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Universal Two-Electron Correlation Operator on Excited States

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UNIVERSAL TWO-ELECTRON CORRELATION OPERATOR ON EXCITED STATES

by

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Bachelor of Science
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Submitted in Partial Fulfillment of the Requirements
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DEDICATION

For my family.

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ABSTRACT

Excited states of chemical systems are extremely important in understanding spectra, chemical phenomena, as well as how a particular compound behaves in reactions. Computationally, excited states are normally very expensive to calculate. The difficulty in calculating these states with wavefunction based methods can be mainly attributed to the calculation of large multi-determinant wavefunctions. One reason to use a complicated multi-determinant wavefunction is to include some of the effects of correlation energy. The quantity of correlation energy can most simply be defined as the reduction in energy caused by any two or more electrons trying to avoid each other. The most common way of avoiding these computational costs is through the use of time-dependent density functional theory (TD-DFT). TD-DFT has an exceptional ratio of accuracy to computational cost because it reduces the many-electron wavefunction to a single-electron density. A single-electron quantity, however, is an improper way to describe an innately two-electron property like correlation energy.

Within this research we seek to alleviate the large computational costs required to calculate excited states with a wavefunction-based method and reduce the costs to near Hartree-Fock theory levels. We do this by using two different inexpensive excited wavefunction methods. First we reduce our multi-determinant wavefunction to a single-determinant wavefunction. The single-determinant wavefunction used in this research comes from delta self-consistent field method (Δ SCF) that essentially creates excited Hartree-Fock states. Secondly we construct the simplest multi-configurational wavefunction using a linear combination of all singly excited states with the method known as configuration interaction singles (CIS). The reduction in wavefunction size,

however, reduces nearly all correlation energy recovered by both methods. This is remedied by modeling correlation energy in a computationally inexpensive manner.

A potentially accurate way to model electron correlation within the single determinant wavefunction formalism is through the expectation value of a linear two-electron operator over the Kohn-Sham single-determinant wavefunction. For practical reasons, it is desirable for such an operator to be universal, i.e. independent of the positions and types of nuclei in a molecule. We choose an operator expanded in a small number of Gaussians as a model for electron correlation. The accuracy of this method is tested by computing atomic and molecular adiabatic excited states in comparison with popular TD-DFT functionals.

The correlation operator combined with Δ SCF is found to be comparable in accuracy to TD-DFT methods for both atomic and molecular excited states. Δ SCF is limited in its applications, however, due to its inability to guarantee orthogonal excited states which leads to unwanted spin contamination. The correlation operator combined with CIS is found to be comparable in accuracy to TD-DFT methods for atomic states but has a significant loss in accuracy for excited molecular states. This drop in accuracy is theorized to be the poor description Hartree Fock theory gives of some ground and excited state wavefunctions.. We offer some possible solutions to these problems in the form of orthogonality constraints and a potential hybrid method of Δ SCF and CIS [1].

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Nearly every electronic structure method is designed to balance computational cost with accuracy. The full configuration interaction method (FCI) can calculate nearly exact information about any property of a chemical system. It does this by including every possible electron configuration in the form of excited determinants. By increasing the system size, however, one can very simply go from a relatively tractable problem to one that would take longer than the age of the universe to complete. This deficiency of FCI illustrates why we must make approximations within electronic structure methods. For FCI, approximations are made that truncate the amount of included excited state determinants to single excitations, double excitations, triple excitations, etc. The methods used to calculate any particular property of chemical systems follow the same chain of logic as the simplification of FCI. Each approximation added will lessen the expense of the method but normally at the cost of some of the accuracy.

The same computational expense and accuracy balance can be found within excited state methods. If highly accurate excited state energies are desired, then one can perform a complete active space self consistent field method (CASSCF) calculation. This soon runs into the same problems where results are quantitatively accurate, however, computational cost grows extremely high for larger systems. It soon becomes clear that the increase in excited state determinants is the cause of the increase of

computational expense. Exactly like FCI, CASSCF can be reduced to restricted active space self consistent field method (RASSCF) that limits the amount of excited state configurations and reduces computational complexity [2].

Many excited state methods have been created that try to avoid this inclusion of more and more determinants to increase accuracy. The most popular method for electronic structure calculations, density functional theory (DFT), avoids using the wavefunction altogether to decrease computational costs. By utilizing the electron density to calculate chemical properties DFT becomes cheaper than nearly all wavefunction-based methods. Density functional theory has an extension for excited states known as time-dependent density functional theory (TD-DFT). Because of TD-DFT's low computational cost and reasonable accuracy, it has become one of the most popular methods for calculating excited states. The use of electron density to calculate properties comes with its own set of particular deficiencies.

The biggest inherent flaw within any DFT method is the use of the electron density. The electron density is used to calculate nearly any property of a chemical system. A problem comes when one tries to calculate a two electron phenomenon with a single electron density. For example one can look at the correlation energy. Correlation energy explicitly comes from two electron interactions. This is impossible to calculate exactly in practice using DFT's one-electron density. Within many modern correlation functionals, however, this is normally compensated for by using many empirically derived parameters rather than ab initio or physically derived coefficients.

During this research we sought to create a wavefunction-based method for excited states that was computationally inexpensive while simultaneously being qualitatively accurate. To do this we avoided density functional theory as well as multi-determinantal wavefunctions. The simplest wavefunction one can create is a single-determinant wavefunction. By using the Hartree-Fock method (HF), one can variationally achieve the best possible ground state single-determinant wavefunction within

the basis set limit. When calculating excited states, however, the HF method is not as useful. The HF method is designed to always build a single determinant wavefunction out of the lowest energy orbitals possible. Because of this, any higher excited energy state initially calculated by the HF method, will always variationally collapse back to the lowest energy same spin state.

1.2 Δ SCF METHOD

The Gill group has shown that a single-determinant wavefunction method does not have to suffer from variational collapse when trying to calculate excited states in a Hartree-Fock like manner [3]. This is possible by changing the criteria for which orbitals become occupied other than only choosing the orbitals of lowest energy. This can be done by choosing occupied orbitals that overlap the most with the orbitals from the previous iteration of the self-consistent field (SCF) cycle. This allows the user to initially choose the excited state electron configuration that the final single-determinant wavefunction is comprised of. This method known as the delta self-consistent field method (Δ SCF) essentially creates an excited HF method that avoids variational collapse back to lower same spin states.

The Δ SCF method is surprisingly accurate for excited states despite utilizing only a single-determinant wavefunction. The single-determinant nature and the formulation of the Δ SCF method does bring its own set of deficiencies. Because the wavefunction is made of a single determinant it omits all possible contributions from other configurations. Many excited states and some ground states require multiple determinants to be fully and accurately described. Without these extra configurations Δ SCF may give qualitatively incorrect descriptions of chemical systems. Even without extra excited determinants, however, Δ SCF has been shown to be a qualitatively accurate method for calculating energies and other properties of many chemical systems [4].

The second notable weakness of the Δ SCF method is introduced by the new operators required to keep the electrons in a given configuration. The calculated excited states are not orthogonal to other lower spin states. This inability to keep excited states orthogonal to each other will allow spin contamination. For open shell systems, spin contamination becomes one of the greatest sources of error within unrestricted HF and Δ SCF theory. Spin contamination occurs when an excited wavefunction begins mixing improperly with lower level excited states of same spatial but different spin symmetry. The error created by the mixing of lower energy spin states creates qualitatively inaccurate wavefunctions for Δ SCF calculations. This deficiency affects all unrestricted post-HF calculations of open shell system.

The third weakness of the Δ SCF method is the total lack of correlation energy. This is a common property that it shares with the HF method. This lack of correlation comes from the mean field treatment of electron repulsion as well as the single determinant wavefunctions of both methods. The correlation energy is normally the smallest contribution to the total energy, however, it is critical for the description of many chemical phenomena such as dispersion, bond breaking, and bond forming.

1.3 CONFIGURATION INTERACTION SINGLES

Although FCI is prohibitively expensive for most chemical systems, it can be truncated by number of excitations to create cheaper and cheaper methods. When FCI is truncated to single excitations it becomes configuration interaction singles (CIS). CIS uses the HF wavefunction as a reference wavefunction and then adds a linear combination of all singly excited configurations. The first full investigation of CIS was done by Pople [5] and found that CIS, severely truncated as it may be, can be surprisingly useful. The determination of the CIS coefficients allows for the CIS to relax energetically and more properly represent excited states. CIS was found to yield accurate properties and geometries of many chemical systems in excited states.

The first benefit of CIS is the low computational cost. CIS is comparable in cost to HF or Δ SCF method. The addition of all first excited state determinants adds a negligible cost to the original HF reference wavefunction. This feature is on account of not having to calculate any extra integrals to include these new states. The second benefit of CIS is the ability to calculate all single excitations simultaneously. This is contrary to the previous Δ SCF method. The Δ SCF method requires an initial ground state calculation as well as an excited state calculation performed for a single excited state electron configuration of interest. The third benefit of CIS is the orthogonality of all excited states to the ground state. This property may possibly be the most important difference from the Δ SCF method. The inability to guarantee the orthogonality of states is the cause of most of the Δ SCF method's deficiencies. CIS does not change the operators so each calculated state remains orthogonal to the ground state. Because of these collected benefits of CIS, it becomes a very good candidate for being used in tandem with the correlation operator.

1.4 CORRELATION OPERATOR

On the quest to create the cheapest yet accurate excited state wavefunction method we begin to neglect critical components that lead to accurate wavefunction descriptions. One of these components is the correlation energy. Correlation energy can be described in two different ways, dynamic and static. Dynamic correlation comes from electrons avoiding each other and trying to reduce their repulsion to a minimum. Static correlation is a consequence of a particular state only being describable by multiple determinants. Reducing the wavefunction model to the Δ SCF method leads to no inclusion of static or dynamic correlation. Creating the wavefunction using the CIS method includes some static correlation but no dynamic correlation. The standard methods of including correlation energy within any system quickly raise the computational cost to much higher than DFT approaches.

The correlation operator was designed to model dynamic correlation energy without greatly increasing the cost of the reference method. The correlation operator is able to model dynamic correlation as the overlaps of all basis functions with the operator augmented with the calculated orbital coefficients. The Δ SCF method contains absolutely no correlation similar to the HF method. For Δ SCF the operator can be evaluated over the chosen basis functions and then included within the SCF procedure or afterwards in a perturbative fashion to model the correlation energy. The Δ SCF correlation operator will be fully discussed in Chapter 2.

The correlation operator mixed with CIS is slightly different. The CIS method includes some correlation for excited states in the form of static correlation. CIS is not a single-determinant method because it includes all singly excited determinants to calculate excited states. These excited determinants, however, do not contribute any correlation energy to the ground state because all of the singly excited determinants are orthogonal to the ground state as described by Brillouin's theorem [6]. CIS still inherently contains no dynamic correlation. Therefore CIS is a promising candidate for treatment with the correlation operator. The full treatment and results of the CIS correlation operator can be found in Chapter 3.

CHAPTER 2

ΔSCF CORRELATION OPERATOR

2.1 METHODS

Energy Expression

The correlation operator is designed as a perturbation to the traditional non-relativistic Born-Oppenheimer Hamiltonian. The traditional Hamiltonian, \hat{H}_0 , normally contains a summation of one-electron terms, \hat{h}_i , and of two-electron interactions, $\frac{1}{r_{ij}}$, but will now contain a perturbation, \hat{H}' , that is a two electron operator known as the correlation operator, \hat{C}_{ij} .

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (2.1)$$

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{i>j} \hat{C}_{ij} \quad (2.2)$$

Energy, E , is evaluated as an expectation value of the modified Hamiltonian in Equation 2.2 over the Kohn-Sham wavefunction, Φ_{KS} .

$$E = \langle \Phi_{KS} | \hat{H} | \Phi_{KS} \rangle \quad (2.3)$$

For the ground state, the energy expression is very similar to the evaluation of density functionals within the Kohn-Sham formulation of DFT. The modified Hamiltonian is analogous to an exchange-correlation functional where exact exchange is used for the exchange portion and the correlation operator is evaluated for the correlation portion. In development of the correlation operator, the single determinant wavefunction Φ_{KS} is varied to only minimize the mean field portion of the total energy. This leads the calculated wavefunction to be identical to a Hartree-Fock wavefunction.

Operator expression

The formulation of the correlation operator first begins with a generic linear operator. Any generic linear operator can be expanded in a complete set of functions g_i and coefficients $O_{i,j}$:

$$\hat{O} = \sum_{i,j} O_{i,j} |g_i\rangle \langle g_j|,$$

with coordinates of functions g_i spanning the operator domain. The translational and rotational invariance of the universal two-electron correlation operator implies that the expansion functions g_i should depend only on a relative coordinate $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ as $g_i = g_i(\vec{r}_{12})$. It is convenient to break the operator into radial and angular parts. Both the semiclassical [7] and the harmonic [8] expressions of the operator are diagonal in the angular variables of 3D vector \vec{r}_{12}

$$\hat{C} = \sum_{l,m,i,j} C_{i,j}^{l,m} |Y_{l,m}(\theta, \phi) g_i(r_{12})\rangle \langle Y_{l,m}(\theta, \phi) g_j(r_{12})|, \quad (2.4)$$

with $\vec{r}_{12} = (r_{12}, \theta, \phi)$ and $Y_{l,m}(\theta, \phi)$ being spherical harmonics.

Previous studies on correlation energy with tight hookium [8] show that the magnitude of the leading expansion coefficients diminishes fast with the increase in l , with the dominant contribution from the spherically symmetric $l = 0$ term, which we label with the superscript s

$$\hat{C}^s = \sum_{i,j} C_{i,j}^s |g_i(r_{12})\rangle \langle g_j(r_{12})|. \quad (2.5)$$

The \hat{C}^s component of the operator is unable to fully describe some electron interactions due to its symmetric nature. It is therefore advantageous to add an anti-symmetric correction. The leading correction to the $l = 0$ term is given by an anti-symmetric $l = 1$ p-term, written in Cartesian representation as

$$\begin{aligned} \hat{C}^p = \sum_{i,j} C_{i,j}^p & \left(|x_{12} g_i(r_{12})\rangle \langle x_{12} g_j(r_{12})| + |y_{12} g_i(r_{12})\rangle \right. \\ & \left. \times \langle y_{12} g_j(r_{12})| + |z_{12} g_i(r_{12})\rangle \langle z_{12} g_j(r_{12})| \right). \end{aligned} \quad (2.6)$$

Two considerations go into the functions chosen for g_i . First it is convenient to choose g_i to be functions with simple matrix elements over atom-centered basis functions, such as a set of even-tempered Gaussians $g_i = \exp(-\alpha_i r_{12}^2)$, $\alpha_i = \alpha_0 \times \beta^i$, with optimally chosen α_0 and β parameters [9]. Secondly g_i is chosen to be eigenfunctions of the harmonic oscillator. Because the harmonic oscillator is so well studied, it will be easier to predict and analyse the properties of the correlation operator.

Correlation energy is known to be nearly independent of the uniform scaling transformation of space [10], and exactly independent of it in the weak correlation limit. This (i) constrains the coefficients $C_{i,j}$ and (ii) requires the set of exponents of the functions g_i be, in principle, infinite. Note that in the case of infinite expansion, the expectation value of the correlation operator should be approximately independent of α_0 . The simplest approach is to limit the expansion of Eq. 2.5 to a *single* term but with the adapted value of exponent α_0 . The adaptation of α_0 is particularly simple when the operator is evaluated in the Atomic Orbital (AO) basis, with each basis function expanded as a linear combination of the primitive (Gaussian or Slater) exponentials. Setting α_0 to be proportional to a mean value of exponents assures the scale invariance of the overall expression. We choose

$$\alpha_0 = \frac{1}{2} \sqrt{\frac{\alpha_1 \alpha_2 \alpha_3 \alpha_4}{\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4} \left(\frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \frac{1}{\alpha_3} + \frac{1}{\alpha_4} \right)} \quad (2.7)$$

as this choice achieves the best overlap between \hat{C}^s and four Gaussian primitives, each on the $\langle bra|$ or $|ket\rangle$ side in the basis function of either electron 1 or 2.

To summarize, the expectation value of the correlation operator over the single determinant Kohn-Sham wavefunction is evaluated as a linear combination over contributions from individual basis functions,

$$\begin{aligned} \langle \Phi_{KS} | \hat{C} | \Phi_{KS} \rangle &= \sum_{\lambda, \mu, \eta, \nu} P_{\lambda, \mu} P_{\eta, \nu} \langle \chi_\lambda(\vec{r}_1) \chi_\eta(\vec{r}_2) | \hat{C}^s + \hat{C}^p | \\ &\times (\chi_\mu(\vec{r}_1) \chi_\nu(\vec{r}_2) - \delta_{\sigma_1, \sigma_2} \chi_\nu(\vec{r}_1) \chi_\mu(\vec{r}_2)) \rangle. \end{aligned} \quad (2.8)$$

The summation runs over all one-electron basis function indices, $P_{\lambda,\mu}$ and $P_{\eta,\nu}$ are one-electron density matrices summed over both spin contributions; $\delta_{\sigma_1,\sigma_2}$ is zero for different spin contributions of the two P matrices, and 1 otherwise. Each basis function, $\chi_\lambda(\vec{r}) = \sum_i b_i^\lambda \exp(-\alpha_i^\lambda(\vec{r} - \vec{R}_\lambda)^2)$, is expressed as a linear combination over the primitive Gaussians, which (using only the \hat{C}^s component as an example) yields

$$\langle \chi_\lambda(\vec{r}_1) \chi_\eta(\vec{r}_2) | \hat{C}^s | \chi_\mu(\vec{r}_1) \chi_\nu(\vec{r}_2) \rangle = \sum_{i,j,k,l} C_{i,j,k,l}^s, \quad (2.9)$$

with the expression for the integral over primitives $C_{i,j,k,l}^s$ given in the Appendix.

Two points about the correlation operator expression are worth emphasizing. First, the Gaussian(s) in the operator expression are centered at the origin of \vec{r}_{12} , regardless of the center positions of the Gaussian basis functions. Second, the \hat{C}^s contribution is usually dominant even when evaluated over p-type atomic or molecular basis functions.

The reduction of the operator expression, essentially to a single Gaussian for each l value, makes it unnecessary to use model systems to derive the $C_{i,j}$ expansion coefficients, or to split the operator into mean-field and response parts, as was done in the tight hookium study [8]. In practice, essentially every density functional model used in quantitative studies adjusts the overall normalization coefficient of the functional contribution. The current version of the correlation operator only contains two parameters used as normalization coefficients to the \hat{C}^s and \hat{C}^p components of the operator. The ratio of the two normalization coefficients corresponds to the correlation energy within the Hooke's law atom. The single coefficient for the \hat{C}^s component has a value of -0.0435159 . The single coefficient for the \hat{C}^p component has a value of -0.0029605 .

Wavefunction model

The correlation operator is designed to give correlation energy as an expectation value over a single-determinant wavefunction. The single-determinant wavefunction is well-known for being deficient in describing excited states, as well as, some ground state systems due to the neglect of extra electron configurations. The single-determinant formalism was chosen due to its simplicity and its accuracy regardless of not including extra excited determinants. The Δ SCF method of describing single-determinant excited states was chosen to be investigated with the correlation operator because it has many desirable qualities for calculating excited states. For ground state calculations the Δ SCF method is the Hartree-Fock method. The Δ SCF method also gives some excited states as long as they have a different symmetry from all other lower energy states. It is normally impossible to constrain a particular symmetry using the traditional SCF procedure without variationally collapsing to the lowest same-symmetry state. It is possible to converge to these higher excited states and avoid variational collapse by using an augmented SCF procedure developed by the Gill group known as the Maximum Overlap Method (MOM). Initial-guess orbitals are occupied for the desired excited state and MOM maximizes overlap between occupied orbitals during each successive SCF iteration. The calculated wavefunction essentially creates HF excited states for states that were impossible to reach using the traditional SCF procedure. The change in the SCF procedure, however, leads to as Gill describes “quasi-orthogonality” [3]. This undesirable property of MOM and Δ SCF will be further discussed in the next section.

The correlation operator is utilized within the Δ SCF formalism in two ways, perturbatively and self-consistently. The perturbative approach maybe adequate because the correlation energy contribution is typically one of the smallest contributions and thus does not perturb the overall wavefunction very significantly. The perturbative approach also allows us to re-adjust the normalization coefficients without redoing

the calculations. The same formulation of the Δ SCF correlation operator also has the option to be used within the self-consistent procedure. The addition of the correlation operator into the self-consistent procedure allows the operator to act as a response term. Instead of acting as a perturbative correction that has no effect on the optimized wavefunction, the operator now dynamically changes the wavefunction through each SCF cycle. This method allows us to see how our model of electronic correlation is able to affect the single determinant wavefunction as it is being optimized rather than perturbatively added to a totally uncorrelated wavefunction.

Basis sets

The correlation operator is evaluated as an expectation value over a single determinant wavefunction. The basis sets were carefully chosen to eliminate any basis set error that may affect the accuracy of the calculated adiabatic excitation energies. Due to the single determinant nature of the wavefunction, it is relatively easy to choose a significantly large basis set to reach the basis set limit. Two different basis sets were used for atomic and molecular calculations respectively. Atomic calculations require far more flexibility within the diffuse domain when calculating excited states. The dependence of the Δ SCF method on the quality of the basis set can be seen in Table 2.1.

Table 2.1 Comparison of the energy of the 3P state of He calculated using the Δ SCF method with basis sets including subsequently more diffuse basis functions. All deviations are from experiment. Energies reported in atomic units.

| Basis | Deviation | % error |
|---------------|-----------|---------|
| 6-311G** | 0.831771 | 107.96 |
| 6-311++G | 0.291918 | 37.89 |
| 6-311(2+,2+)G | 0.291848 | 37.88 |
| 6-311(3+,3+)G | 0.066539 | 8.64 |
| Even-Tempered | -0.040171 | -5.21 |

For atomic calculations we used a modified version of the Universal Gaussian Basis Set (UGBS) [11]. It is based on a fully optimized uncontracted 12s9p atomic basis, augmented in the diffuse region to 17s12p size. The custom basis set is also augmented with even-tempered $9d3f$ uncontracted basis functions. The calculation of molecular excited states does not have as strict of basis set conditions as calculating atomic states. Molecular calculations are not required to have such a large flexibility in the diffuse domain. Because of this we chose to use the large but more traditional G3MP2Large basis set. The G3MP2Large basis set is large enough that basis set error can be neglected for all molecular calculations presented in this investigation.

2.2 RESULTS AND DISCUSSION

The analysis of the results will be split into two data sets: atoms and molecules. All calculations were performed using the developer’s version of the electronic structure package of QCHEM [12]. The value of the correlation energy was computed two separate ways as an expectation value of the correlation operator during the SCF procedure and perturbatively after the SCF procedure while using a spin-unrestricted formalism.

Atoms

Our atomic test set consisted of low-level excited states of the first and second row atoms, shown in Table 2.2. The set contains same-spin and spin-flip excited states. The experimental values are taken from the NIST database [13]. No spin-orbit corrections were used in the calculations. The largest spin-orbit correction in the set would likely be for the sulfur excitation energy. Its magnitude is less than 10^{-3} hartree [14], which is sufficiently small to be neglected. The computed excitation energies are reported as deviations from the experimental values, with positive numbers indicating overestimation of excitation energy. All data are reported in atomic units.

Table 2.2 Atomic excitation energies computed with a custom even-tempered basis set. Experimental excitation energies are taken from NIST [13]. The excitation energies computed with the correlation operator are reported as the deviation from the experiment. Energies reported in atomic units.

| Atom | Transition | $E(exp)$ | $\Delta E(\hat{C}_{Pert})$ | $\Delta E(\hat{C}_{SCF})$ |
|------|-----------------------|----------|----------------------------|---------------------------|
| He | $^1S \rightarrow ^3S$ | 0.728357 | -0.007805 | -0.007809 |
| He | $^1S \rightarrow ^3P$ | 0.770416 | -0.006074 | -0.006081 |
| Li | $^2S \rightarrow ^2P$ | 0.067906 | 0.001697 | 0.001686 |
| Be | $^1S \rightarrow ^3P$ | 0.100140 | -0.012758 | -0.012878 |
| B | $^2P \rightarrow ^2S$ | 0.182434 | 0.013993 | 0.013554 |
| C | $^3P \rightarrow ^5S$ | 0.153790 | -0.006637 | -0.006716 |
| N | $^4S \rightarrow ^4P$ | 0.379470 | 0.009089 | 0.008728 |
| O | $^3P \rightarrow ^5S$ | 0.336113 | -0.000986 | -0.001313 |
| F | $^2P \rightarrow ^4P$ | 0.466595 | -0.004448 | -0.004848 |
| Ne | $^1S \rightarrow ^3P$ | 0.610740 | -0.006299 | -0.006728 |
| Na | $^2S \rightarrow ^2P$ | 0.077258 | 0.001197 | 0.001393 |
| Mg | $^1S \rightarrow ^3P$ | 0.099558 | -0.004104 | -0.004375 |
| Al | $^2P \rightarrow ^4P$ | 0.132251 | -0.004562 | -0.004858 |
| Si | $^3P \rightarrow ^5S$ | 0.151845 | -0.005661 | -0.006007 |
| P | $^4S \rightarrow ^4P$ | 0.254879 | 0.012686 | 0.012129 |
| S | $^3P \rightarrow ^5S$ | 0.239771 | 0.019488 | 0.018888 |
| Cl | $^2P \rightarrow ^2P$ | 0.327866 | 0.021063 | 0.020202 |
| Ar | $^1S \rightarrow ^3P$ | 0.424394 | 0.024937 | 0.023842 |
| RMS | | | 0.011362 | 0.011064 |

The correlation operator data are separated into the self-consistent and perturbative formalisms. For most atoms it can be seen that the self-consistent and perturbative correlation operator are very close in accuracy, with less than a millihartree difference. A more significant difference can be seen for the heavier atoms such as P, S, Cl, and Ar where the difference between the self-consistent and perturbative corrections become more and more pronounced. This is promising since the errors also grow consistently larger for heavier atoms. This is a notable problem and most likely due to the qualitative accuracy of a single-determinant model for the atomic wavefunction used in the test.

The self-consistent and perturbative correlation operator performances are compared to the Δ SCF method, configuration interaction singles (CIS), and TD-DFT

with three popular functionals, B3LYP [15], PBE0 [16], and M06-2X [17]. The TD-DFT and CIS results were calculated with the multiplicities at the ground and excited states rather than allowing the calculations to flip the spins from one multiplicity to another. For example, consider the $^1S \rightarrow ^3S$ transition of helium. The ground state was calculated at a multiplicity of one. The excited triplet was calculated from a multiplicity of three rather than one so as not to require a spin flip in the calculation. This increases the accuracy of all the density functionals and CIS by nearly a factor of 2. The root mean square deviations and mean absolute deviations are given in Table 2.3. Both the self-consistent and perturbative correlation operators outperformed all of the TD-DFT functionals and CIS as well as increasing the accuracy of Δ SCF by a factor of more than 3.

Table 2.3 RMS values and mean absolute deviations for atomic excitation energies obtained with the correlation operator methods, Δ SCF, CIS, and TD-DFT functionals. Energies reported in atomic units.

| Method | RMS | $\langle \Delta E \rangle$ |
|------------------|----------|------------------------------|
| \hat{C}_{Pert} | 0.011362 | 0.009082 |
| \hat{C}_{SCF} | 0.011064 | 0.009002 |
| Δ SCF | 0.039363 | 0.033997 |
| B3LYP | 0.026867 | 0.016720 |
| PBE0 | 0.015897 | 0.010734 |
| M06-2X | 0.018209 | 0.014459 |
| CIS | 0.040393 | 0.034165 |

Molecules

The molecular test set was chosen to include all diatomics made of first row atoms and hydrogen for which experimental excited state geometry and energy are available [18], and with an excited state that did not have a lower level excited state of same

spatial but different spin symmetry. The last restriction is necessary because the spin-unrestricted calculation can become spin-contaminated by mixing with a lower-energy spin state, yielding a qualitatively incorrect excited state wavefunction [19]. The contaminated spin states are often unbound and thus could not be used for adiabatic excitation calculation. The molecular test set and correlation operator results are shown in Table 2.4.

Table 2.4 Diatomic excitation energies computed with the G3MP2Large basis set. Experimental excitation energies are taken from reference [18]. All computed data are reported as the deviation from the experiment. Energies are in atomic units, bond distances are in Angstroms.

| Molecule | $R_e(\text{Grnd})$ | Transition | $R_e(\text{Excit})$ | $E(\text{exp})$ | $\Delta E(\hat{C}_{\text{Pert}})$ | $\Delta E(\hat{C}_{\text{SCF}})$ |
|----------------|--------------------|-------------------------------------|---------------------|-----------------|-----------------------------------|----------------------------------|
| BeH | 1.3431 | $^2\Sigma \rightarrow ^2\Pi$ | 1.3327 | 0.09125 | 0.00716 | 0.00636 |
| BeF | 1.3614 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.3941 | 0.15142 | 0.00790 | 0.00767 |
| BF | 1.262 | $^1\Sigma \rightarrow ^3\Pi$ | 1.308 | 0.13279 | -0.01231 | -0.01279 |
| BO | 1.2049 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.3524 | 0.10861 | -0.01278 | -0.01160 |
| C ₂ | 1.2425 | $^1\Sigma_g \rightarrow ^3\Pi_u$ | 1.3119 | 0.00326 | 0.00346 | 0.00345 |
| CN | 1.1718 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.2327 | 0.04211 | -0.02781 | -0.02327 |
| CO | 1.1281 | $^1\Sigma \rightarrow ^3\Pi_r$ | 1.2093 | 0.22184 | 0.00511 | 0.00103 |
| N ₂ | 1.094 | $^1\Sigma_g \rightarrow ^3\Sigma_u$ | 1.2866 | 0.22874 | 0.05378 | 0.05376 |
| NH | 1.038 | $^3\Sigma \rightarrow ^3\Pi$ | 1.037 | 0.13581 | 0.00604 | 0.00582 |
| OH | 0.9706 | $^2\Pi_i \rightarrow ^2\Sigma$ | 1.0121 | 0.14891 | 0.00636 | 0.00631 |
| RMS | | | | | 0.02052 | 0.01979 |

On average the adiabatic molecular excitation energies are much smaller than the atomic excitation energies. Contrary to the typical atomic system, it is far less common for only a single determinant to be able to properly describe the wavefunction of a molecular system. For instance, the two ΔSCF operators' errors for the excitation energy in CN is more than 50 %. To investigate this issue, we have performed Full Configuration Interaction (FCI) calculations in 9 orbital active space with core electrons frozen, using 6-311G(3d) basis using GAMESS program [20]. Both the ground $^2\Sigma$ and the excited $^2\Pi_i$ states show significant multireference character, as judged by the magnitudes of the determinant expansion coefficients in the wavefunction. The ground state has a second determinant expansion coefficient of 0.1527, and the excited

state has a second determinant expansion coefficient of -0.1262 . The FCI excitation energy is 0.04714 , which is much closer to the experimental value of 0.04211 than the \hat{C}_{Pert} and \hat{C}_{SCF} values of 0.01430 and 0.01884 respectively.

Table 2.5 RMS values and mean absolute deviations for diatomic excitation energies obtained with the correlation operator methods, Δ SCF, CIS, and TD-DFT functionals. Energies reported in atomic units.

| Method | RMS | $\langle \Delta E \rangle$ |
|------------------|---------|----------------------------|
| \hat{C}_{Pert} | 0.02052 | 0.01427 |
| \hat{C}_{SCF} | 0.01979 | 0.01321 |
| Δ SCF | 0.02146 | 0.01734 |
| B3LYP | 0.00736 | 0.00575 |
| PBE0 | 0.01234 | 0.01044 |
| ω B97X | 0.00725 | 0.00593 |
| M06-2X | 0.00730 | 0.00421 |
| CIS | 0.05765 | 0.03830 |

The perturbative and self-consistent correlation operator performances are compared to the Δ SCF method, configuration interaction singles (CIS), and TD-DFT with B3LYP [15], PBE0 [16], ω B97X [21], and M06-2X [17] functionals. The root mean square deviations and mean absolute deviations are given in Table 2.5. Overall, the correlation operator improves the Δ SCF results. Looking at each of the correlation operator results separately we see that the self-consistent form performs superior to the correlation operator as a perturbative correction. Comparing the self-consistent results to the perturbative results can help to reveal how the correlation operator alters the Δ SCF wavefunction. We can see that on average the correlation operator as a response term within the SCF procedure changes the wavefunction in a way that more closely resembles a correlated wavefunction. We find, however, that both correlation operator approaches are inferior to most density functionals used within

TD-DFT method. We theorize that this has to be due to the single-determinant description of the excited states. The gradual improvement from the Δ SCF method to the perturbative correction to the self-consistent correction is very promising.

2.3 CONCLUSIONS

The goal of this research was to test the correlation operator’s ability to accurately model electron correlation in a balanced and computationally inexpensive way. This was achieved by adapting the correlation operator to work in cooperation with the Δ SCF method in a perturbative and self-consistent manner. We found that overall the correlation operator improves the accuracy of the Δ SCF method by more than a factor of three for atomic excitation energies and by several milli-hartrees on average for diatomic systems. We also found that when we compare the two Δ SCF correlation operator versions, the self-consistent version is superior. This was expected due to the response like nature of the self-consistent correlation operator. We see that when the correlation operator is allowed to alter the wavefunction, the orbitals relax even further and most importantly towards yielding the true experimental adiabatic excitation energies.

The results show a true improvement of the Δ SCF method using the correlation operator, however, we are limited by some of the properties of the Δ SCF method. The test set was chosen carefully so as to only show the deficiencies of the correlation operator. Many other molecules could not be tested due to the non-orthogonal states calculated by the Δ SCF method. The combination of the non-orthogonality of the calculated states and the nature of unrestricted Hartree-Fock formalism leads to spin contamination that gives qualitatively inaccurate states. These large errors are unable to be corrected by the small correction that is the correlation operator. This is why we choose the CIS wavefunction model within the next chapter. The more orthogonal states of CIS, in theory, should be a better fit for the correlation operator.

CHAPTER 3

CIS CORRELATION OPERATOR

3.1 METHODS

The CIS correlation operator is almost identical to the perturbative Δ SCF operator. The procedure for evaluating the operator over all basis functions is fully described in Section 2.1 in the previous chapter. Nearly the only difference between the CIS correlation operator and the perturbative Δ SCF correlation operator is the allocation of correlation operator integrals. The CIS method evaluates not just a single determinant wavefunction like the Δ SCF method but all singly excited states. The correlation operator is evaluated over many combinations of singly excited states instead of only one state of interest.

Wavefunction Model

The simplest form of a multi-configurational wavefunction can be obtained from the configuration interaction singles procedure. The full configuration interaction wavefunction is a linear combination of all possible excited electron configurations:

$$|\Psi_{FCI}\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \sum_{i,j,a,b} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{i,j,k,a,b,c} C_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots, \quad (3.1)$$

where i , j , and k are occupied orbitals that are being excited from and a , b , and c are virtual orbitals being excited to. Truncation of equation 3.1 at the first term returns the Hartree-Fock wavefunction and truncation at the second term becomes the definition of the CIS wavefunction.

The CIS wavefunction is chosen to be a linear combination of all possible singly excited determinants for several reasons. It is possible to have a singly excited wavefunction that is made of only one determinant. This procedure would be the equivalent of using one determinant from the many that are within the CIS expansion written generally as: $|\Psi\rangle = |\Phi_i^a\rangle$. The first disadvantage of this approach is that occupied orbital i and virtual orbital a have been variationally optimized for only the ground state. The orbitals will not be relaxed and at their lowest possible energies within this configuration. The evaluation of this wavefunction would be more consistent with the ionization energy of the chemical system rather than the actual excited state. The second disadvantage is that this approach totally neglects any possible degeneracy within the system. Promoting an electron to or from only one degenerate orbital does not completely describe a particular excitation. Excitations to or from degenerate orbitals requires contributions from all degenerate orbitals. Using one unrelaxed, singly excited determinant makes this impossible. These deficiencies are overcome by using a linear combination of all possible singly excited state determinants [5].

The CIS wavefunction is convenient to use for calculating excited states for several reasons. First, the computational cost of calculating the excited states within the CIS formalism negligibly increases the overall computational cost. CIS does not require the calculation of extra integrals because they are all defined within the calculation of the reference Hartree-Fock wavefunction. The most expensive part of the CIS procedure is the transformation from the atomic orbital basis to a molecular orbital basis. This is a very desirable attribute for use with the correlation operator. Nearly all ab-initio wavefunction-based excited state methods are multiple orders of magnitude more computationally expensive than Hartree-Fock theory. CIS is one of the only excited state methods that remains computationally inexpensive compared to an excited state method like TD-DFT.

Second, contrary to the Δ SCF method CIS calculates all singly excited states simultaneously. The formulation of the Δ SCF method only allows for one excited state to be calculated at a time and requires separate subsequent calculations to calculate other states. This property of the CIS method is not only computationally convenient but also gives valuable information about the vertical ordering of states. The CIS method can calculate any number of excited states above the ground state depending on the amount of virtual orbitals that are calculated from the initial Hartree-Fock reference wavefunction. The calculation of these states at any state's given equilibrium bond distance allows the user to see how all of the other states are ordered and are able to compare vertical excitation energies of all states at once. This is also a boon to the user because many points on different excited state potential energy surfaces can be calculated and compared simultaneously. This is all contrary to the Δ SCF method where only single potential energy surface points and single excitation energies can be evaluated with each calculation.

Third, CIS is guaranteed to create excited states that are orthogonal to the ground state. This third property may be the most important advantage over Δ SCF [22]. The guaranteed orthogonality to the ground state within CIS is not matched by the Δ SCF method. Because the wavefunction solutions to the Δ SCF method are calculated using different operators, the excited state wavefunctions cannot therefore be guaranteed to be orthogonal to the ground state or one another. The Δ SCF method can only rely on symmetry to guarantee that certain states are orthogonal to each other. The CIS method relies on the Brillouin theorem. One of the corollaries of this theorem states that any two determinants that differ by only one orbital are completely orthogonal from one another. For CIS this is relevant because $\langle \Phi_i^a | \hat{H} | \Phi_{HF} \rangle = 0$. By definition all singly excited determinants within CIS differ by one orbital from the reference HF wavefunction. This orthogonality constraint within the CIS method is a critical difference between itself and the Δ SCF method.

Energy Expression

The electronic energy of an excited state within configuration interaction singles is evaluated as an expectation value of a sum of an exact non-relativistic electronic Hamiltonian, \hat{H} , that consists of the one-electron terms, \hat{h}_i , and the electron-electron Coulomb interaction, $\frac{1}{r_{ij}}$, and a correlation operator, \hat{C} , evaluated over a wavefunction made of a linear combination of all singly excited determinants, $|\Psi_{CIS}\rangle = C_0|\Phi_0\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle$. When evaluated as an expectation value over the non-relativistic Hamiltonian and correlation operator, we find three distinct hamiltonian matrix elements:

$$H_{00} = \langle \Phi_0 | \hat{H} + \hat{C} | \Phi_0 \rangle \quad (3.2)$$

$$H_{0a} = \langle \Phi_0 | \hat{H} + \hat{C} | \Phi_i^a \rangle \quad (3.3)$$

$$H_{ab} = \langle \Phi_i^a | \hat{H} + \hat{C} | \Phi_j^b \rangle. \quad (3.4)$$

The first matrix element in equation 3.2 returns the ground state Hartree-Fock energy with the calculated value for the correlation operator. This value is the equivalent to evaluating a ground state single determinant wavefunction with the perturbative correlation operator. The second matrix element type in equation 3.3 is the overlap of the reference HF wavefunction with any singly excited determinant over the Hamiltonian with the correlation operator. All matrix elements of this type reduce to only correlation operator elements. Because of the Brillouin theorem, $\langle \Phi_i^a | \hat{H} | \Phi_{HF} \rangle = 0$. Within CIS, the Brillouin theorem does not allow any interaction between the ground state and singly excited determinants. Because the correlation operator integrals are added within the CIS matrix instead of during the SCF procedure for the HF reference wavefunction, this form of the correlation operator does not follow Brillouin's theorem. This means that all $H_{0a} = \langle \Phi_0 | \hat{H} + \hat{C} | \Phi_i^a \rangle$ are equivalent to $H_{0a} = \langle \Phi_0 | \hat{C} | \Phi_i^a \rangle$ allowing for interaction between the singly excited determinants and the reference wavefunction. The third general matrix element in equation 3.4

creates many cross terms between all other singly excited determinants. All of these other matrix elements are easily evaluated using the Slater-Condon rules. A more descriptive evaluation of these matrix elements are found in the Appendix.

The total electronic energy of the ground and excited states are evaluated as eigenvalues of the Hamiltonian matrix. The resultant matrix is diagonal with all the ground and excited state energies along the diagonal. The variational optimization of the CIS coefficients allows all occupied orbitals in each electronic excited state to relax. This allows for the calculated state to better represent the actual excited state wavefunction rather than an ionized state as if the wavefunction only contained a single excited determinant.

3.2 RESULTS AND DISCUSSION

The analysis of the results will be split into two data sets: atoms and molecules. All calculations were performed using the developer’s version of the electronic structure package of QCHEM [12]. The value of the correlation energy was computed as an expectation value of the correlation operator after the SCF procedure of the reference single-determinant wavefunction and used within CIS formalism. All data are calculated while using spin-unrestricted formalism.

Atoms

Our atomic test set consists of low-level excited states of the first and second row atoms, shown in Table 2.2. The set contains same-spin and spin-flip excited states. The experimental values are taken from the NIST database [13]. No spin-orbit corrections were used in the calculations. The computed excitation energies are reported as deviations from the experimental values, with positive numbers indicating overestimation of excitation energy. All data are reported in atomic units.

Table 3.1 Atomic excitation energies computed with a custom even-tempered basis set. Experimental excitation energies are taken from NIST [13]. The excitation energies computed with the correlation operator are reported as the deviation from the experiment. Energies reported in atomic units.

| Atom | Transition | $E(exp)$ | $\Delta E(\hat{C}_{Pert})$ | $\Delta E(\hat{C}_{SCF})$ | $\Delta E(\hat{C}_{CIS})$ |
|------|-----------------------|----------|----------------------------|---------------------------|---------------------------|
| He | $^1S \rightarrow ^3S$ | 0.728357 | -0.007805 | -0.007809 | -0.007809 |
| He | $^1S \rightarrow ^3P$ | 0.770416 | -0.006074 | -0.006081 | -0.006370 |
| Li | $^2S \rightarrow ^2P$ | 0.067906 | 0.001697 | 0.001686 | -0.000441 |
| Be | $^1S \rightarrow ^3P$ | 0.100140 | -0.012758 | -0.012878 | -0.012879 |
| B | $^2P \rightarrow ^2S$ | 0.182434 | 0.013993 | 0.013554 | 0.016129 |
| C | $^3P \rightarrow ^5S$ | 0.153790 | -0.006637 | -0.006716 | -0.020267 |
| N | $^4S \rightarrow ^4P$ | 0.379470 | 0.009089 | 0.008728 | 0.005249 |
| O | $^3P \rightarrow ^5S$ | 0.336113 | -0.000986 | -0.001313 | -0.055413 |
| F | $^2P \rightarrow ^4P$ | 0.466595 | -0.004448 | -0.004848 | -0.042371 |
| Ne | $^1S \rightarrow ^3P$ | 0.610740 | -0.006299 | -0.006728 | 0.001089 |
| Na | $^2S \rightarrow ^2P$ | 0.077258 | 0.001197 | 0.001393 | -0.003662 |
| Mg | $^1S \rightarrow ^3P$ | 0.099558 | -0.004104 | -0.004375 | 0.007010 |
| Al | $^2P \rightarrow ^4P$ | 0.132251 | -0.004562 | -0.004858 | 0.007499 |
| Si | $^3P \rightarrow ^5S$ | 0.151845 | -0.005661 | -0.006007 | -0.002541 |
| P | $^4S \rightarrow ^4P$ | 0.254879 | 0.012686 | 0.012129 | 0.011169 |
| S | $^3P \rightarrow ^5S$ | 0.239771 | 0.019488 | 0.018888 | 0.012876 |
| Cl | $^2P \rightarrow ^2P$ | 0.327866 | 0.021063 | 0.020202 | 0.029001 |
| Ar | $^1S \rightarrow ^3P$ | 0.424394 | 0.024937 | 0.023842 | 0.036735 |
| RMS | | | 0.011362 | 0.011064 | 0.021653 |

The atomic results of the CIS correlation operator are presented in Table 3.1. These results are also compared with the two versions of the Δ SCF correlation operator. Comparing all versions of the correlation operator we find that the CIS operator performs nearly twice as inaccurately as either of the two Δ SCF formulations. We do find that 13 of the 18 tested atomic excitation energies calculated by the CIS correlation operator are comparable or better than the Δ SCF calculations. Between the Δ SCF and CIS versions, however, very large deviations occur for the $^3P \rightarrow ^5S$ oxygen transition and $^2P \rightarrow ^4P$ fluorine transition that severely affect the final RMS. The pattern of decreased accuracy for heavier atoms is evident for the CIS operator just as it can be seen for the Δ SCF operator. This is most likely due to the poor accuracy of describing these atomic wavefunctions using only a single-determinant.

Table 3.2 RMS values and mean absolute deviations for atomic excitation energies obtained with the correlation operator methods, Δ SCF, CIS, and TD-DFT functionals. Energies reported in atomic units.

| Method | RMS | $\langle \Delta E \rangle$ |
|------------------|----------|------------------------------|
| \hat{C}_{CIS} | 0.021653 | 0.015473 |
| \hat{C}_{Pert} | 0.011362 | 0.009082 |
| \hat{C}_{SCF} | 0.011064 | 0.009002 |
| CIS | 0.040393 | 0.034165 |
| Δ SCF | 0.039363 | 0.033997 |
| B3LYP | 0.026867 | 0.016720 |
| PBE0 | 0.015897 | 0.010734 |
| M06-2X | 0.018209 | 0.014459 |

The CIS correlation operator is compared to the perturbative and self-consistent versions of the Δ SCF correlation operator, the Δ SCF method, CIS and TD-DFT with three popular functionals, B3LYP [15], PBE0 [16], and M06-2X [17]. The root mean square deviations and mean absolute deviations are given in Table 3.2. When comparing the data we find that the CIS correlation operator is inferior to both of the Δ SCF operator formulations. Despite this inferiority to the Δ SCF correlation operator, the CIS correlation operator is quite comparable to the TD-DFT functional results. The final point that can be taken out of this is the comparison with just CIS. The CIS correlation operator nearly doubles the accuracy of its base method. Although the results were not as impressive as the Δ SCF correlation operator, it is very encouraging for future studies using CIS like wavefunctions.

Molecules

The molecular test set was chosen to include all diatomics made of first row atoms and hydrogen for which experimental excited state geometry and energy are available [18], and with an excited state that did not have a lower level excited state of same

spatial but different spin symmetry. The last restriction is necessary because the spin-unrestricted calculation can become spin-contaminated by mixing with a lower-energy spin state, yielding a qualitatively incorrect excited state wavefunction [19]. The contaminating spin states are often unbound and thus could not be used for adiabatic excitation calculation. The molecular test set and correlation operator results are shown in Table 3.5.

Table 3.3 RMS values and mean absolute deviations for diatomic excitation energies obtained with the correlation operator methods, Δ SCF, CIS, and TD-DFT functionals. Energies reported in atomic units.

| Method | RMS | $\langle \Delta E \rangle$ |
|------------------|---------|------------------------------|
| \hat{C}_{CIS} | 0.07285 | 0.04751 |
| \hat{C}_{Pert} | 0.02052 | 0.01427 |
| \hat{C}_{SCF} | 0.01979 | 0.01321 |
| CIS | 0.05765 | 0.03830 |
| Δ SCF | 0.02146 | 0.01734 |
| B3LYP | 0.00736 | 0.00575 |
| PBE0 | 0.01234 | 0.01044 |
| ω B97X | 0.00725 | 0.00593 |
| M06-2X | 0.00730 | 0.00421 |

From the results it can be seen that the CIS correlation operator results are very underwhelming compared to the promising atomic results. The CIS correlation operator not only performs poorly compared to the perturbative and self-consistent Δ SCF correlation operators but also makes the results of CIS worse. For example, the $^2\Sigma \rightarrow ^2\Pi_i$ transition of CN increases in error by nearly 11 milli-hartrees from a deviation from experiment of 0.14423 to 0.15501 when including the correlation operator. The biggest problem with these deviations, however, is not the fact that the correlation operator makes the adiabatic excitation energy worse but how inaccurate the CIS method is initially. The CIS method calculates the excitation energy to be

0.14423 hartrees above the experimental value. Within CN it can be seen that CIS calculates the excited state wavefunction completely and qualitatively wrong. This discrepancy between theory and experiment may show that CIS is not able to calculate an accurate enough wavefunction to be able to benefit from the correlation operator. Although the correlation operator can correct some minor errors it is not designed to make huge alterations to incorrect wavefunctions. The same phenomenon occurred for the Δ SCF correlation operator for highly spin contaminated wavefunctions.

The CIS correlation operator performance is compared to the perturbative and self-consistent Δ SCF correlation operator formulations, the Δ SCF method, configuration interaction singles (CIS), and TD-DFT with B3LYP [15], PBE0 [16], ω B97X [21], and M06-2X [17] functionals. The root mean square deviations and mean absolute deviations are given in Table 3.3. From the results it can be seen that the CIS correlation operator is far inferior to all tested TD-DFT functionals as well as its base method CIS. We do not believe that the correlation operator is to blame for these poor results. We can already see that the CIS method performs very poorly with an RMS of 0.05765 and a mean absolute error of 0.03830. Excluding the CIS correlation operator, CIS performs the worst by a factor of 3 over the next worst method. This initially led us to believe that something must be inherently wrong within CIS to have such poor initial results.

To better elucidate this problem, we examine the difference between CIS and the more accurate TD-DFT with the B3LYP functional. We took a closer look at the $^2\Sigma \rightarrow ^2\Pi_i$ transition of BO. CIS deviated from the experimental adiabatic excitation energy of this state by nearly 100 milli-hartrees. The B3LYP functional, however, only had a deviation from experiment of approximately 8 milli-hartrees. These deviations differ by over a factor of 10, therefore, we can almost certainly say that B3LYP creates a much closer example of the exact wavefunction than CIS. Because of this we compare the results of the first three excited state energies of CIS with B3LYP in

Table 3.4. The highlighted sections are the ${}^2\Sigma \rightarrow {}^2\Pi_i$ transition of BO we calculated within this test set. We find that the B3LYP wavefunction accurately describes the ${}^2\Sigma \rightarrow {}^2\Pi_i$ transition as the first excited state. The CIS method, on the other hand, equates the same transition to the third excited state. The CIS method is unable to calculate the proper energy or order of excited states.

Table 3.4 The comparison of the first 3 excited states of the BO molecule calculated with CIS, time-dependent B3LYP, and CIS using the ground state B3LYP wavefunction. Energies reported in atomic units.

| State | CIS | | TD-B3LYP | | CIS(B3LYP) | |
|------------------|------------------------------|------------|------------------------------|------------|------------------------------|------------|
| | Transition | ΔE | Transition | ΔE | Transition | ΔE |
| 3^{rd} Excited | $1\pi \rightarrow 3\sigma$ | 0.22479 | $3\sigma \rightarrow 1\pi^*$ | 0.23149 | $3\sigma \rightarrow 1\pi^*$ | — |
| 2^{nd} Excited | $3\sigma \rightarrow 1\pi^*$ | 0.20586 | $1\pi \rightarrow 1\pi^*$ | 0.19111 | $1\pi \rightarrow 1\pi^*$ | — |
| 1^{st} Excited | $1\pi \rightarrow 1\pi^*$ | 0.19643 | $1\pi \rightarrow 3\sigma$ | 0.11464 | $1\pi \rightarrow 3\sigma$ | — |

We performed one last test, however, to test for the accuracy of CIS in calculating the particular BO excited state. The CIS method is based upon the expansion of the reference HF wavefunction. If CIS is the main culprit for the inability to describe the excited states of BO, then an accurate reference wavefunction used within the CIS formalism should theoretically also calculate the wrong excited state. The B3LYP ground state Kohn-Sham wavefunction when used with CIS rather than the HF reference wavefunction should calculate the wrong order of states. To achieve this we calculated the ground state B3LYP wavefunction and used it as the initial guess with zero SCF iterations within a CIS calculation. The order of the calculated excited states are labeled in Table 3.4 under CIS(B3LYP). When performed in this manner, we find that CIS accurately predicts the order of the first three excited states of BO. This leads us to the conclusion that the reference HF wavefunction may be too poor of a representation of the groundstate wavefunction to accurately describe excited states within CIS using the correlation operator.

Table 3.5 Diatomic excitation energies computed with the G3MP2Large basis set. Experimental excitation energies are taken from reference [18]. All computed data are reported as the deviation from the experiment. No spin-orbit corrections were used in the calculations. Energies are in atomic units, bond distances are in Angstroms.

| Molecule | $R_e(\text{Grnd})$ | Transition | $R_e(\text{Excit})$ | $E(\text{exp})$ | $\Delta E(CIS)$ | $\Delta E(\hat{C}_{CIS})$ | $\Delta E(\hat{C}_{Pert})$ | $\Delta E(\hat{C}_{SCF})$ |
|----------------|--------------------|-------------------------------------|---------------------|-----------------|-----------------|---------------------------|----------------------------|---------------------------|
| BeH | 1.3431 | $^2\Sigma \rightarrow ^2\Pi$ | 1.3327 | 0.09125 | 0.00898 | 0.00934 | 0.00716 | 0.00636 |
| BeF | 1.3614 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.3941 | 0.15142 | 0.00467 | 0.00740 | 0.00790 | 0.00767 |
| BF | 1.262 | $^1\Sigma \rightarrow ^3\Pi$ | 1.308 | 0.13279 | -0.03398 | -0.00586 | -0.01231 | -0.01279 |
| BO | 1.2049 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.3524 | 0.10861 | 0.09329 | 0.13407 | -0.01278 | -0.01160 |
| C ₂ | 1.2425 | $^1\Sigma_g \rightarrow ^3\Pi_u$ | 1.3119 | 0.00326 | 0.00313 | 0.00346 | 0.00346 | 0.00345 |
| CN | 1.1718 | $^2\Sigma \rightarrow ^2\Pi_i$ | 1.2327 | 0.04211 | 0.14423 | 0.15501 | -0.02781 | -0.02327 |
| CO | 1.1281 | $^1\Sigma \rightarrow ^3\Pi_r$ | 1.2093 | 0.22184 | -0.01863 | 0.01914 | 0.00511 | 0.00103 |
| N ₂ | 1.094 | $^1\Sigma_g \rightarrow ^3\Sigma_u$ | 1.2866 | 0.22874 | -0.03607 | 0.09793 | 0.05378 | 0.05376 |
| NH | 1.038 | $^3\Sigma \rightarrow ^3\Pi$ | 1.037 | 0.13581 | 0.01816 | 0.02060 | 0.00604 | 0.00582 |
| OH | 0.9706 | $^2\Pi_i \rightarrow ^2\Sigma$ | 1.0121 | 0.14891 | 0.02189 | 0.02227 | 0.00636 | 0.00631 |
| RMS | | | | | 0.05765 | 0.07285 | 0.02146 | 0.02052 |

3.3 CONCLUSIONS

Our goal for the CIS correlation operator was to model dynamic electron correlation in atoms and molecules in a computationally inexpensive way with a wavefunction based method. We theorized that the CIS approach would give us certain benefits that the Δ SCF method does not have. Two benefits we believed would benefit us the most were the multi-determinant nature of CIS and the orthogonality of all excited states to the ground state. The CIS method does not include any dynamic correlation but does include a small amount of static correlation with the inclusion of all possible singly excited determinants. We believed that the small amount of static correlation would be a benefit because Δ SCF has no inherent correlation within its formulation. The second benefit we believed the CIS method would contribute to our correlation operator was the ability to have orthogonal excited states to the ground state reference Hartree-Fock wavefunction. This would be beneficial to try to eliminate some of the problem Δ SCF has with no guaranteed orthogonality between states other than symmetry.

The value of the correlation operator is relatively insensitive to the quality of the basis set. However, to adequately describe atomic excited states, atomic calculations require far more flexibility within the diffuse domain. For the atomic test set we used a custom even-tempered basis set that consisted of fully optimized uncontracted 12s9p atomic basis, augmented in the diffuse region to 17s12p size. The custom basis set is also augmented with even-tempered $9d3f$ uncontracted basis functions. When used in conjunction with the CIS method we find that the correlation operator calculates atomic excited states comparable to the most popular TD-DFT functionals. Most importantly the correlation operator improved the accuracy of the CIS method by nearly a factor of two. The CIS correlation operator performed inferior to the perturbative and self consistent correlation operator but gave very promising results for study on molecules.

To adequately describe molecular excited states, it is not as necessary to be so flexible in the diffuse domain like atomic calculations. Because of this we chose to use the large but more standard G3MP2Large basis set. The results of the CIS method in conjunction with the correlation operator were found to be problematic. The CIS correlation operator performed far worse than any other compared methods. This includes the CIS method by itself. At first it was believed that the CIS method may be too poor a model for excited states to benefit from the correlation operator, however, we found that it is more likely the HF reference wavefunction. Therefore to use a CIS like method we require a more accurate reference wavefunction. This is part of the future research that will be elaborated upon within the next chapter.

CHAPTER 4

FUTURE OF THE CORRELATION OPERATOR

Based on the conclusions from Chapter 2 and Chapter 3 we found that the primary concerns for the future of this research do not necessarily come from the correlation operator itself but from the underlying methods. At this stage of research we find that the Δ SCF and CIS methods have some critical flaws that have to be overcome to continue. The Δ SCF correlation operator formulations are very promising for the future of this research. The Δ SCF method itself is unable to guarantee orthogonal states other than through symmetry. This limits viable test systems considerably. Within our atomic and molecular test sets we try to limit ourselves to systems whose error can only be attributed to deficiencies within the correlation operator. Because the Δ SCF method contains no other constraint to guarantee orthogonality between excited states and the ground state, we become more and more limited as we increase the size of the test systems. This can be seen by comparing our test set for atoms and molecules. Our atomic test set has at least one viable state for all of the first 17 multi-electron atoms. The molecular test set was originally made of 20 diatomics made of the first row atoms and hydrogen for which experimental excited state geometries and energies were available. This list of 20 molecules became 10 molecules because we were required to choose molecules that were orthogonal by symmetry to lower states to achieve a fair representation of the correlation operator performance.

The non-orthogonality problem of the Δ SCF method can be further seen when investigating larger molecules. Within Table 4.1 we have calculated the adiabatic excitation energies of the benzene molecule for the $^1A_{1g} \rightarrow ^1B_{1u}$ and $^1A_{1g} \rightarrow ^3B_{2u}$

Table 4.1 Comparison of the $^1B_{1u}$ and $^3B_{2u}$ adiabatic excitation energies of benzene calculated using Δ SCF and the Δ SCF correlation operator formulations. Experimental excitation energies are taken from reference [23]. All computed data are reported as the deviation from the experiment. Energies reported in atomic units.

| Transition | $E(exp)$ | $\Delta E(\Delta SCF)$ | $\Delta E(\hat{C}_{Pert})$ | $\Delta E(\hat{C}_{SCF})$ |
|---------------------------------|----------|------------------------|----------------------------|---------------------------|
| $^1A_{1g} \rightarrow ^1B_{1u}$ | 0.17346 | 0.03333 | 0.06725 | 0.08939 |
| $^1A_{1g} \rightarrow ^3B_{2u}$ | 0.20580 | -0.03362 | -0.00125 | -0.01195 |

transitions. The $^1B_{1u}$ state is not orthogonal to lower states while the $^3B_{2u}$ is orthogonal to all lower states by symmetry. For the $^1A_{1g} \rightarrow ^1B_{1u}$ transition the Δ SCF method overestimates the experimental excitation energy by nearly 20 percent because of spin contamination from lower states. With the inclusion of the correlation operator the error increases to 39 percent for the perturbative correction and over 50 percent for the self-consistent correction. The spin contaminated state described by the Δ SCF method adversely affects the performance of the correlation operator causing the error to increase dramatically. In contrast we can see the opposite result with the $^1A_{1g} \rightarrow ^3B_{2u}$ transition of benzene. Because the $^3B_{2u}$ state is guaranteed to be orthogonal to lower states we see how Δ SCF more accurately models the excited wavefunction based on the energy. With the correlation operator the error goes from 16 percent to less than 1 percent for the perturbative correction and 6 percent for the self-consistent correction. The results show promise for the Δ SCF correlation operator on larger more complex molecules, however, we must be able to guarantee orthogonality between more states before this method can be used on larger and more varied systems.

The non-orthogonality problem that can be found within Δ SCF is a problem that plagues many similar methods. A similar problem of non-orthogonality was found in time-independent density functional methods for excited states. Through the use of orthogonally constrained density functional theory (OC-DFT) [24] it was found that one could create variationally optimized Kohn-Sham wavefunctions for excited

states without variational collapse to the ground state. The OC-DFT study found that using orthogonality constraints led to excited state results similar to TD-DFT. To solve our near identical problem we propose an orthogonality constrained Δ SCF method. If we can create orthogonally excited states, we can reduce the influence of lower states on higher states significantly. The results of OC-DFT leads us to believe that an orthogonally constrained Δ SCF may be a promising path to research for further investigation of the correlation operator.

CIS also requires some changes to become a viable method for use with the correlation operator. The performance of CIS was found to be very poor by itself and with correlation operator. Based on the comparison of HF and B3LYP reference wavefunctions we came to the conclusion that the HF wavefunction may be too qualitatively inaccurate of a model to benefit from the correlation operator. Therefore we determined that a more accurate reference wavefunction must be obtained before initiating the CIS or CIS correlation operator method. This leads us to the possibility of a hybrid Δ SCF and CIS method to get the benefits inherent in both methods. For atoms and molecules we have found that the correlation operator increases the accuracy of the Δ SCF method nearly universally for orthogonal states that are not spin contaminated thus creating more qualitatively accurate HF-like wavefunctions. Because of this we can propose that the self consistent or perturbative Δ SCF correlation operator wavefunction be used as the reference wavefunction. The CIS method has the benefit of creating excited state determinants that are guaranteed to be orthogonal to the ground state. The Δ SCF method has no way of guaranteeing that any particular state is orthogonal to other states unless by symmetry. Because the CIS method does not guarantee orthogonality between any of the excited states we also propose to constrain all of the lower states from the state of interest to be orthogonal. This hybrid method could possibly alleviate some of the deficiencies of both methods while accentuating their benefits.

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APPENDIX A

CHAPTER 2: Δ SCF CORRELATION OPERATOR

A.1 CORRELATION OPERATOR MATRIX ELEMENTS

The simplest of the analytical integrals implemented with the correlation operator is the s-type component of the operator combined with four s-type primitives,

$$\begin{aligned}
 C_{1,2,3,4}^s = & \langle C_1 N_1 e^{-\alpha_1(\vec{r}_1 - \vec{R}_1)^2} C_2 N_2 e^{-\alpha_2(\vec{r}_2 - \vec{R}_2)^2} | N_0 e^{-\alpha_0 \vec{r}_{12}^2} \rangle_{\vec{r}_{12}} \\
 & \langle N_0 e^{-\alpha_0 \vec{r}_{12}^2} | C_3 N_3 e^{-\alpha_3(\vec{r}_1 - \vec{R}_3)^2} C_4 N_4 e^{-\alpha_4(\vec{r}_2 - \vec{R}_4)^2} \rangle
 \end{aligned} \tag{A.1}$$

where C_1, C_2, C_3, C_4 are primitive coefficients, N_1, N_2, N_3, N_4 are primitive normalization constants, and N_0 is the correlation operator normalization constant. The outer $\langle \rangle$ bra-ket denotes integration over all coordinates of an electron pair, while the inner $\rangle \langle$ ket-bra of the operator applies only to the intracule coordinate. The latter is labeled with the subscript r_{12} to indicate the distinction. To carry out the integration, it is convenient to transform coordinates of each primitive into intracule, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and extracule, $\vec{p}_{12} = (\vec{r}_1 + \vec{r}_2)/2$, coordinates. In Cartesian representation the overall integral remains separable into x, y, z components.

We use a generating function for all combinations of s- and p-type Gaussian primitives with the correlation operator, by differentiating the following expressions with respect to the Gaussian displacement parameters X_i . Using the x-component as an example and omitting multiplicative coefficients for clarity of notation:

$$\begin{aligned}
& \langle e^{-\alpha_1(x_1-X_1)^2} e^{-\alpha_2(x_2-X_2)^2} | e^{-\alpha_0 x_{12}^2} \rangle_{x_{12}} \langle e^{-\alpha_0 x_{12}^2} | e^{-\alpha_3(x_1-X_3)^2} e^{-\alpha_4(x_2-X_4)^2} \rangle = \\
& C_x e^{-\beta_l(X_2-X_1)^2} e^{-\beta_r(X_4-X_3)^2} e^{-\frac{\gamma_l \gamma_r}{\gamma_l + \gamma_r} (T_l - T_r)^2} \tag{A.2} \\
C_x &= 4\pi \sqrt{\frac{\pi}{(\alpha_1 + \alpha_2 + 4\alpha_0)(\alpha_3 + \alpha_4 + 4\alpha_0)(\gamma_l + \gamma_r)}} , \\
\gamma_l &= \frac{4(\alpha_1 \alpha_2 + \alpha_0(\alpha_1 + \alpha_2))}{4\alpha_0 + \alpha_1 + \alpha_2} , \quad \gamma_r = \frac{4(\alpha_3 \alpha_4 + \alpha_0(\alpha_3 + \alpha_4))}{4\alpha_0 + \alpha_3 + \alpha_4} , \\
\beta_l &= \frac{\alpha_1 \alpha_2 \alpha_0}{(\alpha_1 + \alpha_2)\alpha_0 + \alpha_1 \alpha_2} , \quad \beta_r = \frac{\alpha_3 \alpha_4 \alpha_0}{(\alpha_3 + \alpha_4)\alpha_0 + \alpha_3 \alpha_4} , \\
T_l &= \frac{X_1 + X_2}{2} + \frac{\alpha_0(\alpha_2 - \alpha_1)(X_2 - X_1)}{(\alpha_1 + \alpha_2)\alpha_0 + \alpha_1 \alpha_2} , \\
T_r &= \frac{X_3 + X_4}{2} + \frac{\alpha_0(\alpha_4 - \alpha_3)(X_4 - X_3)}{(\alpha_3 + \alpha_4)\alpha_0 + \alpha_3 \alpha_4} .
\end{aligned}$$

All combinations of four s- and p-type Gaussian primitives were analytically derived and verified using Maple.

APPENDIX B

CHAPTER 3: CIS CORRELATION OPERATOR

B.1 CIS CORRELATION OPERATOR MATRIX ELEMENTS

The evaluation of the matrix elements within the CIS correlation operator are done by using the Slater-Condon rules. All Hamiltonian matrix elements and correlation operator matrix elements are allocated in the same way. Within the following equations \hat{H} will be equivalent to $\sum_i \hat{h}_i + \sum_{i>j} \frac{1}{r_{ij}} + \hat{C}$. The matrix elements are also split into three categories, alpha-alpha, beta-beta, and alpha-beta. The alpha-alpha and beta-beta will be grouped together because they are equivalent to each other. For brevity $N_{\alpha,\beta} \equiv N_\alpha$ or N_β and $\langle ab||cd \rangle \equiv \langle ab|\frac{1}{r_{12}} + \hat{C}|cd \rangle - \langle ab|\frac{1}{r_{12}} + \hat{C}|dc \rangle$.

$\alpha\alpha$ & $\beta\beta$ Integrals

$$\langle \Phi_{ijk\dots}|\hat{H}|\Phi_{ijk\dots}\rangle = \sum_i^{N_{\alpha,\beta}} h_{ii} + \sum_{j>i}^{N_{\alpha,\beta}} \langle ji||ji \rangle \quad (\text{B.1})$$

$$\langle \Phi_{ijk\dots}|\hat{H}|\Phi_{jk\dots}^a\rangle = h_{ia} + \sum_{j\neq i}^{N_{\alpha,\beta}} \langle ij||aj \rangle \quad (\text{B.2})$$

$$\langle \Phi_{jk\dots}^a|\hat{H}|\Phi_{jk\dots}^a\rangle = \sum_{j\neq i}^{N_{\alpha,\beta}} h_{jj} + h_{aa} \sum_{j\neq i}^{N_{\alpha,\beta}} \langle aj||aj \rangle + \sum_{j\neq i, k>j}^{N_{\alpha,\beta}} \langle kj||kj \rangle \quad (\text{B.3})$$

$$\langle \Phi_{ik\dots}^a|\hat{H}|\Phi_{jk\dots}^a\rangle = h_{ji} - \langle ai||aj \rangle - \sum_{i\neq j, k\neq i,j}^{N_{\alpha,\beta}} \langle ki||kj \rangle \quad (\text{B.4})$$

$$\langle \Phi_{jk\dots}^a|\hat{H}|\Phi_{jk\dots}^b\rangle = h_{ab} + \sum_{j\neq i}^{N_{\alpha,\beta}} \langle aj||bj \rangle \quad (\text{B.5})$$

$$\langle \Phi_{jk\dots}^a|\hat{H}|\Phi_{ik\dots}^b\rangle = \langle aj||bi \rangle \quad (\text{B.6})$$

$\alpha\beta$ Integrals

α -occupied: $ijk\dots$ α -virtual: $abc\dots$

β -occupied: $xyz\dots$ β -virtual: $rst\dots$

$$\langle \Phi_{ijk\dots xyz\dots} | \hat{H} | \Phi_{ijk\dots xyz\dots} \rangle = \sum_i^{N_\alpha} \sum_x^{N_\beta} \langle ix || ix \rangle \quad (\text{B.7})$$

$$\langle \Phi_{jk\dots xyz\dots}^a | \hat{H} | \Phi_{ijk\dots xyz\dots} \rangle = \sum_x^{N_\beta} \langle ax || ix \rangle \quad (\text{B.8})$$

$$\langle \Phi_{ijk\dots yz\dots}^r | \hat{H} | \Phi_{ijk\dots xyz\dots} \rangle = \sum_i^{N_\alpha} \langle ir || ix \rangle \quad (\text{B.9})$$

$$\langle \Phi_{jk\dots xyz\dots}^a | \hat{H} | \Phi_{jk\dots xyz\dots}^a \rangle = \sum_x^{N_\beta} \langle ax || ax \rangle + \sum_{j \neq i}^{N_\alpha} \sum_x^{N_\beta} \langle jx || jx \rangle \quad (\text{B.10})$$

$$\langle \Phi_{ijk\dots yz\dots}^r | \hat{H} | \Phi_{ijk\dots yz\dots}^r \rangle = \sum_i^{N_\alpha} \langle ir || ir \rangle + \sum_i^{N_\alpha} \sum_{y \neq x}^{N_\beta} \langle iy || iy \rangle \quad (\text{B.11})$$

$$\langle \Phi_{jk\dots xyz\dots}^a | \hat{H} | \Phi_{jk\dots xyz\dots}^b \rangle = \sum_x^{N_\beta} \langle ax || bx \rangle \quad (\text{B.12})$$

$$\langle \Phi_{ijk\dots yz\dots}^r | \hat{H} | \Phi_{ijk\dots yz\dots}^s \rangle = \sum_i^{N_\alpha} \langle ir || is \rangle \quad (\text{B.13})$$

$$\langle \Phi_{jk\dots xyz\dots}^a | \hat{H} | \Phi_{ik\dots xyz\dots}^a \rangle = - \sum_x^{N_\beta} \langle ix || jx \rangle \quad (\text{B.14})$$

$$\langle \Phi_{ijk\dots yz\dots}^r | \hat{H} | \Phi_{ijk\dots xz\dots}^r \rangle = - \sum_i^{N_\alpha} \langle ix || iy \rangle \quad (\text{B.15})$$

$$\langle \Phi_{jk\dots xyz\dots}^a | \hat{H} | \Phi_{ijk\dots yz\dots}^r \rangle = \langle ax || ir \rangle \quad (\text{B.16})$$

APPENDIX C

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C.1 CHAPTER 2: Δ SCF CORRELATION OPERATOR

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