrices defined. These  $\mathbf{S}^e$  for the regular electronic basis set  $\{\phi_\mu^e\}$ ,  $\mathbf{S}^p$  for the regular electronic basis set  $\{\phi_{\mu'}^p\}$ , and  $\mathbf{S}^g$  for the explicitly correlated basis set between the regular electron and the positron,  $\{\phi_k^g\}$ . With elements of these defined in Equations (235), (236), and (237) respectively. Each basis set is linearly independent but not normally orthogonal. This gives rise to off diagonal elements in the overlap matrix. In addition to this the elements of the Fock operator matrix for each respective basis set were also defined. The Fock operator matrices are  $\mathbf{F}^e$ ,  $\mathbf{F}^p$  and  $\mathbf{F}^g$  for the regular electron, positron and explicitly correlated positron and special electron orbital. Each of the matrices are Hermitian and have the following rank:  $\mathbf{S}^e$  and  $\mathbf{F}^e$  are  $K_e$ ,  $\mathbf{S}^p$  and  $\mathbf{F}^p$  are  $K_p$  and  $\mathbf{S}^g$

and  $\mathbf{F}^g$  are  $K_g$ .

With these definitions for  $\mathbf{F}^p$ ,  $\mathbf{S}^p$ ,  $\mathbf{F}^g$  and  $\mathbf{S}^g$  the integrated Hartree-Fock equations (110) and (105) can be written as

$$\sum_{\nu} \mathbf{F}^e \mathbf{C}_{\nu j}^e = \varepsilon_{pj} \sum_{\nu} \mathbf{S}^e \mathbf{C}_{\nu j}^e \quad j = 1, 2, \dots, K_g \quad (238)$$

$$\sum_{\nu'} \mathbf{F}^p \mathbf{C}_{\nu' j}^p = \varepsilon_{pj} \sum_{\nu'} \mathbf{S}^p \mathbf{C}_{\nu' j}^p \quad j = 1, 2, \dots, K_g \quad (239)$$

$$\sum_{\ell} \mathbf{F}^g \mathbf{C}_{\ell i}^g = \varepsilon_{gi} \sum_{\ell} \mathbf{S}^g \mathbf{C}_{\ell i}^g \quad i = 1, 2, \dots, K_p \quad (240)$$

These equations are the Roothan equations and can be written more succinctly as three coupled matrix equations.

$$\mathbf{F}^e \mathbf{C}^e = \mathbf{S}^e \mathbf{C}^e \boldsymbol{\varepsilon}_e \quad (241)$$

$$\mathbf{F}^p \mathbf{C}^p = \mathbf{S}^p \mathbf{C}^p \boldsymbol{\varepsilon}_p \quad (242)$$

$$\mathbf{F}^g \mathbf{C}^g = \mathbf{S}^g \mathbf{C}^g \boldsymbol{\varepsilon}_g \quad (243)$$

Where  $\mathbf{C}^e$ ,  $\mathbf{C}^p$  and  $\mathbf{C}^g$  are square coefficient expansion matrices each of rank  $K_e$ ,

$K_p$  and  $K_g$  respectively; and are defined as

$$\mathbf{C}^p = \begin{pmatrix} C_{11}^e & C_{12}^e & \cdots & C_{1K_e}^e \\ C_{21}^p & C_{22}^p & \cdots & C_{2K_e}^e \\ \vdots & \vdots & & \vdots \\ C_{K_e1}^p & C_{K_e2}^e & \cdots & C_{K_eK_e}^e \end{pmatrix} \quad (244)$$

(245)

$$\mathbf{C}^p = \begin{pmatrix} C_{11}^p & C_{12}^p & \cdots & C_{1K_p}^p \\ C_{21}^p & C_{22}^p & \cdots & C_{2K_p}^p \\ \vdots & \vdots & & \vdots \\ C_{K_p1}^p & C_{K_p2}^p & \cdots & C_{K_pK_p}^p \end{pmatrix} \quad (246)$$

(247)

$$\mathbf{C}^g = \begin{pmatrix} C_{11}^g & C_{12}^g & \cdots & C_{1K_g}^g \\ C_{21}^g & C_{22}^g & \cdots & C_{2K_g}^g \\ \vdots & \vdots & & \vdots \\ C_{K_g1}^g & C_{K_g2}^g & \cdots & C_{K_gK_g}^g \end{pmatrix} \quad (248)$$

and  $\boldsymbol{\varepsilon}_e$ ,  $\boldsymbol{\varepsilon}_p$  and  $\boldsymbol{\varepsilon}_g$  are diagonal matrices of the orbital energies  $\varepsilon_{ei}$ ,  $\varepsilon_{pi}$  and  $\varepsilon_{gi}$ .

$$\boldsymbol{\varepsilon}_e = \begin{pmatrix} \varepsilon_{e1} & & & \\ & \varepsilon_{e2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \varepsilon_{eK_e} \end{pmatrix} \quad (249)$$

$$\epsilon_p = \begin{pmatrix} \epsilon_{p1} & & & \\ & \epsilon_{p2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_{pK_p} \end{pmatrix} \quad (250)$$

$$\epsilon_g = \begin{pmatrix} \epsilon_{g1} & & & \\ & \epsilon_{g2} & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_{gK_g} \end{pmatrix}. \quad (251)$$

The next subsections will further expand on the development of the elements of each Fock matrix. For general details on the orthogonalization of the basis sets (page 148) and the SCF procedure (page 151) see Appendix B. The next primary section in this chapter will discuss the specif algorithm as implemented in FORTRAN to solve to find wave function for this system.

### **Density Matrices $\mathbf{P}^e$ , $\mathbf{P}^g$ and $\mathbf{P}^p$ .**

As with Ps, both  $\psi^g$  and  $\psi^p$  both have a single filled orbital and therefore Equation (33) is used for determining the density matrix with  $N = 1$  for both expansions so that

$$P_{\mu'\nu'}^p = C_{\mu'1}^p C_{\nu'1}^p \quad (252)$$

$$P_{k,\ell}^g = C_{k1}^g C_{\ell 1}^g \quad (253)$$

Given that the electron model is for RHF, the density matrix for the electrons is given by Equation (34).

$$P_{\mu\nu}^e = 2 \sum_a^{N_r/2} C_{\mu a}^e C_{\nu a}^e \quad (254)$$

### Expression for the Fock Matrices.

This section evaluates the expressions for the Fock matrix elements found in Equations (235), (236) and (237) using the Fock operators from (226), (227) and (228).

### Expression for the Fock Matrix: $F^e$ .

The Fock matrix  $F^e$  is the matrix representation of the Fock Operator  $f^e$  in the basis  $\{\phi_\mu^e\}$ .

$$F_{\mu_1, \nu_1}^e = \int \phi_{\mu_1}^{e*} f^e \phi_{\nu_1}^e d\mathbf{r}_1^e \quad (255)$$

$$= \int \phi_{\mu_1}^{e*} \left( h^e(\mathbf{r}_1^e) + \sum_{a=1}^{K_e/2} [2J_b(\mathbf{r}_1^e) - K_b(\mathbf{r}_1^e)] \right. \\ \left. + \frac{1}{S_{\text{CPEO}}} \int \psi^{p*} \psi^{g*} \Omega_2 \psi^p \psi^g d\mathbf{r}^p d\mathbf{r}_s^e \right) \phi_{\nu_1}^e d\mathbf{r}_1^e \quad (256)$$

$$= \int \phi_{\mu_1}^{e*} \left( h^e(\mathbf{r}_1^e) + \sum_{a=1}^{N_r/2} [2J_b(\mathbf{r}_1^e) - K_b(\mathbf{r}_1^e)] \right. \\ \left. + \frac{1}{S_{\text{CPEO}}} \int \sum_{\mu'=1}^{K_p} C_{\mu'}^{p*} \phi_{\mu'}^{p*} \sum_{k=1}^{K_g} C_k^{g*} \phi_k^{g*} \Omega_2 \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \sum_{\ell=1}^{K_g} C_\ell^g \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \right) \phi_{\nu_1}^e d\mathbf{r}_1^e \quad (257)$$

Where in the basis function approximation

$$S^{\text{CPEO}} = \langle \chi^g \chi^p | \chi^g \chi^p \rangle \quad (258)$$

$$= \left\langle \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^p \sum_{k=1}^{K_g} C_k^g \phi_k^g \middle| \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g \right\rangle \quad (259)$$

$$= \sum_{\mu', \nu'}^{K_p} C_{\mu'}^{p*} C_{\nu'}^p \sum_{k, \ell}^{K_g} C_k^{g*} C_{\ell}^g \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_{\ell}^g \rangle \quad (260)$$

$$= \sum_{\mu', \nu'}^{K_p} \sum_{k, \ell}^{K_g} P_{\mu', \nu'}^p P_{k, \ell}^g \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_{\ell}^g \rangle \quad (261)$$

Continuing now with the Fock matrix derivation  $F^e$ :

$$\begin{aligned} F_{\mu_1, \nu_1}^e &= \int \phi_{\mu_1}^{e*} h^e(\mathbf{r}_1^e) \phi_{\nu_1}^e d\mathbf{r}_1^e + \sum_{a=1}^{N_r/2} \int \phi_{\mu_1}^{e*} \left[ 2J_b(\mathbf{r}_1^e) - K_b(\mathbf{r}_1^e) \right] \phi_{\nu_1}^e d\mathbf{r}_1^e \\ &\quad + \frac{1}{S^{\text{CPEO}}} \sum_{\mu', \nu'} \sum_{k, \ell} P_{\mu', \nu'}^p P_{k, \ell}^g \int \phi_{\mu_1}^{e*} \phi_{\mu'}^{p*} \phi_k^{g*} \Omega_2 \phi_{\mu'}^p \phi_k^g \phi_{\nu_1}^e d\mathbf{r}^p d\mathbf{r}_s^e d\mathbf{r}_1^e \end{aligned} \quad (262)$$

$$\begin{aligned} &= \langle \phi_{\mu_1}^e | h^e(\mathbf{r}_1^e) | \phi_{\nu_1}^e \rangle \\ &\quad + \sum_{\mu_2, \nu_2} P_{\mu_2, \nu_2}^e \left[ \langle \phi_{\mu_1}^e \phi_{\nu_1}^e | \frac{1}{r_{12}} | \phi_{\mu_2}^e \phi_{\nu_2}^e \rangle - \frac{1}{2} \langle \phi_{\mu_1}^e \phi_{\mu_2}^e | \frac{1}{r_{12}} | \phi_{\nu_2}^e \phi_{\nu_1}^e \rangle \right] \\ &\quad + \frac{1}{S^{\text{CPEO}}} \sum_{\mu', \nu'} \sum_{k, \ell} P_{\mu', \nu'}^p P_{k, \ell}^g \langle \phi_{\mu_1}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\nu'}^p \phi_k^g \phi_{\nu_1}^e \rangle \end{aligned} \quad (263)$$

$$\begin{aligned} &= H_{\mu_1, \nu_1}^{\text{core}} + \sum_{\mu_2, \nu_2} P_{\mu_2, \nu_2}^e \left[ \Gamma_{ee}^J(\mu_1, \nu_1; \mu_2, \nu_2) - \frac{1}{2} \Gamma_{ee}^K(\mu_1, \nu_1; \mu_2, \nu_2) \right] \\ &\quad + \frac{1}{S^{\text{CPEO}}} \sum_{k\ell} \sum_{\mu' \nu'} P_{k, \ell}^g P_{\mu' \nu'}^p \Gamma_2(\mu', \nu'; k, \ell; \mu_1, \nu_1) \end{aligned} \quad (264)$$



Where the basis set integrals in Equation (264) are

$$H_{\mu_1, \nu_1}^{\text{core}} \equiv \langle \phi_{\mu_1}^e | h^e(\mathbf{r}_1^e) | \phi_{\nu_1}^e \rangle \quad (265)$$

$$\Gamma_{ee}^J(\mu_1, \nu_1; \mu_2, \nu_2) \equiv \langle \phi_{\mu_1}^e \phi_{\nu_1}^e | \frac{1}{r_{12}} | \phi_{\mu_2}^e \phi_{\nu_2}^e \rangle \quad (266)$$

$$\Gamma_{ee}^K(\mu_1, \nu_1; \mu_2, \nu_2) \equiv \langle \phi_{\mu_1}^e \phi_{\mu_2}^e | \frac{1}{r_{12}} | \phi_{\nu_2}^e \phi_{\nu_1}^e \rangle \quad (267)$$

$$\Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) \equiv \langle \phi_{\mu'}^e \phi_{\nu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle \quad (268)$$

$$S^{\text{CPEO}} = \sum_{\mu', \nu'}^{K_p} \sum_{k, \ell}^{K_g} P_{\mu', \nu'}^p P_{k, \ell}^g \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_{\ell}^g \rangle \quad (269)$$

Equation (264) is the final form for the regular electron Fock matrix.

### Expression for the Fock Matrix: $\mathbf{F}^p$ .

The Fock matrix  $F^p$  is the matrix representation of the Fock Operator  $f^p$  in the basis  $\{\phi_{\mu'}^p\}$ .

$$F_{\mu', \nu'}^p = \int \phi_{\mu'}^{p*} f^p \phi_{\nu'}^p d\mathbf{r}^p \quad (270)$$

$$\begin{aligned} &= \frac{1}{S^{\text{CPEO}}} \int \phi_{\mu'}^{p*} \left( \int \psi^{g*} \Omega_1 \psi^g d\mathbf{r}_s^e + 2 \sum_{a=1}^{N_r/2} \int \psi^{g*} \psi_a^{e*} \Omega_2 \psi^g \psi_a^e d\mathbf{r}_1^e d\mathbf{r}_s^e \right. \\ &\quad \left. - E_G \int \psi^{g*} \psi^g d\mathbf{r}_s^e \right) \phi_{\nu'}^p d\mathbf{r}^p \end{aligned} \quad (271)$$

$$\begin{aligned} &= \frac{1}{S^{\text{CPEO}}} \int \phi_{\mu'}^{p*} \left( \int \sum_{k=1}^{K_g} C_k^{g*} \phi_k^{g*} \Omega_1 \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g d\mathbf{r}_s^e \right. \\ &\quad + 2 \sum_{a=1}^{N_r/2} \int \sum_{k=1}^{K_g} C_k^{g*} \phi_k^{g*} \sum_{\mu_a}^{K_e} C_{\mu_a}^{e*} \phi_{\mu_a}^{e*} \Omega_2 \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g \sum_{\nu_a}^{K_e} C_{\nu_a}^e \phi_{\nu_a}^e d\mathbf{r}_1^e d\mathbf{r}_s^e \\ &\quad \left. - E_G \int \sum_{k=1}^{K_g} C_k^{g*} \phi_k^{g*} \sum_{\ell=1}^{K_g} C_{\ell}^g \phi_{\ell}^g d\mathbf{r}_s^e \right) \phi_{\nu'}^p d\mathbf{r}^p \end{aligned} \quad (272)$$

Where  $S^{\text{CPEO}}$  is now the basis function approximation as given by Equation (261).

$$\begin{aligned}
F_{\mu', \nu'}^p &= \frac{1}{S^{\text{CPEO}}} \int \phi_{\mu'}^{p*} \left( \sum_{k, \ell} P_{k, \ell}^g \int \phi_k^{g*} \Omega_1 \phi_\ell^g d\mathbf{r}_s^e \right. \\
&\quad + \sum_{k, \ell} \sum_{\mu, \nu} P_{k, \ell}^g P_{\mu, \nu}^e \int \phi_k^{g*} \phi_\mu^{e*} \Omega_2 \phi_\ell^g \phi_\nu^e d\mathbf{r}_1^e d\mathbf{r}_s^e \\
&\quad \left. - E_G \sum_{k, \ell} P_{k, \ell}^g \int \phi_k^{g*} \phi_\ell^g d\mathbf{r}_s^e \right) \phi_{\nu'}^p d\mathbf{r}^p \quad (273)
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{S^{\text{CPEO}}} \left( \sum_{k, \ell} P_{k, \ell}^g \int \phi_{\mu'}^{p*} \phi_k^{g*} \Omega_1 \phi_{\nu'}^p \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \right. \\
&\quad + \sum_{k, \ell} \sum_{\mu, \nu} P_{k, \ell}^g P_{\mu, \nu}^e \int \phi_\mu^{e*} \phi_{\mu'}^{p*} \phi_k^{g*} \Omega_2 \phi_\nu^e \phi_{\nu'}^p \phi_\ell^g d\mathbf{r}_1^e d\mathbf{r}^p d\mathbf{r}_s^e \\
&\quad \left. - E_G \sum_{k, \ell} P_{k, \ell}^g \int \phi_{\mu'}^{p*} \phi_k^{g*} \phi_{\nu'}^p \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \right) \quad (274)
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{S^{\text{CPEO}}} \left( \sum_{k, \ell} P_{k, \ell}^g \Gamma_1(\mu', \nu'; k, \ell) + \sum_{k, \ell} \sum_{\mu, \nu} P_{k, \ell}^g P_{\mu, \nu}^e \Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) \right. \\
&\quad \left. - E_G \sum_{k, \ell} P_{k, \ell}^g \Gamma_{1s}(\mu', \nu'; k, \ell) \right) \quad (275)
\end{aligned}$$

Where the new basis set integrals introduced in Equation (275) are

$$\Gamma_1(\mu', \nu'; k, \ell) \equiv \langle \phi_{\mu'}^p \phi_k^g | \Omega_1 | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (276)$$

$$\Gamma_{1s}(\mu', \nu'; k, \ell) \equiv \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (277)$$

Equation (275) is the final form for the positronic Fock matrix.

### Expression for the Fock Matrix: $\mathbf{F}^g$ .

The Fock matrix  $F^g$  is the matrix representation of the Fock Operator  $f^g$  in the basis  $\{\phi_k^g\}$ .

$$F_{\mu', \nu'}^g = \int \phi_k^{g*} f^g \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \quad (278)$$

$$= \frac{1}{S^{\text{CPEO}}} \int \phi_k^{g*} \left( \psi^{p*} \Omega_1 \psi^p + 2 \sum_{a=1}^{N_r/2} \int \psi^{p*} \psi_a^{e*} \Omega_2 \psi^p \psi_a^e d\mathbf{r}_1^e \right. \\ \left. - E_G \psi^{p*} \psi^p \right) \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \quad (279)$$

$$= \frac{1}{S^{\text{CPEO}}} \int \phi_k^{g*} \left( \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^{p*} \Omega_1 \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \right. \\ + 2 \sum_{a=1}^{N_r/2} \int \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^{p*} \sum_{\mu_a}^{K_e} C_{\mu_a}^e \phi_{\mu_a}^{e*} \Omega_2 \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \sum_{\nu_a}^{K_e} C_{\nu_a}^e \phi_{\nu_a}^e d\mathbf{r}_1^e \\ \left. - E_G \sum_{\mu'=1}^{K_p} C_{\mu'}^p \phi_{\mu'}^{p*} \sum_{\nu'=1}^{K_p} C_{\nu'}^p \phi_{\nu'}^p \right) \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \quad (280)$$

Where  $S^{\text{CPEO}}$  is now the basis function approximation as given by Equation (261).

$$F_{\mu', \nu'}^g = \frac{1}{S^{\text{CPEO}}} \left( \sum_{\mu', \nu'} P_{\mu', \nu'}^p \int \phi_k^{g*} \phi_{\mu'}^{p*} \Omega_1 \phi_\ell^g \phi_{\nu'}^p d\mathbf{r}^p d\mathbf{r}_s^e \right. \\ + \sum_{\nu, \mu} \sum_{\nu', \mu'} P_{\nu, \mu}^e P_{\mu', \nu'}^p \int \phi_\mu^{e*} \phi_{\mu'}^{p*} \phi_k^{g*} \Omega_2 \phi_\nu^e \phi_{\nu'}^p \phi_\ell^g d\mathbf{r}_1^e d\mathbf{r}^p d\mathbf{r}_s^e \\ \left. - E_G \sum_{\mu', \nu'} P_{\mu', \nu'}^p \int \phi_{\mu'}^{p*} \phi_k^{g*} \phi_{\nu'}^p \phi_\ell^g d\mathbf{r}^p d\mathbf{r}_s^e \right) \quad (281)$$

$$= \frac{1}{S^{\text{CPEO}}} \left( \sum_{\mu', \nu'} P_{\mu', \nu'}^p \Gamma_1(\mu', \nu'; k, \ell) \sum_{\nu, \mu} \sum_{\nu', \mu'} P_{\nu, \mu}^e P_{\mu', \nu'}^p \Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) \right. \\ \left. - E_G \sum_{\mu', \nu'} P_{\mu', \nu'}^p \Gamma_{1s}(\mu', \nu'; k, \ell) \right) \quad (282)$$

All the integrals presented in the final form for the  $\mathbf{F}^g$  in Equation (282) were previously defined.

## Summary: Matrix Representation of Fock Operators

This section is to aggregate the Fock Operators along with definitions for each element of the operators. There is no new information presented here. The three Fock operators  $\mathbf{F}^e$ ,  $\mathbf{F}^p$  and  $\mathbf{F}^g$  have matrix elements

$$F_{\mu,\nu}^e = H_{\mu_1,\nu_1}^{\text{core}} + \sum_{\mu_2,\nu_2} P_{\mu_2,\nu_2}^e \left[ \Gamma_{ee}^J(\mu_1, \nu_1; \mu_2, \nu_2) - \frac{1}{2} \Gamma_{ee}^K(\mu_1, \nu_1; \mu_2, \nu_2) \right] + \frac{1}{S_{\text{CPEO}}} \sum_{k\ell} \sum_{\mu'\nu'} P_{k,\ell}^g P_{\mu'\nu'}^p \Gamma_2(\mu', \nu'; k, \ell; \mu_1, \nu_1) \quad (283)$$

$$F_{\mu',\nu'}^p = \frac{1}{S_{\text{CPEO}}} \left( \sum_{k,\ell} P_{k,\ell}^g \Gamma_1(\mu', \nu'; k, \ell) + \sum_{k,\ell} \sum_{\mu,\nu} P_{k,\ell}^g P_{\mu,\nu}^e \Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) - E_G \sum_{k,\ell} P_{k,\ell}^g \Gamma_{1s}(\mu', \nu'; k, \ell) \right) \quad (284)$$

$$F_{k,\ell}^g = \frac{1}{S_{\text{CPEO}}} \left( \sum_{\mu',\nu'} P_{\mu',\nu'}^p \Gamma_1(\mu', \nu'; k, \ell) + \sum_{\nu,\mu} \sum_{\nu',\mu'} P_{\nu,\mu}^e P_{\mu',\nu'}^p \Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) - E_G \sum_{\mu',\nu'} P_{\mu',\nu'}^p \Gamma_{1s}(\mu', \nu'; k, \ell) \right) \quad (285)$$

Where the definitions for the integrals and terms are

$$H_{\mu_1, \nu_1}^{\text{core}} = \langle \phi_{\mu_1}^e | h^e(\mathbf{r}_1^e) | \phi_{\nu_1}^e \rangle \quad (286)$$

$$\Gamma_{ee}^J(\mu_1, \nu_1; \mu_2, \nu_2) = \langle \phi_{\mu_1}^e \phi_{\nu_1}^e | \frac{1}{r_{12}} | \phi_{\mu_2}^e \phi_{\nu_2}^e \rangle \quad (287)$$

$$\Gamma_{ee}^K(\mu_1, \nu_1; \mu_2, \nu_2) = \langle \phi_{\mu_1}^e \phi_{\mu_2}^e | \frac{1}{r_{12}} | \phi_{\nu_2}^e \phi_{\nu_1}^e \rangle \quad (288)$$

$$\Gamma_1(\mu', \nu'; k, \ell) = \langle \phi_{\mu'}^p \phi_k^g | \Omega_1 | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (289)$$

$$\Gamma_{1s}(\mu', \nu'; k, \ell) = \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_\ell^g \rangle \quad (290)$$

$$\Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) = \langle \phi_\mu^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_\nu^e \rangle \quad (291)$$

$$S^{\text{CPEO}} = \sum_{\mu' \nu'} \sum_{k \ell} P_{\mu' \nu'}^p P_{k, \ell}^g \Gamma_{1s}(\mu', \nu'; k, \ell) \quad (292)$$

$$E_{G1} = \frac{1}{S^{\text{CPEO}}} \sum_{\mu' \nu'} \sum_{k \ell} P_{\mu' \nu'}^p P_{k, \ell}^g \Gamma_1(\mu', \nu'; k, \ell) \quad (293)$$

$$E_{G2} = \frac{1}{S^{\text{CPEO}}} \sum_{\mu \nu} \sum_{\mu' \nu'} \sum_{k \ell} P_{\mu \nu}^e P_{\mu' \nu'}^p P_{k, \ell}^g \Gamma_2(\mu', \nu'; k, \ell; \mu, \nu) \quad (294)$$

$$E_G = E_{G1} + E_{G2} \quad (295)$$

## Basis Functions

The basis functions to be used in the SCF procedure are the GTFs described in Chapter IV by Equations (39) and (45), repeated here.

$$\phi_\mu^e = x_A^{\ell_i^e} y_A^{m_i^e} z_A^{n_i^e} e^{-\alpha_{\mu'}(r_A^e)^2} \quad (296)$$

$$= (x_A^{\ell_i^e} e^{-\alpha_{\mu'}(x_A^e)^2}) (y_A^{m_i^e} e^{-\alpha_{\mu'}(y_A^e)^2}) (z_A^{n_i^e} e^{-\alpha_{\mu'}(z_A^e)^2}) \quad (297)$$

$$\phi_{\mu'}^p = x_A^{\ell_i^p} y_A^{m_i^p} z_A^{n_i^p} e^{-\alpha_{\mu'}(r_A^p)^2} \quad (298)$$

$$= (x_A^{\ell_i^p} e^{-\alpha_{\mu'}(x_A^p)^2}) (y_A^{m_i^p} e^{-\alpha_{\mu'}(y_A^p)^2}) (z_A^{n_i^p} e^{-\alpha_{\mu'}(z_A^p)^2}) \quad (299)$$

and

$$\phi_\ell^g = e^{-\alpha_\ell(r_s^e - r^p)^2_A} \quad (300)$$

$$= (e^{-\alpha_\ell(x_s^e - x^p)^2})(e^{-\alpha_\ell(y_s^e - y^p)^2})(e^{-\alpha_\ell(z_s^e - z^p)^2}) \quad (301)$$

## The SCF Procedure

With the integrals defined and the various matrices built from the integrals established, it is time to present the computational process used in computing the energy. Figure 12 presents an overview of programming the SCF procedure that will be explained in this section.

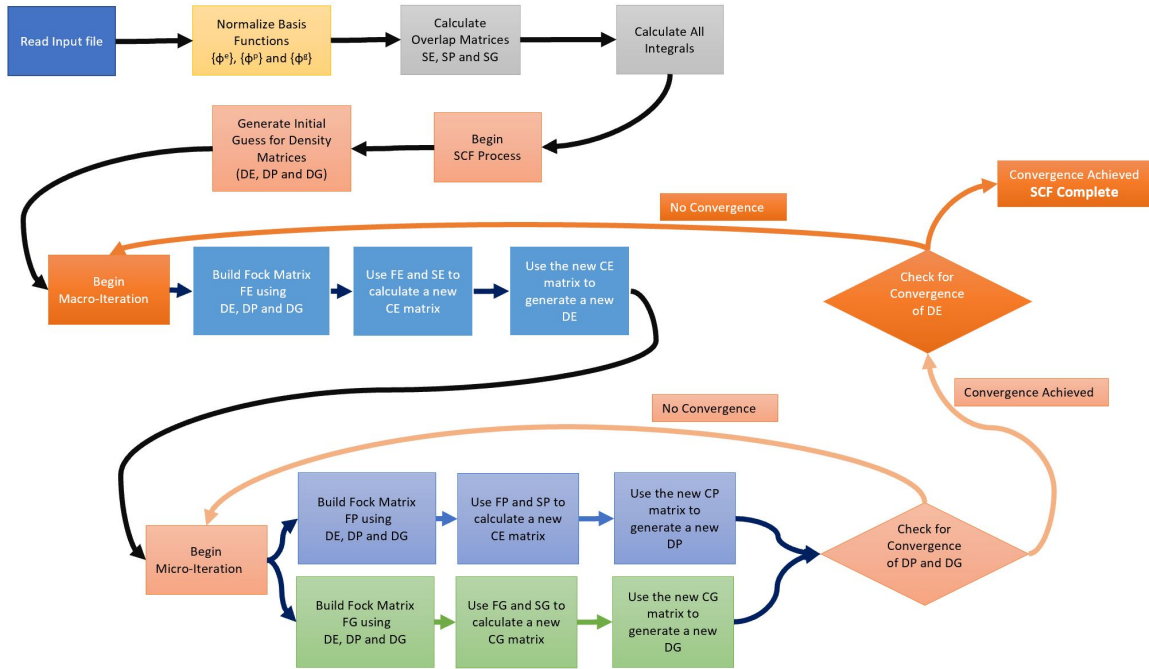


Figure 12. The SCF procedure for calculating the minimum energy for CPEO implementation.

1. Read input
2. Find the Norm for each basis function in  $\{\phi_\mu^e\}$ ,  $\{\phi_{\mu'}^p\}$  and  $\{\phi_k^g\}$ .

3. Calculate the overlap integrals to form the overlap matrices SE, SP and SG as given in Equations (235), (236) and (237). The number of integrals calculated in this step is  $K_e^2 + K_p^2 + K_g^2$
4. Calculate all integrals in Equations (286) through (291). These are the only integrals that will be needed for building the Fock matrices. The number of integrals to be calculated in this step are on the order of  $(K_e)^2(K_p)^2(K_g)^2$ . One for each element of the Hamiltonian in Equation (64)
5. Begin the SCF procedure:
6. Generate initial density matrices DE, DP and DG.
7. Begin Macro-iterations
  - (a) Build Fock matrix FE using DE, DP and DG.
  - (b) Solve the Roothan Equation (241) using FE and SE to get a new CE matrix.
  - (c) Use the new CE matrix to generate a new DE matrix.
  - (d) Begin Micro-iterations
    - i. Build Fock matrices FP and FG using DE, DP and DG.
    - ii. Solve the Roothan Equations (242) and (243) to get a new CP and CG matrices.
    - iii. Use new CP and CG matrices to generate new DP and DG matrices.
    - iv. Determine whether the procedure has converged for DP and DG matrices. If no then repeat micro-iteration using updated DP and DG matrices. If yes then exit micro-iteration.

- (e) Determine whether the procedure has converged for the DE matrix. If no then repeat macro-iteration using updated DE, DP and DG matrices. If yes then exit macro-iteration.

8. SCF procedure complete.

## Annihilation Rate

Using the wavefunction ansatz for  $\Psi^{\text{CPEO}}$ ,

$$\Psi^{\text{CPEO}} = \Phi_0^e(\mathbf{r}^e)\psi^p(\mathbf{r}^p)\psi^g(\mathbf{r}^p, \mathbf{r}^s) \quad (302)$$

and the general 2-photon annihilation rate Equation (62),

$$\lambda_{2\gamma} = 4\pi r_0^2 c \frac{\left\langle \Psi_0 \left| \sum_{i=1}^{N_r} \delta(\mathbf{r}_i^e - \mathbf{r}^p) \right| \Psi_0 \right\rangle}{\langle \Psi_0 | \Psi_0 \rangle} \quad (303)$$

so that

$$\lambda_{2\gamma}^{\text{CPEO}} = \frac{4\pi r_0^2 c}{s^{\text{CPEO}}} \int (\Psi^{\text{CPEO}})^* \left[ \delta(\mathbf{r}^s - \mathbf{r}^p) + \sum_{k=1}^{N_r} \delta(\mathbf{r}_k^e - \mathbf{r}^p) \right] \Psi^{\text{CPEO}} d\mathbf{r}^e d\mathbf{r}^p d\mathbf{r}^s \quad (304)$$

$$= \lambda_{\text{se}} + \lambda_{\text{re}} \quad (305)$$

where  $d\mathbf{r}^e = d\mathbf{r}_1^e d\mathbf{r}_2^e \cdots d\mathbf{r}_{N_r}^e$  and

$$\lambda_{\text{se}} = \frac{4\pi r_0^2 c}{s^{\text{CPEO}}} \int \Psi^{\text{CPEO}} \left[ \delta(\mathbf{r}^s - \mathbf{r}^p) \right] \Psi^{\text{CPEO}} d\mathbf{r}^e d\mathbf{r}^p d\mathbf{r}^s \quad (306)$$

$$\lambda_{\text{re}} = \frac{4\pi r_0^2 c}{s^{\text{CPEO}}} \int \Psi^{\text{CPEO}} \left[ \sum_{k=1}^{N_r} \delta(\mathbf{r}_k^e - \mathbf{r}^p) \right] \Psi^{\text{CPEO}} d\mathbf{r}^e d\mathbf{r}^p d\mathbf{r}^s \quad (307)$$



where the complex conjugate has been dropped due to the pure real functions used in our basis set expansion for the spatial orbitals.  $\lambda_{se}$  is the annihilation term that is associated with the positron and special electron while  $\lambda_{re}$  is the annihilation term associated with the positron and the regular electrons. Since the bulk of the annihilation rate contribution is expected to come from the special electron, only this integral has been calculated thus far.

### Annihilation with the Special Electron.

The  $\lambda_{se}$  can be rewritten as follows:

$$\lambda_{se} = 4\pi r_0^2 c \frac{\left\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \left| \delta(\mathbf{r}^e - \mathbf{r}^p) \right| \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \right\rangle}{\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) | \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \rangle} \langle \Phi_0^e(\mathbf{r}^e) | \Phi_0^e(\mathbf{r}^e) \rangle \quad (308)$$

$$= 4\pi r_0^2 c \frac{\left\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \left| \delta(\mathbf{r}^e - \mathbf{r}^p) \right| \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \right\rangle}{\langle \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) | \psi^p(\mathbf{r}^p) \psi^g(\mathbf{r}^e, \mathbf{r}^p) \rangle} \quad (309)$$

This is the same annihilation rate derived in Chapter V for Ps in Equations (148) through (154). With result from (156)

$$\lambda_{se} = \frac{4\pi r_0^2 c}{S^{\text{Ps}}} \sum_{k,\ell}^{K_g} P_{k\ell}^g \quad (310)$$

Equation (310) will be used for calculation of the annihilation rate for CPEO. The rate will knowingly be smaller than actual rate for the CPEO ansatz as the regular electron annihilation is greater than zero.

## Results

With the theory for CPEO now fully developed a model was implemented for a first show as a proof of concept. This section introduces specifics of the model implementation and then presents results from the model.

## Model Implementation.

The CPEO calculations were implemented using the integration techniques developed from a working NEO-RXCHF-ne model. The explicit correlation in the virtual Ps orbital requires the calculation of multi-particle integrals. The NEO-RXCHF suite of methods implemented efficient and fast integration techniques based on Rys polynomials [10, 42]. The assistance brought to developing a working CPEO model by the leveraging of efficient integration and framework developed in the NEO-RXCHF suite of methods can not be understated.

The RXCHF-ne method had a wavefunction orbital structure similar enough to CPEO. In addition, the presence of the Gaussian type Geminal in the wavefunction ansatz meant that the model could be adapted for modeling CPEO. The wavefunction form for NEO-RXCHF-ne is as follows:

$$\Psi^{\text{R-ne}} = \chi^p(\mathbf{x}^p) \chi_s^e(\mathbf{x}_s^e) g(\mathbf{r}_s^e, \mathbf{r}^p) \Phi_{\text{R-ne}}^e(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_r}^e) \quad (311)$$

where  $g$  is the GTG functions given by

$$g(\mathbf{r}_s^e, \mathbf{r}^p) = \sum_k^{N_{gem}} b_k \exp[-\gamma_k |\mathbf{r}_s^e - \mathbf{r}^p|^2]. \quad (312)$$

The regular electronic integrals for the two system are the same the remaining three

integrals from NEO-RXCHF-ne had to be transformed to those needed for CPEO.

$$\langle \phi_{\mu}^p \phi_{\mu''}^s | g^2 | \phi_{\nu'}^p \phi_{\nu''}^s \rangle \implies \langle \phi_{\mu}^p \phi_k^g | \phi_{\nu'}^p \phi_{\ell}^g \rangle \quad (313)$$

$$\langle \phi_{\mu}^p \phi_{\mu''}^s | g \Omega_1 g | \phi_{\nu'}^p \phi_{\nu''}^s \rangle \implies \langle \phi_{\mu}^p \phi_k^g | \Omega_1 | \phi_{\nu'}^p \phi_{\ell}^g \rangle \quad (314)$$

$$\langle \phi_{\mu}^e \phi_{\mu'}^p \phi_{\mu''}^s | g \Omega_2 g | \phi_{\nu}^e \phi_{\mu'}^p \phi_{\nu''}^s \rangle \implies \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle \quad (315)$$

$$(316)$$

An outline of the main steps taken to build a CPEO model from NEO-RXCHF-ne is as follows.

1. Develop the  $\phi^g$  basis functions from the Geminal Gaussian functionality of RXCHF-ne.
2. Build the CPEO integrals from the existing RXCHF-ne integral routines.
3. Re-code the SCF procedure to build new Fock operators and optimize the coefficients for the basis functions approximating  $\psi^g$ .
4. Input file update for functionality of CPEO basis functions.
5. Re-write main file program to read the new input file, run new integral routines and the new SCF procedure.

### **The Closed Shell restriction for Regular Electrons.**

The theory developed in this chapter restricts the number of regular electrons in the system to be either  $N - r = 1$  or that  $N_r$  be even. Thus a system needs to have a single electron in its outer shell so that the incoming positron can form Ps with the valence electron. An example of this is  $\text{Li} + e^+ \rightarrow e^+ \text{Li}$  or  $\text{PsLi}^+$ . Here Li has 3 electrons and gives up a single electron to form Ps.  $\text{Li}^+$  then has the required 2 regular electrons. The other possibility to model a closed shell system is one where

with Ps joins an already closed shell system. In this case the special electron and the positron are both additions to the base system. A first example of this would be  $\text{Be} + \text{Ps} \rightarrow \text{PsBe}$ . Where Be comes with its four electrons that meet the requirements for an even number of regular electrons. A second example is PsH where H keeps its single electron as the only regular electron.

### **Basis set selection.**

In CPEO there are three type of Orbitals that will be approximated with a finite number of basis functions. Both the electronic and positronic basis functions follow the form put forth in Equations (39) for Gaussian primitives. The electronic basis functions have the additional advantage of using contracted basis sets. The virtual Ps basis set uses a Gaussian type Geminal as introduced in Equation (45).

### **The PsH System.**

PsH is the simplest systems containing positron that has been shown to bind. This system was modeled using the CPEO technique as laid out. calculations were performed using the aug-pcseg-2 electronic basis set [7s3p2d] which has 28 primitive basis functions and 25 contracted basis functions. The basis functions for the positron and virtual Ps calculations were each made up of 10s even tempered basis functions. Table 8 shows results for CPEO compared with SVM and NEO-HF. SVM method is included to be used as a benchmark and is the only system of the three listed that predicts binding. NEO-HF results are also included to provide a comparison to a mean field approach.

In each of the CPEO evaluations provided, the CPU evaluation time is provided for future reference. The calculation were done on an HPE SGI 8600 system located at the Air Force Research Laboratory (AFRL) DoD Super-computing Resource Center

	CPEO	SVM [57, 85]	NEO-HF[2, 85]
Energy:			
H-core	-0.4999		
virtual-Ps	-0.2473		
Interaction	-3.86E-5		
Total	-0.74725	-0.7892	-0.6669
$\langle\delta_{ep}\rangle$ (Bohr $^{-3}$ )	0.4645	0.0489754	0.0032
$\lambda_s$ (10 $^9$ s $^{-1}$ )	93.78	9.8871	0.646
Evaluation time (s)			
Integrals	63.5		
SCF Process	16.8		
Total	80.3		

**Table 8.** Quantities calculated are for PsH. The energy is given in Hartree, electron-positron density,  $\langle\delta_{ep}\rangle$ , is in  $a_o^3$  and the annihilation rate is for singlet annihilation (para-Ps) in ns $^{-1}$ . CPEO method used a 7s3p2d basis set for the electronic basis functions, 10s even tempered positronic ( $e^+$ ) basis functions and 10s even tempered Ps basis functions. The SVM method used 1800 basis functions. NEO-HF used a 6s3p1d basis set.

(DCRC). The code was executed in parallel using a single node with 24 cores.

In all the runs using CPEO the positron orbital,  $\chi^g$ , is dominated by the most diffuse basis function. This leads to a system that is not bound. The total energy for the system is nearly the total of the lone Ps and H atoms combined. The Interaction row in Table 8 is the net energy contribution for the Coulomb potential between the two systems. This potential is negative although very small, suggesting that although the system is unbound there is still some attractive Coulomb force between the Ps and H atom. The dominance of the diffuse orbital for the positron also occurred in NEO-HF and NEO-CI which also did not predict binding of the systems [10].

The special electron singlet annihilation rate is roughly 10 times larger than the singlet annihilation rate for PsH using SVM. This suggests that the correlation within virtual Ps has been captured using the Ps orbital and that since the electron cannot act outside the confines of the completely correlated orbital the probability of finding the electron and the positron in the same location occurs with much greater probability. This is the opposite problem that was encountered with NEO-HF where there

was no Coulomb correlation and the electron and positron did not find each other. This resulted in a low contact density and annihilation rate using NEO-HF.

### **CPEO applied to larger system.**

In this section the CPEO model is run on  $e^+\text{Li}$  and  $e^+\text{Na}$ . Both of these systems will give its outer valence electron to form Ps with the positron. For each system there were three different electronic basis sets used aug-pcseg-0, aug-pcseg-1, and aug-pcseg-2. To reduce the ability of the positron (and therefore the virtual Ps) the basis functions for the positron will be limited to the s-orbitals associated with each of the electronic basis sets. The intent is to keep the virtual Ps in the vicinity of the ionized atom. The basis set for the virtual Ps will be the 10s even tempered basis functions used previously in the Ps and PsH examples used previously.

All of the systems modeled did not show binding using the CPEO method. In the tables below is included a binding energy. In the systems modeled using CPEO as implemented the decay pathway is



Following this pathway the binding energies (BE) are calculated as

$$\text{BE} = E(e^+A) - E(\text{Ps}) - E(A^+) \quad (318)$$

where  $E(X)$  is the energy of species X.

The annihilation rates shown are for the two-photon singlet electron-positron (para-Ps) annihilation. For CPEO the singlet annihilation rate given for with the special electron only. This was defined in Equation (310).

### **The $e^+\text{Li}$ System.**

In modeling the  $e^+\text{Li}$  the three electronic basis sets have the following orbitals: aug-pcseg-0 7s2p, aug-pcseg-1 9s4p, aug-pcseg-2 12s5p2d. With positronic basis sets made of the corresponding s orbitals only associated with each basis set. The Ps basis set was fixed at 10s for each run.

Table 9 gives the results for each of the three runs. The total energy decreased slightly with the larger basis sets. This was primarily a result of better electronic energy associated with the  $\text{Li}^+$  core. The virtual-Ps energy in aug-pcseg-0 run is the highest and was due primarily to an increase in the kinetic energy of the positron. None of the three systems showed binding. It is worth noting though that the dominant orbital for the positron was not the most diffuse orbital for both the aug-pcseg-1 and aug-pcseg-2 runs. When a very diffuse orbital was added to the system the positron density was dominated by this orbital.

The annihilation rate for each of the three runs was more than 10-times too large, similar to the  $\text{PsH}$  system and Ps results already discussed. An observation that can be made and will hold is that the annihilation rate for each system modeled remained 93 /ns. This again suggests that the rigid nature of the virtual Ps orbital does not allow for the variation that the system needs to occur. Also, in the CPEO system as implemented there is little to no basis function allowance for the special electron or positron to move outside of the completely correlated Ps orbital.

### **The $e^+\text{Na}$ System.**

In modeling the  $e^+\text{Na}$ , the three electronic basis sets have the following orbitals: aug-pcseg-0 10s6p, aug-pcseg-1 13s8p, aug-pcseg-2 16s10p2d. The positronic basis sets are from the corresponding s orbitals only as associated with each basis set. The Ps basis set was fixed at 10s for each run.

	aug-pceg-0	aug-pceg-1	aug-pceg-2	SVM[70, 77]
Basis Functions:				
$e^-$ Primitive	16	21	39	
$e^-$ Contracted	10	13	20	
Positron	7	9	12	
Ps - GTGs	10	10	10	
Energy:				
Li <sup>+</sup> -core	-7.224	-7.232	-7.235	
virtual-Ps	-0.2280	-0.2364	-0.2381	
Interaction	-2.82E-3	1.38E-3	1.10E-3	
Total	-7.449	-7.467	-7.472	-7.53208
Binding Energy	-1.18E-4	-8.9E-5	-5.0E-5	0.00217
$\langle\delta_{ep}\rangle$ (Bohr <sup>-3</sup> )	0.458	0.461	0.459	0.034698
$\lambda_s$ (10 <sup>9</sup> s <sup>-1</sup> )	92.62	93.07	92.60	6.9956
Evaluation time (s)				
Integrals	2.8	7.3	129.3	
SCF Process	7.0	20.4	86.6	
Total	9.8	27.7	215.9	

**Table 9.** Quantities calculated are for  $e^+\text{Li}$ . The energy is given in Hartree, electron-positron contact density,  $\langle\delta_{ep}\rangle$ , is in  $a_o^3$  and the annihilation rate is for singlet annihilation (para-Ps) in ns<sup>-1</sup>.

Table 10 gives the results for each of the three runs. The total energy decreased slightly with the larger basis sets. The decrease was again primarily a result of better electronic energy associated with the Li+ core. The virtual-Ps energy remained relatively constant in each of the three runs. None of the three systems showed binding and the positron orbital was dominated by the most diffuse orbital for each run. The contact density and therefore the annihilation rate follows the same pattern that has already been laid out.



	aug-pceg-0	aug-pceg-1	aug-pceg-2	FCSVM [70, 73]
Basis Functions:				
$e^-$ Primitive	28	37	58	
$e^-$ Contracted	14	14	30	
Positron	10	13	16	
Ps - GTGs	10	10	10	
Energy:				
Na <sup>+</sup> -core	-161.455	-161.653	-161.666	
virtual-Ps	-0.2326	-0.2385	-0.2398	
Interaction	8.01E-4	6.04E-4	5.26E-4	
Total	-161.6913	-161.8911	-161.9055	
Binding Energy	(0.0032)	(0.0025)	(0.0021)	1.61E-4
$\langle\delta_{ep}\rangle$ (Bohr <sup>-3</sup> )	0.4606	0.4613	0.4617	0.03846
$\lambda_s$ (10 <sup>9</sup> s <sup>-1</sup> )	92.99	93.13	93.20	7.764
Evaluation time (s)				
Integrals	18.5	48.9	403	
SCF Process	17.5	52.6	271	
Total	35.0	101.5	674	

**Table 10.** Quantities calculated are for  $e^+\text{Na}$ . The energy is given in Hartree, electron-positron contact density,  $\langle\delta_{ep}\rangle$ , is in  $a_o^3$  and the annihilation rate is for singlet annihilation (para-Ps) in ns<sup>-1</sup>.

## VII. Summary and Concluding Remarks

### Discussion.

The energy levels of the three systems modeled did not support the positron being bound. In general the positron occupied the most diffuse positron basis function. The annihilation time was over 10 times too high which was a direct result of the contact density being too large. A good reason for this is that the positron and electron did not have a degree of freedom given in the model to manifest one without the other. To this end the correlating the positron and the electron in virtual Ps bound to a system was successful.

As stated in Chapter III and by [73, 52] the  $\text{PsA}^+$  state is virtual Ps in the field of a polarized atom, but the reality is that the bound positron is in a superposition, that of the Ps and the  $e^+$  state, with one or the other being more dominant. The CPEO model as implemented did not allow the flexibility to create the superposition of the two states that is observed in working models of a bound positron.

### Future Efforts: CPEO 2.0.

The virtual Ps orbital as implemented was only given s orbitals. If this were expanded to include at least p shaped orbitals it would allow the virtual Ps to have an elongated or polarized form. providing this flexibility could go far in increasing the accuracy of the model and decreasing the contact density of the positron and the special electron.

The NEO-HF method provided for the electron and the positron each to have their own orbitals. This led (especially at the Hartree-Fock level) to little or no Coulomb correlation between the positron and other electrons. The CPEO method sacrificed Fermi-correlation amongst the electrons by designating a special electron.

This approach captures Coulomb correlation between the special electron and the regular electron. However, this structure is overly correlated. A hybrid approach would be expected to have improved results over either of the two methods.

A hybrid approach can be imagined as shown in Figure 13. NEO-HF seeks to optimize the state where the positron,  $e^+$  is bound to the system, A. CPEO seeks to optimize the state where Ps is bound to the ionized system,  $A^+$ . The addition an overlap would balance the superposition of NEO-HF and CPEO and variationally optimize the weights for the basis functions across the two states.

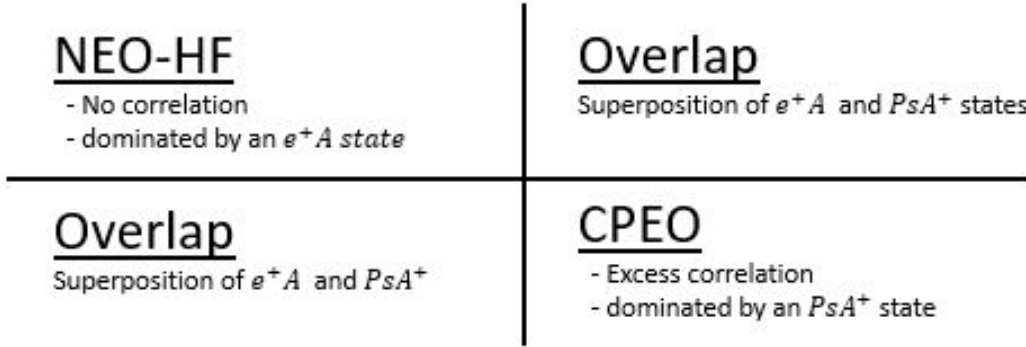


Figure 13. A schematic for a hybrid model utilizing both the NEO-HF and CPEO methods. The NEO-HF seeks to optimize the state where the positron,  $e^+$  is bound to the system, A. CPEO seeks to optimize the state where Ps is bound to the ionized system,  $A^+$ . The addition of an overlap would balance the superposition of NEO-HF and CPEO and variationally optimize the weights for the basis functions across the two states.

This hybrid approach can in some measure be realized by using the CPEO method as outlined in this dissertation with a modification to the virtual Ps orbital basis functions so that Equation (231) would be written as such

$$\psi^g(\mathbf{r}^p, \mathbf{r}^e) = \sum_{k=1}^{K_g} C_k^g \phi_k^g(\mathbf{r}^p, \mathbf{r}^e) \quad (319)$$

$$= \sum_{k=1}^{K_{g1}} C_k^{g1} \phi_k^{g1}(\mathbf{r}^p, \mathbf{r}^e) + \sum_{k=1}^{K_{g2}} C_k^{g2} \phi_k^{g2}(\mathbf{r}^e) \quad (320)$$

Where  $K_{g1} + K_{g2} = K_g$ ,  $\phi_k^{g1}(\mathbf{r}^p, \mathbf{r}^e)$  would have the same form as in Equation (301) but with the added polarization that comes from the addition of p and d orbitals as explained in Chapter IV.

$$\phi_k^{g1}(\mathbf{r}^p, \mathbf{r}^e) = x_{Ps}^{\ell_i^{g1}} y_{Ps}^{m_i^{g1}} z_{Ps}^{n_i^{g1}} e^{-\alpha_k(r_s^e - r^p)^2}. \quad (321)$$

where

$$x_{Ps} = x_s^e - x^p \quad (322)$$

$$y_{Ps} = y_s^e - y^p \quad (323)$$

$$z_{Ps} = z_s^e - z^p \quad (324)$$

and  $\phi_k^{g2}(\mathbf{r}^e)$  is a basis function for the special electron centered on an atomic centered with the form

$$\phi_k^{g2}(\mathbf{r}^e) = x_A^{\ell_i^{g2}} y_A^{m_i^{g2}} z_A^{n_i^{g2}} e^{-\alpha_{\mu'}(r_A^e)^2} \quad (325)$$

Expanding the basis functions for the virtual Ps orbital as done in equation (320) would increased the number of integrals among the basis function to expand from six

to 15 as follows.

$$1. \langle \phi_{\mu_1}^e | h^e(\mathbf{r}_1^e) | \phi_{\nu_1}^e \rangle \quad (326)$$

$$2. \langle \phi_{\mu_1}^e \phi_{\nu_1}^e | \frac{1}{r_{12}} | \phi_{\mu_2}^e \phi_{\nu_2}^e \rangle \quad (327)$$

$$3. \langle \phi_{\mu_1}^e \phi_{\mu_2}^e | \frac{1}{r_{12}} | \phi_{\nu_2}^e \phi_{\nu_1}^e \rangle \quad (328)$$

$$4. \langle \phi_{\mu'}^p \phi_k^g | \Omega_1 | \phi_{\nu'}^p \phi_\ell^g \rangle \longrightarrow \langle \phi_{\mu'}^p \phi_k^{g1} | \Omega_1 | \phi_{\nu'}^p \phi_\ell^{g1} \rangle, \langle \phi_{\mu'}^p \phi_k^{g1} | \Omega_1 | \phi_{\nu'}^p \phi_\ell^{g2} \rangle, \\ \langle \phi_{\mu'}^p \phi_k^{g2} | \Omega_1 | \phi_{\nu'}^p \phi_\ell^{g1} \rangle, \langle \phi_{\mu'}^p \phi_k^{g2} | \Omega_1 | \phi_{\nu'}^p \phi_\ell^{g2} \rangle \quad (329)$$

$$5. \langle \phi_{\mu'}^p \phi_k^g | \phi_{\nu'}^p \phi_\ell^g \rangle \longrightarrow \langle \phi_{\mu'}^p \phi_k^{g1} | \phi_{\nu'}^p \phi_\ell^{g1} \rangle, \langle \phi_{\mu'}^p \phi_k^{g1} | \phi_{\nu'}^p \phi_\ell^{g2} \rangle, \\ \langle \phi_{\mu'}^p \phi_k^{g2} | \phi_{\nu'}^p \phi_\ell^{g1} \rangle, \langle \phi_{\mu'}^p \phi_k^{g2} | \phi_{\nu'}^p \phi_\ell^{g2} \rangle \quad (330)$$

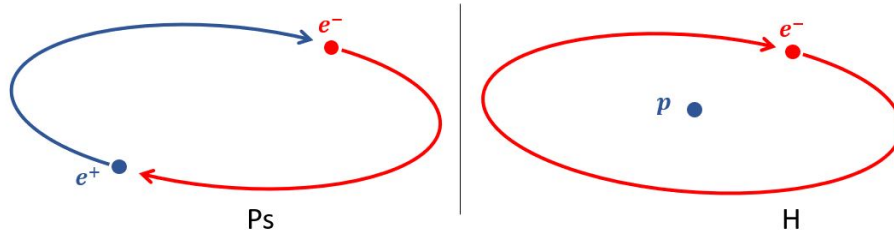
$$6. \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle \longrightarrow \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle, \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle, \\ \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle, \langle \phi_{\mu}^e \phi_{\mu'}^p \phi_k^g | \Omega_2 | \phi_{\mu'}^p \phi_k^g \phi_{\nu}^e \rangle \quad (331)$$

Here the red and blue integrals would need to be coded to model this system. The olive green integrals here correspond to the CPEO quadrant of chart in figure 13, the red integrals correspond to the overlap parts of the quad chart and the blue integrals to that of a modified NEO-HF.

These upgrades would use the CPEO theory to give the special electron to act freely without the positron and to the degree that the electron is not correlated with the positron the positron would move freely within its orbital structure. This would fall short though of a true hybrid using NEO-HF since there would still be the loss of Fermi-correlation between the special and regular electrons.

## Appendix A. Shrödinger Solution to a Two Particle System

This Chapter will focus on the wavefunctions and attributes of the Ps and Hydrogen (H) atoms. While the Ps atom consist of an electron and a positron orbiting their mutual center of mass, the Hydrogen atom has an electron that orbits a nearly stationary proton as shown in Figure 8. Both these are are neutral systems with the single electron of charge  $-e$  and the positron or proton with a charge of  $+e$ . The study of these atoms provide a qualitative insight into the research objective of this prosecutes. The H atom because it forms the basis of understanding for atomic quantum chemistry. The Ps atom because of the virtual Ps that can be formed when a positron get close enough to an atom to bond.



**Figure 14.** The positronium atom on the left consists of an electron and a positron orbiting their mutual center of mass. A Hydrogen atom has an electron that orbits a nearly stationary proton. While the picture depicts the motion of particles in a plane, the motion being considered is in three dimensions.

A two particle system that only has a central field is the only atomic system for which an exact solution to the time independent Shrödinger equation exists. The following sections will setup the two particle problem and its transformation to the equivalent one body problem. Using the solution, a number of expectation values or average values for the two body problem can be derived. The final section will bring these attributes together to compare and contrast the Ps and H atom systems.

## Two-Particle Systems

The wavefunction,  $\Psi(\mathbf{r}, t)$ , for a single particle is a function of the spatial coordinates  $\mathbf{r}$ , and time  $t$ . The wavefunction for a system of two particles would include the coordinate of both particles,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , as well as time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t). \quad (332)$$

The Shrödinger equation for this system is given by

$$i \frac{d\Psi}{dt} = \mathcal{H}\Psi, \quad (333)$$

where  $\mathcal{H}$  is the Hamiltonian for the system:

$$\mathcal{H} = -\frac{1}{2m_1}\nabla_1^2 - \frac{1}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t). \quad (334)$$

Here  $m_1$  and  $m_2$  refer to the respective masses for particle 1 or particle 2, and  $\nabla_i^2$  indicate differentiation with respect to the coordinates of particle  $i$  (either 1 or 2).

In order to give statistical interpretation to the wavefunction meaning it must be normalized so that

$$\langle \Psi(\mathbf{r}_1, \mathbf{r}_2, t) | \Psi(\mathbf{r}_1, \mathbf{r}_2, t) \rangle = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = 1. \quad (335)$$

Then the statistical interpretation allows for

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (336)$$

to give the probability of finding particle one in the volume  $d\mathbf{r}_1$  and particle 2 in the volume  $d\mathbf{r}_2$ .

Given that the potential is time-independent:

$$V(\mathbf{r}_1, \mathbf{r}_2, t) = V(\mathbf{r}_1, \mathbf{r}_2). \quad (337)$$

A complete set of solutions can be found by separation of variables with a time dependant solution for  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  being given by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt} \quad (338)$$

where the spatial wavefunction  $\psi$  satisfies the time independent Shrödinger equation

$$-\frac{1}{2m_1}\nabla_1^2\psi - \frac{1}{2m_2}\nabla_2^2\psi + V(\mathbf{r}_1, \mathbf{r}_2)\psi = E\psi, \quad (339)$$

and E is the total energy of the system.

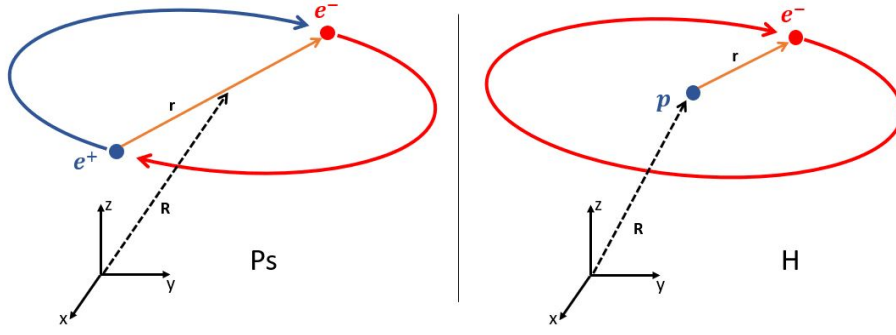
### The Equivalent One-Body Problem

The interaction potential for the two particle system given in equation (337) only depends on the vector  $\mathbf{r}$  between the two particles:  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ . Attributing particle one with a charge of  $+e$  and particle two a charge of  $-e$

$$V(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} = -\frac{1}{\|\mathbf{r}\|}. \quad (340)$$

With the Coulumbic potential being the only potential in our system, the time independent Shrödinger equation, equation (339), can be separated into its translational motion,  $\mathbf{R}$ , and the relative motion,  $\mathbf{r}$ , of the two particles as shown in Figure 15.





**Figure 15.** These two different two-body problems are reduced to the same 1-body equivalent problem in  $\mathbf{R}$  and  $\mathbf{r}$ .

These transformation coordinates are

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad (341)$$

$$\mathbf{R} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}. \quad (342)$$

Here,  $|\mathbf{r}|$  is the distance between the two particles and  $\mathbf{R}$  is vector pointing to the center of mass of the system. In order to do the coordinate transformation equations (341) and (342) are solved for  $\mathbf{r}_1$  and  $\mathbf{r}_2$  to get

$$\mathbf{r}_1 = \mathbf{R} + \frac{\mu}{m_1} \mathbf{r} \quad (343)$$

$$\mathbf{r}_2 = \mathbf{R} - \frac{\mu}{m_2} \mathbf{r} \quad (344)$$

where the reduced mass  $\mu$  is

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (345)$$

### Coordinate Transformation: The Potential.

In the new coordinate system the potential energy from equation (340) is given by

$$V(\mathbf{R}, \mathbf{r}) = -\frac{1}{\|\mathbf{R} + \frac{\mu}{m_1}\mathbf{r} - \mathbf{R} + \frac{\mu}{m_2}\mathbf{r}\|} = -\frac{1}{\|\mathbf{r}\|} \quad (346)$$

### Coordinate Transformation: The Laplacian.

The coordinate transformation of the Laplacian for  $\mathbf{r}_1$  from  $\{\mathbf{r}_1, \mathbf{r}_2\}$  to  $\{\mathbf{R}, \mathbf{r}\}$  is given by

$$\nabla_{\mathbf{r}_1}^2 \psi(\mathbf{r}_1, \mathbf{r}_2) = \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_1} \psi(\mathbf{r}, \mathbf{R}) \quad (347)$$

$$= \nabla_{\mathbf{r}_1} \cdot \left[ \frac{\mu}{m_2} \nabla_{\mathbf{R}} + \nabla_{\mathbf{r}} \right] \psi(\mathbf{r}, \mathbf{R}) \quad (348)$$

$$= \frac{\mu}{m_2} \nabla_{\mathbf{R}} \cdot \left[ \frac{\mu}{m_2} \nabla_{\mathbf{R}} + \nabla_{\mathbf{r}} \right] \psi(\mathbf{r}, \mathbf{R}) + \nabla_{\mathbf{r}} \cdot \left[ \frac{\mu}{m_2} \nabla_{\mathbf{R}} + \nabla_{\mathbf{r}} \right] \psi(\mathbf{r}, \mathbf{R}) \quad (349)$$

$$= \left( \frac{\mu}{m_2} \right)^2 \nabla_{\mathbf{R}}^2 \psi(\mathbf{r}, \mathbf{R}) + 2 \frac{\mu}{m_2} (\nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{r}}) \psi(\mathbf{r}, \mathbf{R}) + \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}, \mathbf{R}). \quad (350)$$

In a similar fashion, the coordinate transformation of the Laplacian for  $\mathbf{r}_2$  from  $\{\mathbf{r}_1, \mathbf{r}_2\}$  to  $\{\mathbf{R}, \mathbf{r}\}$  is

$$\nabla_{\mathbf{r}_2}^2 \psi(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{\mu}{m_1} \right)^2 \nabla_{\mathbf{R}}^2 \psi - 2 \frac{\mu}{m_1} (\nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{r}}) \psi + \nabla_{\mathbf{r}}^2 \psi. \quad (351)$$

### The Time Independent Shrödinger Equation.

Putting all this into the time independent Shrödinger equation, equation (339), gives

$$\begin{aligned}
H\psi &= \left[ -\frac{1}{2m_1}\nabla_1^2 - \frac{1}{2m_2}\nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2) \right] \psi \\
&= -\frac{1}{2} \left[ \frac{\mu^2}{m_1 m_2^2} \nabla_{\mathbf{R}}^2 + \frac{2\mu}{m_1 m_2} \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} + \frac{1}{m_1} \nabla_{\mathbf{r}}^2 + \frac{\mu^2}{m_2 m_1^2} \nabla_{\mathbf{R}}^2 \right. \\
&\quad \left. - \frac{2\mu}{m_2 m_1} \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} + \frac{1}{m_2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \psi \\
&= -\frac{1}{2} \left[ \frac{\mu^2}{m_1 m_2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_{\mathbf{R}}^2 + \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right] \psi \\
&= E\psi.
\end{aligned} \tag{352}$$

Note that:

$$\left( \frac{1}{m_1} + \frac{1}{m_2} \right) = \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{\mu}, \tag{353}$$

and

$$\frac{\mu^2}{m_1 m_2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) = \frac{\mu}{m_1 m_2} = \frac{1}{m_1 + m_2}. \tag{354}$$

Using equations (353) and (354) in equation (352), the time-independent Shrödinger equation for this system in  $\{\mathbf{r}, \mathbf{R}\}$  is

$$-\frac{1}{2(m_1 + m_2)} \nabla_{\mathbf{R}}^2 \psi - \frac{1}{2\mu} \nabla_{\mathbf{r}}^2 \psi + V(\mathbf{r})\psi = E. \tag{355}$$

Equation (355) is separable by letting  $\psi = \psi_{\mathbf{r}}(\mathbf{r})\psi_{\mathbf{R}}(\mathbf{R})$  and dividing by  $\psi_r\psi_R$ :

$$\left[ -\frac{1}{2(m_1 + m_2)} \frac{1}{\psi_{\mathbf{R}}} \nabla_{\mathbf{R}}^2 \psi_{\mathbf{R}} \right] + \left[ -\frac{1}{2\mu} \frac{1}{\psi_{\mathbf{r}}} \nabla_{\mathbf{r}}^2 \psi_{\mathbf{r}} + V(\mathbf{r}) \right] = E \quad (356)$$

The first term in equation (356) depends only on  $\mathbf{R}$  and the second on  $\mathbf{r}$ , so each is a constant;  $E_R$  and  $E_r$  respectively:

$$-\frac{1}{2(m_1 + m_2)} \nabla_R^2 \psi_R = E_R \psi_R \quad (357)$$

$$-\frac{1}{2\mu} \nabla_r^2 \psi_r + V(\mathbf{r}) \psi_r = E_r \psi_r, \quad (358)$$

with

$$E_r + E_R = E. \quad (359)$$

This means that the center of mass,  $\mathbf{R}$ , moves like a free particle and the motion of particle 2 with respect to particle 1 is the same as if we had a single particle subject to the potential  $V$  with the relative positions of the two particles given by equations (343) and (344).

### The Shrödinger Equation in Spherical Coordinates

With out any outside forces acting on the two particle system and without loss of generality, a reference frame for a coordinate system can be assigned so that  $\mathbf{R} = \mathbf{0}$ . This reduces the equations (343) and (344) for the relative motion of the particles to

$$\mathbf{r}_1 = \frac{\mu}{m_1} \mathbf{r}, \quad (360)$$

$$\mathbf{r}_2 = -\frac{\mu}{m_2} \mathbf{r}, \quad (361)$$

The time independent Shrödinger equation to be solved is

$$\mathcal{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (362)$$

Where  $\mathbf{r}$  is taken to be in spherical coordinates and

$$\mathcal{H} = -\frac{1}{2\mu r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + V(r). \quad (363)$$

This is the same form as that of the hydrogen atom in a non-relativistic solution.

Where  $\Psi(r, \theta, \phi)$  is separable so that

$$\Psi_{n,\ell,m_\ell}(r, \theta, \phi) = R_{n,\ell}(r) \Theta_{\ell,m_\ell}(\theta) \Phi_{m_\ell}(\phi) \quad (364)$$

$$= R_{n,\ell}(r) Y_\ell^{m_\ell}(\theta, \phi), \quad (365)$$

is the solution to the equation [25, 32, 61] where the three quantum numbers,  $\{n, \ell, m_\ell\} \in \mathbb{Z}$ , are restricted so that

$$n \geq 1 \quad (366)$$

$$0 \leq \ell \leq n \quad (367)$$

$$-\ell \leq m_\ell \leq \ell, \quad (368)$$

and

$$R_{n,\ell}(r) = \underbrace{\sqrt{\frac{(n-\ell-1)!}{2n[(n+1)!]^3}} \left(\frac{2\mu}{n}\right)^{\ell+\frac{1}{2}}}_{\text{normalization constant}} \underbrace{L_{n+\ell}^{2\ell+1}\left(\frac{2r\mu}{n}\right)}_{\text{associated Laquerre polynomials}} \underbrace{r^\ell e^{-r\mu/n}}_{\text{exponential}}, \quad (369)$$

$$Y_\ell^{m_\ell} = \underbrace{\sqrt{\frac{2\ell+1}{4\pi}} \frac{(\ell-|m_\ell|)!}{(\ell+|m_\ell|)!}}_{\text{normalization constant}} \underbrace{P_\ell^{|m_\ell|}(\cos\theta)}_{\text{associated Legendre polynomials}} \underbrace{e^{im_\ell\phi}}_{\text{complex exponential}}. \quad (370)$$

### Commuting Operators of $\Psi(r, \theta, \phi)$ .

The the three commuting operators of the solution,

$$\Psi_{n,\ell,m_\ell}(r, \theta\phi) = R_{n,\ell}(r)Y_\ell^{m_\ell}(\theta, \phi), \quad (371)$$

to the time independent Shrödinger equation (362) are  $\mathcal{H}$ ,  $L^2$  and  $L_z$ . With  $\mathcal{H}$  as given in (363) and

$$L^2 = -\left[ \frac{1}{\sin\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \quad (372)$$

$$L_z = -i \frac{\partial}{\partial\phi} \quad (373)$$

The wavefunctions,  $\Psi_{n,\ell,m_\ell}(r, \theta\phi)$ , of this system are eigenfunctions of the Hamiltonian operator as well as being eigenfunctions of the operators  $L^2$ , the total angular momentum operator squared; and the z part of the angular momentum,  $L_z$ . The

eigenvalue equations are

$$\mathcal{H}\Psi_{n,\ell,m_\ell}(r, \theta\phi) = E_n\Psi_{n,\ell,m_\ell}(r, \theta\phi), \quad (374)$$

$$L^2\Psi_{n,\ell,m_\ell}(r, \theta\phi) = \ell(\ell + 1)\Psi_{n,\ell,m_\ell}(r, \theta\phi), \quad (375)$$

$$L_z\Psi_{n,\ell,m_\ell}(r, \theta\phi) = m_\ell\Psi_{n,\ell,m_\ell}(r, \theta\phi). \quad (376)$$

With the eigenvalues for  $E_n$  of the Hamiltonian given by

$$E_n = -\frac{\mu}{2n^2}. \quad (377)$$

The eigenvalues of  $L^2$  are  $\ell(\ell + 1)$  and of  $L_z$  are  $m_\ell$  with the conditions for valid values of  $n, \ell$ , and  $m_\ell$  given in equations (366), (367), and (368). Any unique combination of the eigenvalues will produce a unique solution to the time independent Schrödinger equation (362).

## Expectation Values

In 3-dimensions the expectation value of a given property  $A$  is given by using the operator representing that property  $\hat{A}$ :

$$\langle A \rangle = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_{-\infty}^\infty r^2 dr \Psi^*(r, \theta\phi) \hat{A} \Psi(r, \theta\phi) \quad (378)$$

### Radial Expectation Values.

The first property to compute is the average distance  $r$  between the two particles in our system. This is given by calculating the expectation value of  $r$  in the lowest energy state  $\Psi_{100}$  or  $1s$  orbital.

$$\langle r \rangle_{1s} = \int_0^{2\pi} \int_0^\pi \int_{-\infty}^\infty \Psi_{100}^* r \Psi_{100} r^2 \sin\theta dr d\theta d\phi \quad (379)$$

where  $\Psi_{100}$  is calculated from equation (371) using equations (369) and (370):

$$\Psi_{100} = \Psi_{100}^* = \frac{1}{\sqrt{\pi}} \mu^{3/2} e^{-r\mu}. \quad (380)$$

Then using the integral

$$\int_0^\infty x^N e^{-ax} dx = \frac{n!}{a^{n+1}}, \quad (381)$$

equation (380) is used to evaluate the expectation value of  $\langle r \rangle_{1s}$  in equation (379):

$$\langle r \rangle_{1s} = \frac{1}{\pi} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_{-\infty}^\infty \mu^3 r^3 e^{-2r\mu} dr}_{\mu^3 3! (\frac{1}{2\mu})^4} \quad (382)$$

$$= \frac{3}{2\mu}. \quad (383)$$

So the expectation value for the distance between the two particles is  $\frac{3}{2\mu}$  where  $\mu$  is the reduced mass given in equation (345). This can then be used to find  $\langle r_1 \rangle_{1s}$  and  $\langle r_2 \rangle_{1s}$  for the two particles. First using equations (360) and (361) we can get the magnitude of  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in terms of  $\mathbf{r}$ .

$$r_1 = \|\mathbf{r}_1\| = \left\| \frac{\mu}{m_1} \mathbf{r} \right\| = \frac{\mu}{m_1} r \quad (384)$$

$$r_2 = \|\mathbf{r}_2\| = \left\| \frac{\mu}{m_2} \mathbf{r} \right\| = \frac{\mu}{m_2} r \quad (385)$$

Given that  $\mu, m_1$  and  $m_2$  are constants and only scale the result of integration for expectation values, using (384) and (385) along with equation (383) the expectation values for  $r_1$  and  $r_2$  can be found:

$$\langle r_1 \rangle_{1s} = \left\langle \frac{\mu}{m_1} r \right\rangle_{1s} = \frac{\mu}{m_1} \langle r \rangle_{1s} = \frac{3}{2m_1} \quad (386)$$

$$\langle r_2 \rangle_{1s} = \left\langle -\frac{\mu}{m_2} r \right\rangle_{1s} = \frac{\mu}{m_2} \langle r \rangle_{1s} = \frac{3}{2m_2}. \quad (387)$$



### The Most Probable Radial Values.

The radial probability density is obtained by multiplying the square of the radial wavefunction by a spherical shell volume element:

$$\text{Prob}(\text{in } dr \text{ at } r) = |R_{n,\ell}(r)|^2 dV = 4\pi r^2 |R_{n,\ell}(r)|^2 dr = P_{n,\ell}(r) dr \quad (388)$$

$$P_{n,\ell}(r) = 4\pi r^2 |R_{n,\ell}(r)|^2. \quad (389)$$

Since  $P_{n,\ell}(r)$  is a probability it will always be greater than 0. Therefore the maximum of the function is the “most probable” value of  $r$ , denoted:  $r^{\text{mp}}$ .  $r^{\text{mp}}$  is found by taking a derivative of (389) and setting it equal to 0 then solving for  $r^{\text{mp}}$ , i.e.

$$\frac{d}{dr} P_{n,\ell} = 0 \quad (390)$$

This is obtained for the ground state,  $1s$ , radial distribution function using equation (369) with  $n = 1$  and  $\ell = 0$ :

$$\frac{d}{dr} P_{1,0}(r) = \frac{d}{dr} 4\pi r^2 \left[ \frac{1}{\sqrt{\pi}} \mu^{3/2} e^{-r\mu} \right]^2 \quad (391)$$

$$= \frac{d}{dr} 4\mu^3 r^2 e^{-2r\mu} \quad (392)$$

$$= 2r e^{-2r\mu} (1 - r\mu) \quad (393)$$

$$= 0, \quad (394)$$

$$\therefore r^{\text{mp}} = \frac{1}{\mu} \text{ or } 0. \quad (395)$$

$P_{1,0}(0) = 0$  is a minimum for a probability density functions. While  $P_{1,0}(\frac{1}{\mu}) = 4\mu^3 e^{-2} > 0$ , therefore  $r = \frac{1}{\mu}$  is the maximum for  $P_{1,0}(r)$ . This means that while the average value of the distance between the two particles is given by equation (383),  $\langle r \rangle_{1s} = \frac{3}{2\mu}$ , the most probable distance between the particles is,  $r^{\text{mp}} = \frac{1}{\mu}$ .

Now to find the most probable value of  $r_1$  and  $r_2$ . This is done using equations (384) and (385) with equation (395):

$$r_1^{\text{mp}} = \frac{\mu}{m_1} r^{\text{mp}} = \frac{1}{m_1} \quad (396)$$

$$r_2^{\text{mp}} = \frac{\mu}{m_2} r^{\text{mp}} = \frac{1}{m_2} \quad (397)$$

### Expectation Values: Potential and Kinetic Energy.

The expectation value of the potential energy of the two particle problem in the 1s ( $\Psi_{100}$ ) state is done in similar fashion to that of  $\langle r_1 \rangle_{1s}$  and  $r^{\text{mp}}$ . Using equation (378) with the potential, equation (346), as the operator  $A$  for  $\Psi_{100}$ .

$$\langle V \rangle_{1s} = -\frac{1}{\pi} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_{-\infty}^\infty \mu^3 r e^{-2r\mu} dr}_{\mu^3 1! (\frac{1}{2\mu})^2} \quad (398)$$

$$= -\mu \quad (399)$$

The expectation value for the kinetic energy can be found by subtracting the expected potential energy, equation (399) from the Total energy equation, equation (377). For the 1s state,  $n=1$  so that:

$$\langle T \rangle_{1s} = E_1 - \langle V \rangle_{1s} \quad (400)$$

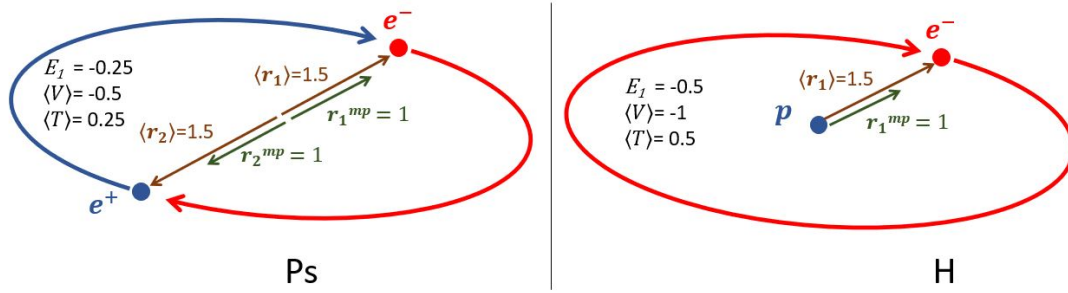
$$= -\frac{\mu}{2} + \mu \quad (401)$$

$$= \frac{\mu}{2} \quad (402)$$

### Non-relativistic: Hydrogen vs. Positronium

Using the information developed in the previous sections, it is time to look at the Ps and H systems. In each of these cases the electron will be assigned as particle 1,

with mass  $m_1 = 1$ . For the Ps the second particle is the positron with mass  $m_2 = 1$ , the same as that for the electron. The H atom has the proton as the second particle with a mass that is 18.36.1 times larger than the electron. The reduced mass  $\mu$  from equation (345) is 0.5 for the Ps and 0.9995 for the H. The reduced mass is the key difference in calculation for the energy level  $E_n$ , equation (377), and expectation values for,  $\langle r \rangle_{1s}$ ,  $r^{\text{mp}}$ ,  $\langle V \rangle_{1s}$ , and  $\langle T \rangle_{1s}$ . Each of these results is then used to get the equivalent value for the electron and positron in Ps, as well as the electron and proton in H. These values are shown in Table 11 and Figure 16 for Ps and H. Table 11 also shows values for the H atom with the nucleus not being treated as an infinite point charge.



**Figure 16.** These two different two-body problems are reduced to the same 1-body equivalent problem in  $R$  and  $r$ .

From Table 11 it is observed that while  $\langle r \rangle_{1s}$  for H is twice that for Ps, the  $\langle r_1 \rangle_{1s}$  for the electron in both Ps and H is the same and matches  $\langle r_2 \rangle_{1s}$  for the positron in Ps. This is the same for the  $r^{\text{mp}}$  values for the electron in both models and the positron in Ps. This suggests that the electron in both systems have the same spatial orbital, and that the positron shares that same spatial orbital. The key difference being in the Energy values. The H atom has a ground state energy that is twice that of the Ps. The expectation of the potential in both systems is all Columbic. In Ps the particles stay twice as far away from each other as the proton and electron in the H atom. This results in half the  $\langle V \rangle_{1s}$  for the Ps atom as the H atom. The kinetic

energy in the H system is all with the electron, and  $\langle T \rangle_{1s}$  for the H is twice that of the Ps. In Ps the kinetic energy of the electron and positron are equal. This means that the electron in the Ps has one quarter of the kinetic energy as the electron in the H atom.

Property	Calculation	Value for Ps	Value for H
$m_1$	—	1	1
$m_2$	—	1	1836.15
$\mu$	$\frac{m_1 m_2}{m_1 + m_2}$	0.5	0.99946
$\langle r \rangle_{1s}$	$\frac{3}{2\mu}$	3	1.499
$\langle r_1 \rangle_{1s}$	$\frac{3}{2m_1}$	1.5	1.5
$\langle r_2 \rangle_{1s}$	$\frac{3}{2m_2}$	1.5	0.00082
$r^{\text{mp}}$	$\frac{1}{\mu}$	2	1.00054
$r_1^{\text{mp}}$	$\frac{1}{m_1}$	1	1
$r_2^{\text{mp}}$	$\frac{1}{m_2}$	1	0.00054
$E_1$	$-\frac{\mu}{2n^2}$	-0.250	-0.49972
$\langle V \rangle_{1s}$	$-\mu$	-0.5	-0.99946
$\langle T \rangle_{1s}$	$\frac{\mu}{2}$	0.250	0.49972

**Table 11.** Comparison of expectation values between Ps, and H. All units are in atomic units as provided in table 3.

## Appendix B. Theoretical Background

### Hartree-Fock Theory

The Hartree Fock (HF) approximation is regarded as the fundamental step in quantum chemistry [26, 33]. HF is used to solve the many-body problem using the postulates of quantum mechanics and certain approximations that will be identified when made. The development in this Appendix follows closely the development laid out in Szabo [87].

The electronic structure problem a single-particle time-dependant Shrödinger equation is given by

$$\left( -\frac{1}{2m}\nabla^2 + V(\mathbf{r}) \right) |\Psi(\mathbf{r}, t)\rangle = i\frac{d}{dt} |\Psi(\mathbf{r}, t)\rangle \quad (403)$$

where  $m$  is the mass of the particle and  $|\Psi(\mathbf{r}, t)\rangle$  is the wave function of the system and,  $V(\mathbf{r})$  is the potential energy of the particle at the given position  $\mathbf{r}$ . The operator,  $\mathcal{H}$ ,

$$\mathcal{H} = \left( -\frac{1}{2m}\nabla^2 + V(\mathbf{r}) \right) \quad (404)$$

is the Hamiltonian for the system.  $|\Psi(\mathbf{r}, t)|^2$  is the probability density at position  $\mathbf{r}$  and time  $t$  and gives the probability of finding the particle in a volume element  $\delta\mathcal{V}$  around  $\mathbf{r}$  at time  $t$  by  $|\Psi(\mathbf{r}, t)|^2\delta\mathcal{V}$ . With the assumption that the wavefunction can be written as

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r})\Phi(t)$$

the wavefunction is separable and by use of separation of variables the time independent Shrödinger

$$\mathcal{H} |\Psi(\mathbf{r})\rangle = E |\Psi(\mathbf{r})\rangle \quad (405)$$

where  $E$  is the separation constant or energy eigenvalue. The time-dependent equation

is given by

$$-i\frac{d}{dt}\Phi(t) = E\Phi(t). \quad (406)$$

The time independent Shrödinger equation is the one that will be the focus of HF theory.

### The Many-body Molecular Hamiltonian .

Solving the Shrödinger equation for a system of many interacting particles requires the extension of equation (405). This is done for the system to that shown in Figure 17 where there are  $N_e$  electrons and  $N_c$  nuclei. The molecular Hamiltonian for this system can be written as

$$\begin{aligned} \mathcal{H} = & \underbrace{-\sum_i^{N_e} \frac{1}{2} \nabla_{\mathbf{r}_i}^2}_{\hat{T}_e} - \underbrace{\sum_i^{N_c} \frac{1}{2M_i} \nabla_{\mathbf{R}_i}^2}_{\hat{T}_n} \\ & - \underbrace{\sum_i^{N_e} \sum_j^{N_c} \frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}}_{\hat{V}_{ne}} + \underbrace{\frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}_{ee}} + \underbrace{\sum_i^{N_c} \sum_j^{N_c} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|}}_{\hat{V}_{nn}}, \end{aligned} \quad (407)$$

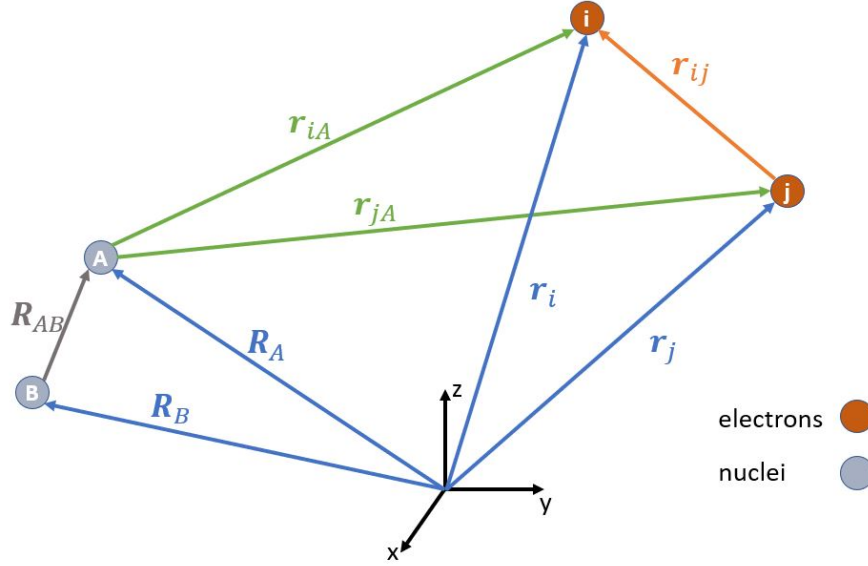
Where  $\mathbf{r}$  refers to electron's coordinates and  $\mathbf{R}$  refers to the nuclei coordinates.  $M$  refer to nuclear masses and  $Z$  to the charge of the nuclei. The operators  $\hat{T}_e$  and  $\hat{T}_n$  refer to the kinetic energy of the electrons and nuclei respectively. The operators  $\hat{V}_{ne}$ ,  $\hat{V}_{ee}$ , and  $\hat{V}_{nn}$  are refer to the electrostatic cumulative interaction between each electron and each nucleus, each pair of electrons, and each pair of nuclei respectively. Equation (407) can be re-written as

$$\mathcal{H} = -\hat{T}_e - \hat{T}_n - \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}. \quad (408)$$

The non-relativistic, time-independent Shrödinger equation for this system is

$$\mathcal{H} |\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\rangle = E |\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\rangle \quad (409)$$

where E is the total energy of the system.



**Figure 17. Three particle molecular coordinate system:**  $e$  = electron;  $p$  = positron;  $A$  = classical nucleus.

### Born-Oppenheimer approximation.

Since each electron and each nucleus can move in 3-dimensional space there are  $3N_e + 3N_c$  degrees of freedom. Using  $N = N_e + N_c$  there are  $N(N-1)/2!$  interacting pairs. For  $N > 2$  this becomes an analytically unsolvable problem that falls into the "NP-complete" problem with difficulty  $O(e^N)$ . Therefore we begin making approximations to make the problem more tractable. The first approximation is known as the Born-Oppenheimer approximations where the nucleus as a fixed point charge.

First take note that the mass of a nucleus weighs approximately 1836 times that of the electron (i.e.  $M \gg m$ ). Due to the high mass of the nuclei, the nuclei will

move slow relative to the set of all electrons  $\{\mathbf{r}_i\}$ . This allows for the approximation that the position of all the nuclei  $\{\mathbf{R}_i\}$  are fixed relative to the electrons. Given that the nuclei are fixed  $\hat{T}_n = 0$  and  $\hat{V}_{nn} = C$  where  $C$  is a constant. This is equivalent to treating the nuclei as classical point charges. Given that  $\hat{V}_{nn} = C$  it effects the total energy but not the electronic energy and wavefunction.

Using the Born-Oppenheimer approximation the electronic Shrödinger equation is written as

$$\mathcal{H}_{elec} |\Psi_{elec}\rangle = E_{elec} |\Psi_{elec}\rangle . \quad (410)$$

where  $\Psi_{elec}$  is a function of only the set of electrons,  $\{\mathbf{r}_i\}$ . The electronic Hamiltonian operator  $\mathcal{H}_{elec}$  is

$$\mathcal{H}_{elec} = -\hat{T}_e - \hat{V}_{ne} + \hat{V}_{ee}. \quad (411)$$

### Spin Orbitals.

The term "orbital" is used to refer to a 1-electron wavefunction. A spin orbital consists of both spatial orbital and a spin. The spatial orbital is specified by using spatial coordinates (ex.  $x, y, z$ ) and the spin is specified by the spin function. In this document the spatial coordinates will be given by  $\mathbf{r}$  where  $\mathbf{r} = (x, y, z)$ . The spin function is  $\omega$  where

$$\omega \rightarrow \text{spin} = \begin{cases} |\alpha\rangle - \text{spin up} \\ |\beta\rangle - \text{spin down}, \end{cases} \quad (412)$$



with

$$\begin{aligned}\langle\alpha|\alpha\rangle &= \langle\beta|\beta\rangle = 1 \\ \langle\alpha|\beta\rangle &= \langle\beta|\alpha\rangle = 0 \\ \{|\alpha\rangle, |\beta\rangle\} &\text{ are orthonormal.}\end{aligned}$$

The spin orbital refers to both the Cartesian coordinates and the spin. In this document the spin orbital coordinates will be given by  $\mathbf{x}$  where  $\mathbf{x} = (\mathbf{r}, \omega) = (x, y, z, \omega)$ .

The spatial orbital will be given by  $\phi(\mathbf{r})$ . If the spatial wavefunction is normalized,  $\langle\phi|\phi\rangle = 1$  then  $\phi^*(\mathbf{r})\phi(\mathbf{r})d^3\mathbf{r}$  is the probability of finding electron 1 near the point . In addition, if the set  $\{\phi_i\}$  is "complete" then  $f(\mathbf{r}) = \sum_i a_i\phi_i(\mathbf{r})$  for any  $f(\mathbf{r})$ . The  $\{a_i\}$  can be found from  $a_i = \langle\phi_i|f\rangle$ .

The spin orbital will always be given as  $\chi(\mathbf{x})$  where

$$\underbrace{\chi(\mathbf{x}_1)}_{\substack{\text{spin} \\ \text{orbital}}} = \underbrace{\phi(\mathbf{r}_1)}_{\substack{\text{spatial} \\ \text{orbital}}} \underbrace{\sigma(\omega_1)}_{\text{spin function}}. \quad (413)$$

This means that for a given spin orbital there are two possibilities for the same spatial orbital to be paired with one of two spins as follows:

$$\chi(\mathbf{x}_1) = \begin{cases} \phi(\mathbf{r}_1) |\alpha\rangle \\ \phi(\mathbf{r}_1) |\beta\rangle . \end{cases} \quad (414)$$

### Slater Determinants.

This section will cover the antisymmetry principal to deal with the fact that electrons are indistinguishable. To begin with it should be noted that in the electric

Hamiltonian, Equation (411) there is no spin. The Pauli exclusion principle is a quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously. This means that two electrons cannot occupy the same orbital with the same spin. This is fixed by enforcing the anti-symmetry principle. The anti-symmetry principle says that if any two electrons in the wavefunction are swapped the wavefunction remains the same with the exception that the sign has changed. This is shown below.

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \mathbf{x}_j, \dots, \mathbf{x}_{N_e}) = -\Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \mathbf{x}_i, \dots, \mathbf{x}_{N_e}) \quad (415)$$

for all  $1 \leq \{i, j\} \leq N_e$ .

In order to satisfy the anti-symmetric property of the total electronic wavefunction V. Fock [26] proposed in 1930 to use what termed a Slater determinant. A Slater determinant is a determinant constructed from spin orbitals. Being a determinant, it obeys the antisymmetry principle and serves as a natural choice for electronic wavefunctions. Formalizing this to an arbitrary size ( $N_e$ ) is done by

$$\Psi(\{\mathbf{x}_i\}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_{N_e}(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_{N_e}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_{N_e}) & \chi_2(\mathbf{x}_{N_e}) & \dots & \chi_{N_e}(\mathbf{x}_{N_e}) \end{vmatrix} \quad (416)$$

$$= |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_{N_e}(\mathbf{x}_{N_e})\rangle \quad (417)$$

$$= |\chi_1\chi_2\dots\chi_{N_e}\rangle, \quad (418)$$

where the rows in equation (416) are individual electronic coordinates and the columns

are individual spin orbitals. Clearly, if any two electrons are in the same spin orbital then  $\Psi = 0$  and if any two spin orbitals are the same  $\Psi = 0$ . The Slater Determinant is the default wavefunction for all of HF theory.

### Restricted and Unrestricted Determinants.

All spin orbitals have a spin part and a spatial part. In the spin part for a given spatial orbital there can be a spin up electron  $\alpha$  or a spin down electron  $\beta$ . This allows each spatial orbital to be occupied by two electrons, with orthogonal spins.

In a restricted determinant the electrons that are in the same spatial orbital, one with  $\alpha$  and one with  $\beta$  spin, are paired together near the same energy. The restricted determinant requires the spatial orbital to be the same. This is generally applicable to a systems with closed shells where each occupied orbital has two electrons.

In an unrestricted determinant the spatial orbitals for the spin  $\alpha$  and spin  $\beta$  electrons can be different. Unrestricted determinants can more accurately reflect the physical situation by allowing the spatial orbitals of the paired electrons to be different and thereby can have different energies. Unrestricted determinants are most applicable to open shell systems.

The difference between restricted determinants and unrestricted determinants is illustrated below. This illustrated here for the ground state determinant  $|\Psi_o\rangle$ :

$$|\Psi_0\rangle = |\chi_1\chi_2\chi_3\chi_4\cdots\chi_{N_e-1}\chi_{N_e}\rangle \quad (419)$$

$$= |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_{N_e/2}\bar{\phi}_{N_e/2}\rangle, \quad (420)$$

where  $\phi_i = \phi_i|\alpha\rangle$  and  $\bar{\phi}_i = \phi_i|\beta\rangle$ . Where equation (419) is an unrestricted determinant and will be used for Unrestricted Hartree-Fock (UHF) theory. Equation (420) is a restricted determinant and is used in Restricted Hartree-Fock (RHF) where halving the number of distinct spatial orbitals can be exploited to simplify the method.

### Electron Integrals.

Re-writing the electronic Shrödinger equation from equation (410) while dropping the *elec* subscript gives

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle. \quad (421)$$

Letting  $|\Psi_0\rangle$  be the ground state (lowest energy state) for the wavefunction  $|\Psi\rangle$ . This wavefunction is given by the the unrestricted determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_{N_e}\rangle \quad (422)$$

with the energy,  $E_0$  (ground state energy) , of the wave function being the expectation value of the Hamiltonian operator,  $\mathcal{H}$ , given by

$$E = \langle\Psi_0|\mathcal{H}|\Psi_0\rangle. \quad (423)$$

The Hamiltonian is that from equation (411) without the subscript *elec*.

$$\mathcal{H} = -\hat{T}_e - \hat{V}_{ne} + \hat{V}_{ee}. \quad (424)$$

This Hamiltonian can be separates into two types of operators.

$$\text{1-electron operator: } \hat{h}_i \quad (425)$$

$$\text{2-electron operator: } \frac{1}{r_{ij}}, \quad (426)$$

The one electron operator is defined as

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_A^{N_c} \frac{Z_A}{r_{iA}}. \quad (427)$$

where the distance  $r_{iA}$  refers to the distance between the electron  $i$  and the  $A^{\text{th}}$  nuclei so that

$$\hat{T}_e + \hat{V}_{ne} = \sum_i^{N_e} \hat{h}_i, \quad (428)$$

The two electron operator  $\frac{1}{r_{ij}}$  is used to create the  $\hat{V}_{ee}$  term of the Hamiltonian:

$$\hat{V}_{ee} = \sum_i^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}}, \quad (429)$$

where the distance  $r_{ij}$  refers to the distance between the  $i$ th and the  $j$ th electrons.

Using these new operators, the total Energy from equation (423) is given by

$$E_0 = \sum_i^{N_e} \langle \Psi_0 | \hat{h}_i | \Psi_0 \rangle + \sum_i^{N_e} \sum_{j>i}^{N_e} \langle \Psi_0 | \frac{1}{r_{ij}} | \Psi_0 \rangle \quad (430)$$

$$= E_1 + E_2, \quad (431)$$

where  $E_1$  is given by

$$E_1 = \sum_i^{N_e} [i | \hat{h} | i]. \quad (432)$$

Here the 1 electron integral is defined by

$$\begin{aligned} [i | \hat{h} | i] &= [\chi_i | \hat{h}_1 | \chi_i] \\ &= [\chi_i(1) | \hat{h}_1 | \chi_i(1)] \\ &= \int d\mathbf{x}_1 \chi_i^*(1) \hat{h}_1 \chi_i(1) \\ &= \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) \hat{h}_1 \chi_i(\mathbf{x}_1). \end{aligned} \quad (433)$$

$E_2$  is given by

$$E_2 = \sum_i^{N_e} \sum_{j>i}^{N_e} ([ij|ij] - [ij|ji]) \quad (434)$$

with the two electron integral defined by

$$\begin{aligned} [ij|kl] &= [\chi_i \chi_j | \chi_k \chi_l] \\ &= [\chi_i(1) \chi_j(2) | \chi_k(1) \chi_l(2)] \\ &= [\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)] \\ &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \chi_k^*(2) \chi_l(2) \\ &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2). \end{aligned} \quad (435)$$

This notation is common usage in quantum chemistry and will be used here. Equation (430) can now be re-written as

$$E_0 = \sum_i^{N_e} \underbrace{[i|\hat{h}|i]}_A + \sum_i^{N_e} \sum_{j>i}^{N_e} \underbrace{[ii|jj]}_B - \underbrace{[ij|ji]}_C \quad (436)$$

where  $A$  is the core energy,  $B$  is referred to as the Coulomb energy, and  $C$  is referred to as the exchange energy. It is worth noting that the Coulomb potential in  $B$  is the electrostatic interaction that exists between all pairs of electrons. The exchange interaction only exists between electrons with the same spin, i.e. if  $\sigma(\omega_1) \neq \sigma(\omega_2)$  then  $[ij|ji] = 0$ .

### Spin Integration for RHF.

Using the simplification for restricted determinants used in RHF the integrals from the previous section can be simplified by integrating out the spin. A quick note on notation will be helpful. Integration represented by square brackets  $[ \ ]$  includes spin and thus is integration over all the coordinates of the spin orbital. Round brackets,

( ) are used to integration over only the spatial orbitals. Reducing the spin orbital integration to just spatial integration for RHF is done for the core energy integral as follows.

$$\begin{aligned}
[i|\hat{h}|i] &= \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) \hat{h}_1 \chi_i(\mathbf{x}_1) \\
&= \int d\mathbf{r}_1 d\omega_1 \phi_i^*(\mathbf{r}_1) \sigma_i^*(\omega_1) \hat{h}_1 \phi_i(\mathbf{r}_1) \sigma_i^*(\omega_1) \\
&= \int d\omega_1 \sigma_i^*(\omega_1) \sigma_i^*(\omega_1) \int d\mathbf{r}_1 \phi_i(\mathbf{r}_1) \hat{h}_1 \phi_i(\mathbf{x}_1) \\
&= \int d\mathbf{r}_1 \phi_i(\mathbf{r}_1) \hat{h}_1 \phi_i(\mathbf{x}_1) \\
&= (i|\hat{h}|i)
\end{aligned} \tag{437}$$

Doing the same thing for the 2-electron integral yields:

$$\begin{aligned}
[ij|kl] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) \\
&= \int d\omega_1 \sigma_i^*(\omega_1) \sigma_j(\omega_1) \int d\omega_2 \sigma_k^*(\omega_2) \sigma_l(\omega_2) \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \frac{1}{r_{12}} \phi_k^*(\mathbf{r}_2) \phi_l(\mathbf{r}_2) \\
&= \delta_{\sigma_i, \sigma_j} \delta_{\sigma_k, \sigma_l} \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \frac{1}{r_{12}} \phi_k^*(\mathbf{r}_2) \phi_l(\mathbf{r}_2) \\
&= \delta_{\sigma_i, \sigma_j} \delta_{\sigma_k, \sigma_l} (ij|kl),
\end{aligned} \tag{438}$$

where  $\delta_{\sigma_i, \sigma_j} = 1$  if the spin functions are the same,  $\sigma_i = \sigma_j$ , and  $\delta_{\sigma_i, \sigma_j} = 0$  if the spin functions are not the same,  $\sigma_i \neq \sigma_j$ . This is then applied to both the Coulomb energy

integral to get

$$\begin{aligned} [ii|jj] &= \delta_{\sigma_i, \sigma_i} \delta_{\sigma_j, \sigma_j} (ii|jj) \\ &= (ii|jj) \end{aligned} \tag{439}$$

$$\tag{440}$$

and the exchange energy integral for

$$\begin{aligned} [ij|ji] &= \delta_{\sigma_i, \sigma_j} \delta_{\sigma_j, \sigma_i} (ij|ji) \\ &= \delta_{\sigma_i, \sigma_j} (ij|ji) \end{aligned} \tag{441}$$

In RHF when the wavefunctions is expressed as a single determinant of  $N_e$  doubly occupied spatial orbitals, equation (420), then the integration over the spin orbitals for equation (436) gives the follow energy for RHF.

$$E_0 = 2 \sum_i^{N_e/2} (i|\hat{h}|i) + \sum_i^{N_e/2} \sum_{j>i}^{N_e/2} (2(ii|jj) - (ij|ji)) \tag{442}$$

### **Coulomb and Exchange Operators.**

The Coulomb and exchange operators in the energy, equation (436) and (442), can be re-written more succinctly with the following notation.

The integrals  $[ii|jj]$  for the Coulomb force can be written using a Coulomb Oper-



ator  $J_j$ :

$$\begin{aligned}
[i|j] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(1) \chi_i(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_j(2) \\
&= \int d\mathbf{x}_1 \chi_i^*(1) \int d\mathbf{x}_2 \chi_j^*(2) \frac{1}{r_{12}} \chi_j(2) \chi_i(1) \\
&= \int d\mathbf{x}_1 \chi_i^*(1) J_j \chi_i(1) \\
&= [i|J_j|i],
\end{aligned} \tag{443}$$

where

$$J_j(1) \chi_i(1) = \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \chi_i(1). \tag{444}$$

In like fashion, but involving the exchange operator  $K_j$ , the integral  $[ij|ji]$  becomes

$$\begin{aligned}
[ij|ji] &= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_i(2) \\
&= \int d\mathbf{x}_1 \chi_i^*(1) \int d\mathbf{x}_2 \chi_j^*(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1) \\
&= \int d\mathbf{x}_1 \chi_i^*(1) K_j \chi_i(1) \\
&= [i|K_j|i],
\end{aligned} \tag{445}$$

where

$$K_j(1) \chi_i(1) = \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1). \tag{446}$$

### Minimum Determinant Energy.

Using the ground-state determinant wavefunction, from equation (419)

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_{N_e}\rangle \quad (447)$$

$$= |12\cdots ab\cdots N_e\rangle, \quad (448)$$

the energy  $E_0$  is a functional of the spin orbitals  $\{\chi_a\}$ :

$$E_0[\{\chi_a\}] = \langle\Psi_0|\mathcal{H}|\Psi_0\rangle. \quad (449)$$

The next step is to use the variational principal in order to get the lowest possible ground state energy of the system. This is done by minimizing the energy  $E_0[\{\chi_a\}]$  with respect to the spin orbital, subject to the constraint that the spin orbitals remain orthonormal,

$$\int d\mathbf{x}_1 \chi_a^*(1)\chi_b(1) = [a|b] = \delta_{ab} \quad (450)$$

The Lagrangian is then going to be a functional of the set of spin orbitals

$$\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_a^{N_e} \sum_b^{N_e} \varepsilon_{ab}([a|b], -\delta_{ab}) \quad (451)$$

where  $E_0$  is the energy from (436)

$$E_0[\{\chi_a\}] = \sum_a^{N_e} [a|\hat{h}|a] + \frac{1}{2} \sum_a^{N_e} \sum_b^{N_e} ([aa|bb] - [ab|ba]) \quad (452)$$

and  $\varepsilon_{ab}$  are the Lagrange multipliers. Since energy is a physical property (an observable) the  $\mathcal{L}$  is real. Also,  $[a|b] = [b|a]^*$  so the Lagrange multipliers are elements of a

Hermitian matrix with

$$\varepsilon_{ab} = \varepsilon_{ab}^*. \quad (453)$$

The minimization of  $E_0$  subject to (450) is obtained by minimizing  $\mathcal{L}$ . This is done by varying the spin orbitals an infinitesimal amount

$$\chi_a \rightarrow \chi_a + \delta\chi_a \quad (454)$$

and set the first variation in  $\mathcal{L}$  equal to zero,

$$\delta\mathcal{L}[\{\chi_a\}] = \delta E_0[\{\chi_a\}] - \sum_a^{N_e} \sum_b^{N_e} \varepsilon_{ab} \delta[a|b] = 0. \quad (455)$$

Equation (455) follows directly from equation (451) since the variation of the constant  $\delta_{ab}$  is zero. Now,

$$\begin{aligned} \varepsilon_{ab} \delta[a|b] &= \sum_a^{N_e} \sum_b^{N_e} \varepsilon_{ab} ([\delta a|b] + [a|\delta b]) \\ &= \sum_a^{N_e} \sum_b^{N_e} (\varepsilon_{ab} [\delta a|b] + \varepsilon_{ab}^* [\delta a|b]^*), \end{aligned} \quad (456)$$

and

$$\begin{aligned} \delta E_0[\{\chi_a\}] &= \sum_a^{N_e} ([\delta a|\hat{h}|a] + [a|\hat{h}|\delta a]) \\ &+ \frac{1}{2} \sum_a^{N_e} \sum_b^{N_e} ([\delta a a|b b] + [a \delta a|b b] + [a a|\delta b b] + [a a|b \delta b]) \\ &- \frac{1}{2} \sum_a^{N_e} \sum_b^{N_e} ([\delta a b|b a] + [a \delta b|b a] + [a b|\delta b a] + [a b|b \delta a]). \end{aligned} \quad (457)$$

The following transitive relationships can be shown using the definitions of the integrals from equations (433) and (435):

$$[\delta a|\hat{h}|a] = [\delta a|\hat{h}|a]^* \quad (458)$$

$$[\delta aa|bb] = [a\delta a|bb]^* = [aa|\delta bb] = [aa|b\delta b]^* \quad (459)$$

$$[\delta ab|ba] = [a\delta b|ba]^* = [ab|\delta ba] = [ab|b\delta a]^*. \quad (460)$$

Using the transitive properties from (458), (459), and (460); equation (455) becomes

$$\begin{aligned} \delta E_0[\{\chi_a\}] &= \sum_a^{N_e} ([\delta a|\hat{h}|a] + [a|\hat{h}|\delta a]) \\ &\quad + \sum_a^{N_e} \sum_b^{N_e} ([\delta aa|bb] - [\delta ab|ba] + [\delta aa|bb]^* - [\delta ab|ba]^*) \\ &= \sum_a^{N_e} \left( [\delta a|\hat{h}|a] + \sum_b^{N_e} ([\delta aa|bb] - [\delta ab|ba]) \right) \\ &\quad + \sum_a^{N_e} \left( [\delta a|\hat{h}|a]^* + \sum_b^{N_e} ([\delta aa|bb]^* - [\delta ab|ba]^*) \right) \end{aligned} \quad (461)$$

Then using the definitions for the Coulomb and exchange operators in equations (444) and (446)

$$\begin{aligned} \delta E_0[\{\chi_a\}] &= \sum_a^{N_e} \left( [\delta a|\hat{h}|a] + \sum_b^{N_e} ([\delta a|J_b|a] - [\delta a|K_b|a]) \right) \\ &\quad + \sum_a^{N_e} \left( [\delta a|\hat{h}|a]^* + \sum_b^{N_e} ([\delta a|J_b|a] - [\delta a|K_b|a])^* \right) \\ &= \sum_a^{N_e} \left[ \delta a \left| \hat{h} + \sum_b^{N_e} (J_b - K_b) \right| a \right] + \sum_a^{N_e} \left[ \delta a \left| \hat{h} + \sum_b^{N_e} (J_b - K_b) \right| a \right]^* \end{aligned} \quad (462)$$

Using equations (462) and (456) the first variation in  $\mathcal{L}$ , equation (455), becomes

$$\begin{aligned}
\delta\mathcal{L} &= \sum_a^{N_e} \left( \left[ \delta a \left| \hat{h} + \sum_b^{N_e} (J_b - K_b) \right| a \right] - \sum_b^{N_e} \varepsilon_{ab} [\delta a | b] \right) \\
&\quad + \sum_a^{N_e} \left( \left[ \delta a \left| \hat{h} + \sum_b^{N_e} (J_b - K_b) \right| a \right] - \sum_b^{N_e} \varepsilon_{ab} [\delta a | b] \right)^* \\
&= \sum_a^{N_e} \int d\mathbf{x}_1 \delta\chi_a^*(1) \left\{ \hat{h}(1) \chi_a(1) + \sum_b^{N_e} (J_b(1) - K_b(1)) \chi_a(1) - \sum_b^{N_e} \varepsilon_{ab} \chi_b(1) \right\} \\
&\quad + \left[ \sum_a^{N_e} \int d\mathbf{x}_1 \delta\chi_a^*(1) \left\{ \hat{h}(1) \chi_a(1) + \sum_b^{N_e} (J_b(1) - K_b(1)) \chi_a(1) - \sum_b^{N_e} \varepsilon_{ab} \chi_b(1) \right\} \right]^* \\
&= 0
\end{aligned} \tag{463}$$

The vanishing of  $\delta\mathcal{L}[E_0]$  for an arbitrary variation  $\delta\chi_a$  and  $\delta\chi_a^*$  is satisfied by the condition

$$\left[ \hat{h}(1) + \sum_b^{N_e} (J_b(1) - K_b(1)) \right] \chi_a(1) = \sum_b^{N_e} \varepsilon_{ab} \chi_b(1) \tag{464}$$

The quantity in the square brackets in equation (464) is the definition of the Fock operator.

$$f(1) = \hat{h}(1) + \sum_b^{N_e} (J_b(1) - K_b(1)) \tag{465}$$

The Fock operator in equation (465) is a single electron operator. The summation over the Coulomb and exchange operators represent a 1-electron approximation to the behavior of that electron in the field of the other  $N_e - 1$  electrons. The sum in (465) represents an average potential (Coulomb and exchange) felt by that 1-electron.

The spin orbitals then take the form

$$f|\chi_a\rangle = \sum_b^{N_e} \varepsilon_{ab} |\chi_b(1)\rangle \quad (466)$$

which are not in their canonical eigenvalue form. A single determinant wavefunction  $|\Psi_0\rangle$  formed from a set of spin orbitals  $\{\chi_a\}$  can be mixed among the orbitals without changing the expectation value  $E_0 = \langle\Psi_0|\mathcal{H}|\Psi_0\rangle$ . The canonical form can be obtained by taking a unitary transformation on the Lagrange multipliers.

### Canonical Spin Orbitals.

The orbitals generated by the Hartree-Fock equations are not unique. Any set of orbitals obtainable by a unitary transformation that leaves the total wavefunction invariant would produce another set of spin orbitals,  $\{\chi'_a\}$  where

$$\chi'_a = \sum_b U_{ab} \chi_b \quad (467)$$

$$[a'|b'] = \delta_{ab}. \quad (468)$$

Given that  $\varepsilon_{ab}$  form a Hermitian matrix, see equation (453), it is always possible to form a unitary matrix  $\mathbf{U}$  such that

$$\varepsilon' = \mathbf{U}^\dagger \varepsilon \mathbf{U} \quad (469)$$

is a transformation that makes  $\varepsilon'$  a diagonal matrix. However, the Fock operator,  $f$ , is defined in terms of the original spin orbitals  $\{\chi_a\}$  and not in terms of the canonical spin orbitals  $\{\chi'_a\}$ . To show that the Fock operator is invariant under a unitary transformation the various parts are examined. The core operator,  $\hat{h}$  does not depend on the spin orbitals, so only the Coulomb and exchange operators are

considered, equations (444) and (446). The transformed sum for these operators from equation (464) is

$$\sum_b^{N_e} J'_b(1) \chi_a(1) = \sum_b^{N_e} \int d\mathbf{x}_2 \chi'_b{}^*(2) \frac{1}{r_{12}} \chi'_b(2) \chi_a(1) \quad (470)$$

$$= \sum_c \int d\mathbf{x}_2 \left( \sum_c U_{bc}^* \chi_c^*(2) \right) \frac{1}{r_{12}} \left( \sum_d U_{bd} \chi_d^*(2) \right) \quad (471)$$

$$= \sum_c^{N_e} \sum_d^{N_e} \left[ \sum_b^{N_e} \mathbf{U}_{cb}^\dagger \mathbf{U}_{bd} \right] \int d\mathbf{x}_2 \chi_c^*(2) \frac{1}{r_{12}} \chi_d(2) \chi_a(1), \quad (472)$$

but

$$\sum_b^{N_e} \mathbf{U}_{cb}^\dagger \mathbf{U}_{bd} = \delta_{cd} \quad (473)$$

so that

$$\begin{aligned} \sum_b^{N_e} J'_b(1) \chi_a(1) &= \sum_c^{N_e} \int d\mathbf{x}_2 \chi_c(2) \frac{1}{r_{12}} \chi_c(2) \chi_a(1) \\ &= \sum_c^{N_e} J_c(1) \chi_a(1) \end{aligned} \quad (474)$$

Thus the sum of the Coulomb operators is invariant to a unitary transformation of the spin orbitals. In an identical manner it can be shown that the exchange operator is invariant to any arbitrary unitary transformation. Hence, the Fock operator,  $f$ , is invariant as well and can now be written as

$$f(1) |\chi_a(1)\rangle = \varepsilon_a |\chi_a(1)\rangle \quad (475)$$

## Restricted Spin Orbitals

Recall from equation (420) that

$$\begin{aligned}
|\Psi_0\rangle &= |\chi_1\chi_2\chi_3\chi_4\cdots\chi_{N_e-1}\chi_{N_e}\rangle \\
&= |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_{N_e/2}\bar{\phi}_{N_e/2}\rangle,
\end{aligned} \tag{476}$$

where the number of distinct spin orbitals was halved by pairing the spins in each orbital with the restriction that the energy of each electron in the pair is the same. This applies to systems with closed orbitals so the number of electrons is even. i.e.  $N_e/2$  is an integer. Having converted the wave equation to spatial orbitals, the general spin orbital Hartree-Fock equation,  $f(1)\chi_a(1) = \varepsilon_a\chi_a$ , needs to be converted to a spatial eigenvalue equation where each of the spatial orbitals is doubly occupied. Remembering that  $\chi_a(\mathbf{x}_1) = \psi_a(\mathbf{r}_1)\sigma(\omega_1)$

$$f(\mathbf{x}_1)\psi_a(\mathbf{r}_1)\sigma(\omega_1) = \varepsilon_a\psi_a(\mathbf{r}_1)\sigma(\omega_1) \tag{477}$$

Multiplying then on the left by  $\sigma(\omega_1)$  and integrating over spin gives

$$\left[ \int d\omega_1 \sigma^*(\omega_1) f(\mathbf{x}_1) \sigma(\omega_1) \right] \psi_a(\mathbf{r}) = \varepsilon_a \psi_a(\mathbf{r}). \tag{478}$$

Recall that the spin orbital Fock operator acting on  $\chi_a$  is

$$\begin{aligned}
f(\mathbf{x}_1)\chi_a(\mathbf{x}_1) &= \hat{h}(\mathbf{x}_1)\chi_a(\mathbf{x}_1) + \sum_b^{N_e} \left( J_b(\mathbf{x}_1) - K_b(\mathbf{x}_1) \right) \chi_a(\mathbf{x}_1) \\
&= \hat{h}(\mathbf{x}_1) + \sum_b^{N_e} \int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_b(\mathbf{x}_2) \chi_a(\mathbf{x}_1) \\
&\quad - \sum_b^{N_e} \int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_a(\mathbf{x}_2) \chi_b(\mathbf{x}_1).
\end{aligned} \tag{479}$$



If the closed shell Fock operator is

$$f^{\text{cs}}(\mathbf{r}_1) = \int d\omega_1 \sigma^*(\omega_1) f(\mathbf{x}_1) \sigma(\omega_1) \quad (480)$$

then

$$f^{\text{cs}}(\mathbf{r}_1) \psi_a(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) \psi_a(\mathbf{r}_1) + \quad (481)$$

$$\begin{aligned} & + \sum_b^{N_e} \int d\omega_1 d\mathbf{x}_2 \sigma^*(\omega_1) \chi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_b(\mathbf{x}_2) \sigma(\omega_1) \psi_a(\mathbf{r}_1) \\ & - \sum_b^{N_e} \int d\omega_1 d\mathbf{x}_2 \sigma^*(\omega_1) \chi_b^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_b(\mathbf{x}_1) \sigma(\omega_2) \psi_a(\mathbf{r}_2) \\ & = \varepsilon_a \psi_a(\mathbf{r}_1) \end{aligned} \quad (482)$$

where the integration over  $d\omega_1$  was performed in the expression involving  $\hat{h}(\mathbf{r}_1)$ . The closed shell sum over the occupied spin orbitals includes two equal sums over the spatial orbitals: one with spin  $\sigma(\omega_i) = \alpha(\omega_i)$  and the other with spin  $\sigma(\omega_i) = \beta(\omega_i)$ . Therefore

$$f^{\text{cs}}(\mathbf{r}_1) \psi_a(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) \psi_a(\mathbf{r}_1) + \quad (483)$$

$$\begin{aligned} & + \sum_b^{N_e} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_b^*(\mathbf{r}_2) \alpha^*(\omega_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_2) \alpha(\omega_2) \alpha(\omega_1) \psi_a(\mathbf{r}_1) \\ & + \sum_b^{N_e} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_b^*(\mathbf{r}_2) \beta^*(\omega_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_2) \beta(\omega_2) \alpha(\omega_1) \psi_a(\mathbf{r}_1) \\ & - \sum_b^{N_e} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_b^*(\mathbf{r}_2) \alpha^*(\omega_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_1) \alpha(\omega_1) \alpha(\omega_2) \psi_a(\mathbf{r}_2) \\ & - \sum_b^{N_e} \int d\omega_1 d\omega_2 d\mathbf{r}_2 \alpha^*(\omega_1) \psi_b^*(\mathbf{r}_2) \beta^*(\omega_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_1) \beta(\omega_1) \alpha(\omega_2) \psi_a(\mathbf{r}_2) \\ & = \varepsilon_a \psi_a(\mathbf{r}_1) \end{aligned} \quad (484)$$

In performing the integration over the spin the first three spin integrals integrate to 1 and the last term to 0. This gives two equal Coulomb terms and a single exchange term so that

$$f^{\text{cs}}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) + \quad (485)$$

$$\begin{aligned} & + 2 \sum_b^{N_e/2} \int d\mathbf{r}_2 \psi_b^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_2) \psi_a(\mathbf{r}_1) \\ & - \sum_b^{N_e/2} \int d\mathbf{r}_2 \psi_b^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \\ & = \varepsilon_a \psi_a(\mathbf{r}_1). \end{aligned} \quad (486)$$

The closed shell Fock operator then has the form,

$$f^{\text{cs}}(\mathbf{r}_1) = \hat{h}(\mathbf{r}_1) + \sum_b^{N_e/2} \left( 2J_b^{\text{cs}}(\mathbf{r}_1) - K_b^{\text{cs}}(\mathbf{r}_1) \right) \quad (487)$$

where the spatial Coulomb and exchange operators are

$$J_b^{\text{cs}}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \int d\mathbf{r}_2 \psi_b(\mathbf{r}_2) \frac{1}{r_{12}} \psi_b(\mathbf{r}_2) \psi_a(\mathbf{r}_1). \quad (488)$$

$$K_b^{\text{cs}}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \int d\mathbf{r}_2 \psi_b(\mathbf{r}_2) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1).. \quad (489)$$

### The Roothaan Equations for RHF.

Having eliminated spin, the calculation of orbitals becomes equivalent to the problem of solving the spatial integro-differential equation

$$f^{\text{cs}}(\mathbf{r}_1)\psi_a(\mathbf{r}_1) = \varepsilon_a \psi_a(\mathbf{r}_1). \quad (490)$$

Since this equation can not be solved exactly a set of spatial basis functions is introduced and the differential equation is converted to a set of algebraic equations and solved by standard matrix techniques. To this end a set of  $K$  known basis functions is introduced

$$\{\phi_\mu(\mathbf{r})|\mu = 1, 2, \dots, K\} \quad (491)$$

where the unknown spatial orbitals are represented as a linear expansion of the basis functions.

$$\psi_a = \sum_{\mu}^K C_{\mu a} \phi_\mu, \quad a = 1, 2, \dots, K \quad (492)$$

Since the expansion is limited to a finite number,  $K$ , it is not complete. Having introduced an incomplete expansion another approximation to the wavefunction has been introduced. If the set  $\{\phi_{mu}\}$  were complete the expansion would not introduce further room for error.

A matrix equation for  $C_{\mu a}$  is obtained by substituting equation (492) into the Hartree-Fock equation (490). Using the index  $\nu$

$$f^{\text{cs}}(1) \sum_{\nu} C_{\nu a} \phi_\nu(1) = \varepsilon_a \sum_{\nu} C_{\nu a} \phi_\nu(1) \quad (493)$$

This equation is turned into a matrix equation by left multiplication of  $\phi_\mu^*(1)$  and integrating:

$$\sum_{\nu} C_{\nu a} \int d\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) = \varepsilon_a \sum_{\nu} C_{\nu a} \int d\mathbf{r}_1 \phi_\mu^*(1) \phi_\nu(1) \quad (494)$$

In this equation 2 matrices can be defined:

1. The overlap matrix  $\mathbf{S}$  has elements

$$S_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1) \phi_\nu(1). \quad (495)$$

The  $\mathbf{S}$  matrix is a  $K \times K$  Hermitian matrix.

2. The Fock matrix  $\mathbf{F}$  has elements

$$F_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1) f^{\text{cs}}(1) \phi_\nu(1) \quad (496)$$

The  $\mathbf{F}$  matrix is also a  $K \times K$  Hermitian matrix. It is a matrix representation of the Fock operator with in the set of basis functions  $\{\phi_\mu\}$ .

With these definitions for  $\mathbf{S}$  and  $\mathbf{F}$  equation (494) can be written as

$$\sum_{\nu} F_{\nu\mu} C_{\nu a} = \varepsilon_a \sum_{\nu} S_{\nu\mu} C_{\nu a} \quad a = 1, 2, \dots, K. \quad (497)$$

These are the Roothan equations which can be written in single matrix form

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (498)$$

Where  $\mathbf{C}$  is a  $K \times K$  matrix of the expansion coefficients  $C_{\mu a}$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1K} \\ C_{21} & C_{22} & \dots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \dots & C_{KK} \end{pmatrix} \quad (499)$$

and  $\boldsymbol{\varepsilon}$  is a diagonal matrix of the orbital energies  $\varepsilon_a$ ,

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & & \\ & \varepsilon_2 & & \mathbf{0} \\ & & \ddots & \\ \mathbf{0} & & & \varepsilon_K \end{pmatrix}. \quad (500)$$

The columns of  $\mathbf{C}$  describe the spatial orbitals, for example, the coefficients describing  $\psi_1$  are in the first column of  $\mathbf{C}$  while the second column are those for  $\psi_2$ , etc.

### The Charge Density.

In the closed-shell system of a single determinant, as that described by the spatial wavefunction in equation (492), the total charge density is given by

$$\rho(\mathbf{r}) = 2 \sum_a^{N_e/2} |\psi_a|^2 \quad (501)$$

such that  $\rho(\mathbf{r})d\mathbf{r}$  is the probability of finding an electron in  $d\mathbf{r}$  at  $\mathbf{r}$ . Equation (501) shows that the total charge density is a sum of the charge densities for each of the electrons. Using the orbital expansions from equation (492) the expression in (501) becomes

$$\begin{aligned} \rho(\mathbf{r}) &= 2 \sum_a^{N_e/2} \psi_a^*(\mathbf{r})\psi_a(\mathbf{r}) \\ &= 2 \sum_a^{N_e/2} \sum_{\mu} C_{\nu a}^* \phi_{\nu a}^*(\mathbf{r}) \sum_{\mu}^K C_{\mu a} \phi_{\mu}(\mathbf{r}) \\ &= \sum_{\mu\nu} \left[ 2 \sum_a^{N_e/2} C_{\nu a}^* C_{\mu a} \right] \phi_{\mu}^*(\mathbf{r})\phi_{\mu}(\mathbf{r}) \\ &= \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}^*(\mathbf{r})\phi_{\mu}(\mathbf{r}) \end{aligned} \quad (502)$$

where the density matrix is defined as

$$P_{\mu\nu} = 2 \sum_a^{N_e/2} C_{\nu a}^* C_{\mu a} \quad (503)$$

The density matrix,  $\mathbf{P}$  is completely specifies the charge density given the set of basis functions  $\{\phi_\mu\}$ .

### The Fock Matrix.

The Fock matrix is the matrix representation of the Fock operator in the basis  $\{\phi_\mu\}$ , see equation (496)

$$\begin{aligned} F_{\mu\nu} &= \int d\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \\ &= \int d\mathbf{r}_1 \phi_\mu^*(1) \hat{h}(1) \phi_\nu(1) + \sum_a^{N_e/2} \int d\mathbf{r}_1 \phi_\mu^*(1) [2J_a(1) - K_a(1)] \phi_\nu(1) \\ &= H_{\mu\nu}^{\text{core}} - G_{\mu\nu} \end{aligned} \quad (504)$$

where the core Hamiltonian is defined as

$$\begin{aligned} H_{\mu\nu}^{\text{core}} &= \int d\mathbf{r}_1 \phi_\mu^*(1) \hat{h}(1) \phi_\nu(1) \\ &= \int d\mathbf{r}_1 \phi_\mu^*(1) \left[ -\frac{1}{2} \nabla_1^2 \right] \phi_\nu(1) + \int d\mathbf{r}_1 \phi_\mu^*(1) \left[ -\sum_A^{N_c} \frac{Z_A}{r_{iA}} \right] \phi_\nu(1) \end{aligned} \quad (505)$$

and  $G_{\mu\nu}$  as

$$\begin{aligned}
G_{\mu\nu} &= \sum_a^{N_e/2} \int \mathbf{r}_1 \phi_\mu^*(1) [2J_a(1) - K_a(1)] \phi_\nu(1) \\
&= \sum_a^{N_e/2} \int d\mathbf{r}_1 \phi_\mu^* \left[ 2(\mu\nu|aa) - (\mu a|a\nu) \right] \phi_\nu(1) \\
&= \sum_a^{N_e/2} \sum_{\lambda\sigma} C_{\lambda a}^* C_{\sigma a} \left[ 2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu) \right] \\
&= \sum_a^{N_e/2} \sum_{\lambda\sigma} P_{\sigma\lambda} \left[ (\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right]. \tag{506}
\end{aligned}$$

Fock matrix contains both the one electron part,  $H_{\mu\nu}^{\text{core}}$ , and the two electron part  $G_{\mu\nu}$ .  $\mathbf{G}$  depends on  $\mathbf{P}$  and the two electron integrals

$$(\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\mu^*(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda^*(2) \phi_\sigma(2). \tag{507}$$

The Fock matrix as defined depends on the density matrix  $\mathbf{P}$  which from equation (503) depends on the expansion coefficients matrix  $\mathbf{C}$ . Thus

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon}, \tag{508}$$

and so the Roothan equations are nonlinear and will need to be solved in an iterative fashion.

### **Basis Set Orthogonalization.**

The basis sets are not always an orthonormal sets. While normalized, they may not be orthogonal. The following is one procedure that can be used to orthogonalize the basis functions.

Given a set of functions  $\{\phi_\mu\}$  that are not orthogonal,

$$\int d\mathbf{r} \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) = S_{\mu\nu} \quad (509)$$

it will always be possible to find a transformation matrix  $\mathbf{X}$  such that

$$\phi'_\mu = \sum_\nu \mathbf{X}_{\mu\nu} \phi_\nu \quad \mu = 1, 2, \dots, K \quad (510)$$

is a transformation to a new set of functions  $\{\phi'_\mu\}$  that is an orthonormal set,

$$\int d\mathbf{r} \phi'_\mu{}^*(\mathbf{r}) \phi'_\nu(\mathbf{r}) = \delta_{\mu\nu}. \quad (511)$$

To derive  $\mathbf{X}$ , substitute the transformation equation (510) into (511) to get

$$\begin{aligned} \int d\mathbf{r} \phi'_\mu{}^*(\mathbf{r}) \phi'_\nu(\mathbf{r}) &= \int d\mathbf{r} \left[ \sum_\lambda \mathbf{X}_{\lambda\mu}^* \phi_\lambda^*(\mathbf{r}) \right] \left[ \sum_\sigma \mathbf{X}_{\sigma\nu} \phi_\sigma(\mathbf{r}) \right] \\ &= \sum_\lambda \sum_\sigma \mathbf{X}_{\lambda\mu}^* \int d\mathbf{r} \phi_\lambda^*(\mathbf{r}) \phi_\sigma(\mathbf{r}) \mathbf{X}_{\sigma\nu} \\ &= \sum_\lambda \sum_\sigma \mathbf{X}_{\lambda\mu}^* S_{\lambda\sigma} \mathbf{X}_{\sigma\nu} \\ &= \delta_{\mu\nu}. \end{aligned} \quad (512)$$

Equation (512) can be written as the matrix equation

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I}. \quad (513)$$

Since  $\mathbf{S}$  is Hermitian it can be diagonalized by a unitary matrix  $\mathbf{U}$

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \quad (514)$$



where  $\mathbf{s}$  is a diagonal matrix of the eigenvalues of  $\mathbf{S}$ .

Using a procedure called symmetric orthogonalization, described in [87], the inverse of the square root of  $\mathbf{S}$  is used to get  $\mathbf{X}$

$$\mathbf{X} \equiv \mathbf{S}^{-1/2} = \mathbf{U} \mathbf{s}^{-1/2} \mathbf{U}^\dagger. \quad (515)$$

$\mathbf{S}^{-1/2}$  comes from diagonalizing  $\mathbf{S}$  to form  $\mathbf{s}$ , then taking the inverse square root of each eigenvalue to form the matrix  $\mathbf{s}^{-1/2}$  and then “un-diagonalizing” using  $\mathbf{U}^\dagger$ , as shown in (515). Since  $\mathbf{S}$  is Hermitian the  $\mathbf{S}^{-1/2}$  is also Hermitian. Substituting (515) into (513),

$$\mathbf{S}^{-1/2} \mathbf{S} \mathbf{S}^{-1/2} = \mathbf{S}^{-1/2} \mathbf{S}^{1/2} = \mathbf{S}^0 = 1 \quad (516)$$

shows that  $\mathbf{X}$  is an orthogonalizing transformation matrix.

To make use of  $\mathbf{X}$  consider  $\mathbf{C}'$ , a new coefficient matrix related to  $\mathbf{C}$  by

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \quad \mathbf{C} = \mathbf{X} \mathbf{C}'. \quad (517)$$

Then substituting  $\mathbf{C} = \mathbf{X} \mathbf{C}'$  into the Roothan equation (508) gives

$$\mathbf{F} \mathbf{X} \mathbf{C}' = \mathbf{S} \mathbf{X} \mathbf{C}' \boldsymbol{\varepsilon}. \quad (518)$$

Then left multiplying by  $\mathbf{X}^\dagger$  gives

$$(\mathbf{X}^\dagger \mathbf{F} \mathbf{X}) \mathbf{C}' = (\mathbf{X}^\dagger \mathbf{S} \mathbf{X}) \mathbf{C}' \boldsymbol{\varepsilon} \quad (519)$$

Defining a new matrix  $\mathbf{F}'$  by

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad (520)$$

and using it and equation (513)

$$\mathbf{F}' \mathbf{C}' = \mathbf{C}' \boldsymbol{\epsilon} \quad (521)$$

These equations are still non-linear since  $\mathbf{F}'$  is still a function of  $\mathbf{C}'$ , however working in the new basis the overlap matrix  $\mathbf{C}$  is the identity. The transformed Roothan equations can be solved for  $\mathbf{C}'$  by diagonalizing  $\mathbf{F}'$ . Given  $\mathbf{C}'$ ,  $\mathbf{C}$  can be obtained from equation (517). The intermediate primed matrices are the Fock matrix and expansion coefficients in the orthogonalized basis.

### Self-Consistent Field Procedure.

With all the theory covered, its now time for the actual computation process. The algorithm used to find the orbitals which represent the minimum energy orbitals for a given system for a given atomic orbital basis set is called the Self-Consistent-Field (SCF) procedure. SCF is as follows:

1. Specify a molecule:  $\{\mathbf{R}_A\}$  set of nuclear coordinate,  $\{Z_A\}$  atomic numbers, and a basis set  $\{\phi_\mu\}$ .
2. Calculate the required integrals:  $S_{\mu\nu}$ , equation (495);  $H_{\mu\nu}^{\text{core}}$ , equation (505); and  $(\mu\nu|\lambda\sigma)$ , equation (506) and (507).
3. Diagonalize the overlap matrix  $\mathbf{S}$  and obtain a transformation matrix  $\mathbf{X}$ , equation (515).
4. Obtain a first guess at the density matrix  $\mathbf{P}^{(0)}$ .

5. Calculate the matrix  $\mathbf{G}^{(i)}$ , equation (506), from the density matrix  $\mathbf{P}^{(i-1)}$  and the two electron integrals  $(\nu\mu|\lambda\sigma)$ .
6. Add  $\mathbf{G}^{(i)}$  to the core-Hamiltonian to obtain the Fock matrix  $\mathbf{F}^{(i)} = \mathbf{H}^{\text{core}} + \mathbf{G}^{(i)}$ .
7. Calculate the transformed Fock matrix  $\mathbf{F}'^{(i)} = \mathbf{X}^\dagger \mathbf{F}^{(i)} \mathbf{X}$ .
8. Diagonalize  $\mathbf{F}'^{(i)}$  to obtain  $\mathbf{C}'^{(i)}$  and  $\epsilon^{(i)}$ .
9. Calculate  $\mathbf{C}^{(i)} = \mathbf{X} \mathbf{C}'^{(i)}$ .
10. Form a new density matrix  $\mathbf{P}^{(i)}$  from  $\mathbf{C}^{(i)}$ , equation (503).
11. Determine if  $\mathbf{P}^{(i-1)} \approx \mathbf{P}^{(i)}$ 
  - if yes then go to 12
  - if no then go to 5
12. Use  $\mathbf{C}$  to calculate expectation values.

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