A Second-Order Møller–Plesset Perturbation Theory Energy Decomposition Analysis for Intermolecular Interactions: Design, Implementation, and Application

by

JONATHAN E THIRMAN

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Martin P. Head-Gordon, Chair
Professor William H. Miller
Professor Berend Smit
Professor Joel E. Moore

Spring 2017
A Second-Order Møller–Plesset Perturbation Theory Energy Decomposition Analysis for Intermolecular Interactions: Design, Implementation, and Application

Copyright 2017
by
JONATHAN E THIRMAN
Abstract

A Second-Order Møller–Plesset Perturbation Theory Energy Decomposition Analysis for Intermolecular Interactions: Design, Implementation, and Application

by

JONATHAN E THIRMAN

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Martin P. Head-Gordon, Chair

This thesis is concerned with the development an analysis for decomposing the binding energy of second-order Møller–Plesset perturbation theory into physically meaningful components. This can be defined as an extension to the previous work on an absolutely localized molecular orbitals based EDA for Hartree–Fock. The decomposition of the correlation energy proceeds though physically motivated constrained intermediate wave functions and corrects the HF description of frozen interaction, polarization, and charge transfer, while adding a description of dispersion that is only possible at the correlated level. This method is implemented efficiently and the performance of the implementation is tested. The EDA is then applied to systems of chemical interest to help resolve questions related to intermolecular interactions.
To my parents,
Karen and Michael
Contents

List of Figures iv

List of Tables vii

1 Introduction 1
   1.1 The Schrödinger Equation .............................................. 1
   1.2 The Hartree-Fock Approximation ....................................... 4
   1.3 Correlation Methods .................................................... 8
   1.4 Perturbation Theory ..................................................... 8
   1.5 Energy Decomposition .................................................. 11
   1.6 Outline ................................................................. 14

2 Electrostatics in intermolecular correlation 17

3 An EDA for MP2 based on ALMOs 26
   3.1 Introduction ............................................................. 26
   3.2 Theory ................................................................. 28
   3.3 Results ................................................................. 39
   3.4 Conclusions ............................................................ 53

4 Efficient Implementation of MP2 EDA and Application to Anion-π Interactions 55
   4.1 Introduction ............................................................. 55
   4.2 Brief review of the MP2 EDA .......................................... 57
   4.3 Implementation ........................................................ 58
   4.4 Performance ............................................................ 64
   4.5 Application: anion-π interactions .................................... 68
   4.6 Conclusions ............................................................. 76

5 Probing the Interplay Between Electrostatics and Charge Transfer in Halogen Bonding 78
List of Figures

2.1 Four different geometries of the water dimer. The stretched geometry is based on the S22 equilibrium geometry. The other three geometries each have equivalent monomers with bond length of 0.9584 Å and bond angle of 104.46°. .......................... 19
2.2 RIMP2 binding energy curves for the water dimer in four different geometries. .......................... 20
2.3 RIMP2 correlation binding energy curves for the water dimer in four different geometries, along with a CCSD(T) value (the diamonds) at 5.5 Å for each. .......................... 20
2.4 Correlation binding energy (CBE) curves for water dimer in the stretched equilibrium geometry, in three different basis sets. (The auxiliary basis set corresponds to the main basis set in each case.) .......................... 21
2.5 Correlation binding energy of the water dimer in the stretched equilibrium geometry vs. difference in dipole interaction from HF to MP2. As the center of the charge distribution does not affect the dipole moment, the centers of the charge distributions are chosen to be 0.35 Å farther apart than the O-O separation. .......................... 23
2.6 Log-log plot (natural logarithm) of absolute value of CBE for water in the aligned and anti-aligned geometries. .......................... 23
3.1 The three types of double excitations: on fragment (upper row), charge conserving (middle row), and charge transferring (bottom row), schematically illustrated for a two-fragment system. .......................... 29
3.2 (a) MP2 part of the EDA (i.e. the correlation correction) for HCl exposed to uniform electric fields of varying strength. (b) Unrelaxed version of the MP2 part of the EDA for HCl exposed to uniform electric fields of varying strength. .......................... 40
3.3 log-log plot of the MP2 part (i.e. the correlation contribution) of the EDA for He interacting with a point charge at varying distances. .......................... 41
3.4 (a) Percentage difference between the HF and MP2 densities (b) log-lin plot of $\Delta E_{\text{froz}}$ from density and from EDA. .......................... 42
3.5 (a) HF EDA and (b) MP2 EDA (including the HF contribution) for the He dimer as a function of separation. .......................... 43
3.6 log-log plot for dispersion component of He dimer EDA. .......................... 44
3.7 (a) HF EDA, (b) MP2 EDA, and (c) log-log plot of the correlation part of the MP2 EDA for the chloride-argon system as a function of separation. .......................... 45
3.8 (a) HF EDA, (b) MP2 EDA, and (c) log-log plot of the correlation part of the MP2 EDA for the water dimer as a function of center of mass separation. 46
3.9 (a) HF EDA and (b) MP2 EDA for water dimer rotated between two orientations: equilibrium on the left and aligned on the right. The x axes are both the dimensionless coordinate of transformation. 48
3.10 (a) \( \Delta E \), (b) \( \Delta E_{\text{pol}} \), (c) \( \Delta E_{\text{frz}} \), (d) \( \Delta E_{\text{CT}} \), and (e) \( \Delta E_{\text{disp}} \) for water dimer rotated between two orientations, in three different basis sets. All x axes are the dimensionless coordinate of transformation. 50
3.11 (a) HF EDA and (b) MP2 EDA for the \( \text{H}_2\text{O}-\text{ClF} \) system on the lowest energy path between two symmetry equivalent minima. Left and right are the minima, and the middle is the planar transition state. The x axes are both the dimensionless coordinate of transformation. 52

4.1 Algorithm for \( I \) 61
4.2 Algorithm for multiplication by \( \Delta \) 63
4.3 A log-log plot of time per conjugate gradient iteration vs. number of water molecules, with a cubic fit line 65
4.4 A plot of time per conjugate gradient iteration vs. number of threads 66
4.5 A log-log plot of time to compute \( I \) vs. number of water molecules, with a cubic fit line 66
4.6 A plot of time to compute \( I \) vs. number of threads 67
4.7 Q-Chem RIMP2 time (excluding SCF) vs EDA time 68
4.8 Q-Chem RIMP2 time (excluding SCF) vs EDA time 68
4.9 Binding energy of six different anion-\( \pi \) interactions 69
4.10 (a) Frozen interaction and (b) sum of polarization, charge transfer, and dispersion for six different anion-\( \pi \) interactions 70
4.11 EDA for chloride-benzene interaction 71
4.12 Hartree-Fock EDA for chloride-benzene interaction 72
4.13 Frozen interaction of chloride and benzene vs truncated multipole expansions of the classical electrostatic interaction, log-log plot 73
4.14 Lin-log plot of difference between frozen interaction and multipole approximation to classical electrostatic interaction 73
4.15 Lin-log plot of differences between frozen interactions and multipoles approximation to classical electrostatic interaction 74
4.16 Binding energy of three different anion-\( \pi \) interactions, with an angled path 75
4.17 Frozen energy differences between three different anion-\( \pi \) interactions, with an angled path 76

5.1 Binding energy of \( \text{CX}_3\text{I}^-\text{Y}^- \), for \( X=\text{F}, \text{Cl}, \text{Br}, \text{I} \) and \( Y=\text{F}, \text{Cl}, \text{Br} \) 82
5.2 Charge transfer energy of \( \text{CX}_3\text{I}^-\text{Y}^- \), for \( X=\text{F}, \text{Cl}, \text{Br}, \text{I} \) and \( Y=\text{F}, \text{Cl}, \text{Br} \) 83
5.3 Electrostatic energy of \( \text{CX}_3\text{I}^-\text{Y}^- \), for \( X=\text{F}, \text{Cl}, \text{Br}, \text{I} \) and \( Y=\text{F}, \text{Cl}, \text{Br} \) 83
5.4 (a) EDA for Cl$_4$F$^-$ (b) EDA for Cl$_4$Cl$^-$. The geometry is fully optimized at each I-Y$^-$ distance ................................................................. 84
5.5 (a) EDA for CF$_3$I-F$^-$ (b) EDA for CI$_4$F$^-$ .................................................. 86
5.6 CX$_3$I dipole moment at different constrained I-F distances ......................... 88
5.7 Optimum C-I bond length at different constrained I-F distances .................... 88
5.8 EDA for C(NO$_2$)$_3$I-F$^-$ ................................................................. 89
List of Tables

2.1 Dipole moments (in debye) for the two water molecules in the stretched equilibrium geometry with three different methods. ........................................... 22

2.2 Correlation contributions to the intermolecular interaction energies of small complexes from the A24 database, evaluated at the equilibrium geometry and at a geometry where the monomers are translated apart by 3/7 Å. RIMP2 is used with the aug-cc-pVQZ basis set and the corresponding auxiliary basis, without counterpoise correction and with the frozen core approximation. Values in parentheses are evaluated via attenuated RIMP2 with the aug-cc-pVTZ basis set: RIMP2(terfc, aTZ), also with the frozen core approximation. .......................... 24

3.1 HF and MP2 EDA for water dimer in two geometries (in kJ/mol) ............. 49

4.1 Number of conjugate gradient iterations vs number of water molecules, for four different algorithms. G denotes using the isolated fragment excitations as an initial guess, P denotes preconditioning with the diagonal elements of $\Delta$, GP both, and $\emptyset$ neither. .................................................. 65

4.2 Significant multipole moments for substituted benzenes. Units are D·Å$^{-1}$. .... 74

5.1 Adiabatic EDA. All energies in kJ/mol. Dipole moment is of CI$_4$. ............. 85

5.2 Adiabatic EDA. All energies in kJ/mol. Dipole moment is of CX$_3$I. Numbers for CI$_4$--F$^-$ repeated from table 5.1 for ease of comparison .......................... 87
Acknowledgments

I would like to thank all the people who made this work possible. Most important is my adviser, Martin Head-Gordon, who taught me most of what I know about quantum chemistry and all of what I know about being a scientist. I am grateful to him for providing support as well as invaluable insights as I worked on the research described here. I would also like to thank the entire Head-Gordon group, whose collective knowledge has helped me greatly at every stage along the way. This especially includes Narbe Mardirossian for being the main person with whom I discussed most of my ideas, Paul Horn for helping me understand the background of the work, and Eric Sundstrom, David Stück, Yuezhi Mao, and Ehud Tsivion for other help and discussion over the years.
Chapter 1

Introduction

1.1 The Schrödinger Equation

In quantum mechanics, systems are represented as complex Hilbert spaces. All information about each possible state of that system is associated (up to normalization and a phase factor) with a vector in that space, known as the state vector and usually denoted $|\psi\rangle$. Observables are represented by Hermitian operators $A$. The possible measurements of $A$ are its eigenvalues $a_i$, and the states corresponding to these measurements are the associated eigenvectors, such that if the system is in one of those states, then $A |\psi_i\rangle = a_i |\psi_i\rangle$. As the eigenvectors of a Hermitian operator form an orthonormal basis for the space, any possible state can be represented as a linear combination of the eigenvectors. Assuming the eigenvalues are discrete and of multiplicity one, we have $|\psi\rangle = \sum b_i |\phi_i\rangle$, where $|\phi_i\rangle$ is the eigenvector of $A$ corresponding to eigenvalue $a_i$. When $|\psi\rangle$ is not an eigenvector of $A$, the measurement of the observable will not have a definite value, but may take on any value with nonzero coefficient in $|\psi\rangle$. If $|\psi\rangle$ is normalized, the expectation value will be $\langle \psi | A |\psi\rangle$, where $\langle \psi |$ is the Hermitian conjugate of $|\psi\rangle$. This is equal to $\sum |b_i|^2 a_i$, so we see that the probability associated with measurement $a_i$ is $|b_i|^2$.

A state vector only represents a state at a particular time, so the state as a function of time may be represented as $|\psi(t)\rangle$. The time evolution of any system is given by the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$  \hspace{1cm} (1.1)

where $H$ is the Hamiltonian operator and $\hbar$ is the reduced Planck constant ($\frac{\hbar}{2\pi}$). The quantum Hamiltonian operator, analogous to the classical Hamiltonian, is defined as $T + V$, the sum of kinetic and potential energy. In chemistry, we often interested in the stationary states of a system. While the Schrödinger equation only allows the zero state to be unchanging with time, we can separate $|\psi(t)\rangle$ into $|\psi\rangle f(t)$, a time invariant state multiplied by some function that is not acted upon by $H$. Doing so gives the equation $(i\hbar \frac{d}{dt} f(t)) |\psi\rangle = f(t) H |\psi\rangle$. For this to be true at all times, we can separate into two eigenvalue equations with a shared con-
constant: \( E |\psi\rangle = H |\psi\rangle \) and \( i\hbar \frac{d}{dt} f(t) = Ef(t) \). The second gives the solution \( f(t) = e^{-(i/\hbar)Et} \), while the first is the time-independent Schrödinger equation:

\[
H |\psi\rangle = E |\psi\rangle
\]  

(1.2)

We see that the only possible stationary states are the eigenstates of the Hamiltonian operator. Because the Hamiltonian corresponds to the observable of energy, these are the same as states with definite energy, which is the constant \( E \) in the above equations. The time evolution of a stationary state is therefore only a changing phase factor, but because observables do not depend on phase, all observables of a stationary state are constant with respect to time.

For a non-relativistic, many particle system, \( T = \sum_{i}^{N} \frac{p_{i}^2}{2m_{i}} \) where \( p_{i} \) is the momentum and \( m_{i} \) is the mass associated with the \( i \)th particle. The potential energy \( V = \sum_{i}^{N} \sum_{j>i}^{N} V_{ij} \) can be described pairwise. However, general individual potential energy terms are only easy to describe in the position representation. To do this, we can introduce the resolution of the identity \( \int_{R} \cdots \int_{R} |x_{1} \cdots x_{N}\rangle \langle x_{1} \cdots x_{N}| dx_{1} \cdots dx_{N} \) between \( V \) and \( |\psi\rangle \). The state vector \( |x_{1} \cdots x_{N}\rangle \) represents the state with particle 1 exactly localized at \( x_{1} \) and so on. These are the eigenstates of the potential energy operators, so potential energy can be described as a function of the position of the particles: \( V_{ij} |x_{1} \cdots x_{N}\rangle = |x_{1} \cdots x_{N}\rangle V(x_{i}, x_{j}) \). This leaves the product \( \langle x_{1} \cdots x_{N}|\psi\rangle \). Since this is a number dependent on each position, we can call it a function – the wave function \( \Psi(x_{1}, \ldots, x_{N}) \). The spatial part of the wave function does not include all information about a state. In particular, it excludes spin as we will see later. We can also multiply by \( \langle x'_{1} \cdots x'_{N}| \) on left of both sides of equation 1.2. This converts the left side’s \( |\psi\rangle \) into the wave function. On the right, it creates the product \( \langle x'_{1} \cdots x'_{N}|x_{1} \cdots x_{N}\rangle \). This is equal to the product of Dirac deltas \( \delta(x'_{1} - x_{1}) \cdots \delta(x'_{N} - x_{N}) \), which is the equivalent of orthonormality for this continuous representation. The deltas require each position to be equal and remove the integrals. This leaves the kinetic energy part of the Hamiltonian. It looks like \( \sum_{i}^{N} \frac{1}{2m_{i}} \langle x'_{1} \cdots x'_{N}|p_{i}^2|\psi\rangle \). The momentum operator is like the spatial equivalent of the Hamiltonian operator, in that \( -i\hbar \frac{\partial}{\partial x_{i}} |\psi\rangle = p_{x_{i}} |\psi\rangle \), or in vector notation \( -i\hbar \nabla_{i} |\psi\rangle = p_{i} |\psi\rangle \). Putting this all together yields the wave function version of the time-independent Schrödinger equation:

\[
E\Psi(x_{1}, \ldots, x_{N}) = \left( -\hbar^2 \sum_{i}^{N} \frac{1}{2m_{i}} \nabla_{i}^2 + \sum_{i}^{N} \sum_{j>i}^{N} V(x_{i}, x_{j}) \right) \Psi(x_{1}, \ldots, x_{N})
\]  

(1.3)

Additionally, when the only force is the electrostatic force, Coulomb’s law applies, and \( V(x_{i}, x_{j}) = \frac{1}{4\pi\varepsilon_{0}} \frac{Z_{i}Z_{j}e^{2}}{|x_{i} - x_{j}|} \), where \( Z_{i} \) is the charge of the \( i \)th particle and \( e \) is the fundamental charge. Furthermore, we may work in atomic units, where \( \varepsilon_{0} = \frac{1}{4\pi} \) and \( \hbar, e, \) and the electron mass are all equal to 1. This leads to the complete equation

\[
E\Psi(x_{1}, \ldots, x_{N}) = \left( -\sum_{i}^{N} \frac{1}{2m_{i}} \nabla_{i}^2 + \sum_{i}^{N} \sum_{j>i}^{N} \frac{Z_{i}Z_{j}}{|x_{i} - x_{j}|} \right) \Psi(x_{1}, \ldots, x_{N})
\]  

(1.4)
This is a partial differential equation with infinite solutions that form a basis for all possible $N$ particle wave functions. However, it is not in general possible to solve because the potential energy term means that every variable is coupled to every other variable. One very useful simplifying assumption is the Born–Oppenheimer approximation\cite{1}. It says that the electronic and nuclear degrees of freedom may solved separately. When solving the electronic wave function, the locations of the nuclei can be treated as fixed parameters rather than as variables. This is in effect like saying the nuclei weigh infinitely much relative to the electrons. As even the lightest nucleus weighs nearly 2000 times more than an electron, this will usually be a reasonable assumption. In fact, the Born–Oppenheimer approximation will be good when the relevant electronic wave functions are far apart in energy. This is most cases that we are concerned with, though there are chemically interesting situations where this is not true (such as photochemistry). With the Born–Oppenheimer approximation, the Schrödinger equation can be rewritten as

$$E \Psi(x_1, \ldots, x_n) = \left( -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 + V_{nn} + \sum_{i} V_n(x_i) + \sum_{i} \sum_{j>i} \frac{1}{|x_i - x_j|} \right) \Psi(x_1, \ldots, x_n) \tag{1.5}$$

The mass may be omitted because only the kinetic energy of electrons is being considered and the electron mass is 1 in atomic units. The summation here is only over the electrons. $V_{nn}$ is the nuclear repulsion energy $\sum_{i}^{N} \sum_{j>i}^{N} \frac{Z_i Z_j}{|x_i - x_j|}$, where the capital indices run over the nuclei, and is a constant that does not affect the solution of the equation. $V_n(x_i)$ is the one electron potential energy, the electron-nuclear attraction, equal to $-\sum_{i} Z_i |x_i - x_i|$. Analytic solutions are not possible for more than one electron, but the one electron case is called the hydrogen-like atom and has an exact solution. Because of the spherical symmetry of the potential, it is easier to represent the wave function in spherical polar coordinates. The solutions have separate radial and angular parts, and have three different parameters describing all the possible solutions. The wave function can written $\Psi(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$. The parameters are called quantum numbers. The principal quantum number $n$ determines the energy of the solution according to the equation $E_n = -\frac{Z^2}{n^2}$, where $Z$ is the nuclear charge. The angular momentum quantum number $l$ determines the magnitude of the orbital angular momentum as $\sqrt{l(l+1)}$. Finally, the magnetic quantum number $m$ partially determines the direction of the orbital angular momentum, with the $z$ component equal to $m$. Because the $L_z$ operator does not commute with the $L_x$ or $L_y$ operator, it is not possible for a quantum state state to have a completely determined orbital angular momentum direction. The possible values for the quantum numbers are $n > 0$, $l < n$ and $-l \leq m \leq l$. The angular part, $Y_{lm}(\theta, \phi)$ is a spherical harmonic. The exact formula for the radial part is not important, but it includes an exponential decay whose rate depends of $n$ multiplied by a polynomial depending on both $n$ and $l$. The polynomial gives the wave function radial nodes, while the exponential decay causes the long range behavior to go as $e^{-r}$.

While no analytical solution can be found for more than electron, the hydrogen-like solution can be used as the start for an approximation. However, we must first consider one additional complication that occurs with more than one electron – spin statistics. In addition
to all the properties that arise from the spatial wave function, electrons have an additional intrinsic amount of angular momentum known as spin. This can take on one of two possible values, $-\frac{1}{2}$ and $\frac{1}{2}$. To account for this $x_i$ can be considered to include an additional dummy parameter $\omega$ that is related to spin (so $x_i = \{x_i, y_i, z_i, \omega_i\}$). Spin has two orthonormal basis functions: $\alpha(\omega)$, the spin function for spin $\frac{1}{2}$ electrons, and $\beta(\omega)$, the spin function for spin $-\frac{1}{2}$ electrons. The orthogonality condition is $\int \alpha(\omega) \beta(\omega) d\omega = 0$, and all other spin functions can be built as a linear combination of $\alpha$ and $\beta$.

Spin has two major implications. The first is wave function antisymmetry. All electrons are identical, completely indistinguishable particles. The fact that they have been labeled from 1 to $n$ is just for notational convenience — swapping two labels would have no effect on the physical state described. As the physical meaning of a state vector is independent of its phase, that means swapping two labels can multiply the vector by a root of unity. But not all of those are possible. As the permutation multiplies the state by a constant, it can be thought of as an operator that physically meaningful states must be an eigenvector of: $P_{12} |\psi\rangle = z |\psi\rangle$, where $P_{12}$ permutes the first two indices. But since switching two indices twice is the same as doing nothing, $P_{12}^2 = I$. Therefore, $z^2 = 1$, and 1 and $-1$ are the only two possible values. However, as a result of being spin-$\frac{1}{2}$ particles, the value for electrons must be $-1$ for a valid state. Therefore, all wave functions must be antisymmetric with respect to swapping two indices.

The second is related to the fact that inner products must take spin into account as well as the spatial coordinates. The wave functions we are concerned with will have each electron with a spin component of either $\alpha$ or $\beta$ rather than some combination of them. That means wave functions with non-matching spin components for a given electron will be orthogonal. Also, the Hamiltonians we will use commute with spin, so the product $\langle \psi | H | \phi \rangle$ will be zero when spins don’t match.

This is all the information needed to specify the many electron wave function problem, but a full solution is not practical. The function $\Psi(x_1, \cdots, x_n)$ is very complicated as the value for any one electron depends of the location of all the others. Furthermore, there is a potential energy term for each pair of electrons, preventing any separation of variables. Because all this correlation makes the problem impossible to solve, the simplest approximation ignores the correlation between electrons and describes them all independently.

## 1.2 The Hartree–Fock Approximation

There are two simple routes to ignoring the effect of electron correlation. The first is finding the optimum uncorrelated wave function for the exact Hamiltonian in accordance with the variational principle, and the second is finding the exact solution to an approximate mean field Hamiltonian where the potential felt by each electron is just the averaged probability distribution of the others. In fact, both of these routes lead equivalently to the Hartree–Fock Approximation[2–4]. The first is easier to think about for describing the method itself, while
the second is simpler for the purposes of perturbative corrections. But first, it is necessary
to discuss the concept of an uncorrelated wave function.

1.2.1 Slater Determinants

The multivariable nature of $\Psi(x_1, \cdots, x_n)$ prevents the discussion of each electron separately. Focusing on a two electron case for simplicity, the probability of finding an electron
at $x_1$ is highly dependent on where the other electron is. However, with a simpler function
such as $\Phi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2)$, this is not the case. The function $\Phi(x_1, x_2)$ with a fixed
$x_2$ is the same regardless of its actual value other than a multiplicative constant. In the
language of probability, $P(e_1 \text{ at } x_1 \cap e_2 \text{ at } x_2) = \phi_1(x_1)^2\phi_2(x_2)^2 = P(e_1 \text{ at } x_1)P(e_2 \text{ at } x_2)$,
so the locations of the electrons are independent. The functions $\phi_1$ and $\phi_2$ describe one
electron independently and are called orbitals. They are spin orbitals when they have a spin
component and spatial orbitals when they do not. This wave function which is a product
of orbitals is called a Hartree product. However, the fact that the probability statement
had to specify $e_1$ and $e_2$ when electrons are indistinguishable hints at the major flaw. Hartree
products are not antisymmetric, and so do not describe physically possible states. The
simplest way to correct this is to force the function to be antisymmetric by redefining it as $\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} (\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2))$ (the prefactor is for normalization). The
locations of the two electrons are no longer perfectly uncorrelated if they have the same spin.
In particular, the probability of both electrons being at the same point with the same spin is
zero. However, the descriptions are as separate as possible for an antisymmetric function and
the only correlation is in spin statistics, so this type of wave function is called uncorrelated.

The extension of this to arbitrary numbers of electrons is called the Slater determinant[5, 6]:

$$
\Phi(x_1, x_2, \ldots, x_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_n(x_1) \\
\phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_n(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(x_n) & \phi_2(x_n) & \cdots & \phi_n(x_n)
\end{vmatrix}
$$

which can be denoted as $|\phi_1 \cdots \phi_n|$. For convenience, the orbitals are required to be ortho-
normal, though the important thing is the space they span. The determinant has the
property that it is linear in every row and column and also antisymmetric with respect to
exchanging rows or columns. This makes it perfect for creating antisymmetric wave func-
tions. One implication is that two identical columns cause the determinant to be zero, as no
antisymmetric wave function can have the same orbital twice. This is a reflection of the
Pauli principle, which states that only one electron can occupy a given spin orbital[7]. In the
restricted, closed shell case, each spatial orbital exists in a spin $\alpha$ and spin $\beta$ spin orbital, so
the determinant is $|\phi_{\alpha\alpha}\phi_{\beta\beta} \cdots \phi_{\alpha\beta}\phi_{\beta\alpha}|$. This allows each spatial orbital to appear twice in the
determinant, which is the origin of the more familiar version of the Pauli principle, which says
each orbital may be occupied twice – once by an electron of each spin. Slater determinants
also have the nice property that matrix elements $\langle \psi_a | H | \psi_b \rangle$ can calculated according to the
fairly simple Slater-Condon rules. The rest will be introduced as needed, but when both sides of the matrix element are the same Slater determinant, \( \langle \psi | F | \psi \rangle = \sum_i \int \phi_i^*(x) f \phi_i(x) dx \) and \( \langle \psi | G | \psi \rangle = \sum_i \sum_j \int \int \phi_i^*(x) \phi_j^*(x') g \phi_i(x) \phi_j(x') dx dx' \), where \( G \) is an operator that’s a sum of two electron terms, such as the electron repulsion operator, and \( F \) is an operator that’s a sum of one electron terms, such as the rest of the Hamiltonian. This makes Slater determinants good to use as a basis for wave functions.

1.2.2 The Variational Principle

As the Schrödinger equation must be solved approximately, it is necessary to have a way to evaluate approximations. Because the exact solutions form a basis for the space, it is possible to express any approximate solution by a linear combination of exact solutions, \( |\phi\rangle = \sum_i c_i |\psi_i\rangle \), with \( \sum_i c_i = 1 \). The expected value of the energy is \( \langle \psi | H | \psi \rangle = \sum_i c_i^2 E_i \). Since the ground state energy \( E_0 \) is lowest of all eigenvalues of \( H \), the expectation value must be greater than or equal to it. When \( |\psi_0\rangle \) is unique, equality is only achieved when \( |\phi\rangle = |\psi_0\rangle \). Therefore, we see that the expectation value of the energy for a trial wave function can never underestimate the correct ground state energy, and minimizing the energy is a valid way to find an approximation.

1.2.3 Basis Sets

The variational principle with Slater determinants nearly defines an approximation method for the Schrödinger equation, but still missing is a space of possible Slater determinants to minimize over. The solution to this is expansion in a finite basis set. The possible orbitals \( \phi_i \) of the Slater determinant can be expressed as linear combinations of these basis functions \( \phi_i = \sum_\mu C_{\mu i} \chi_\mu \), with the requirement that the different orbitals be orthonormal. Since the basis functions will not in general be orthonormal, the orthonormality condition becomes \( \langle \phi_i | \phi_j \rangle = \sum_\mu C_{\mu i} S_{\mu \nu} C_{\nu j} = \delta_{ij} \), where \( S \) is the overlap matrix \( S_{\mu \nu} = \langle \chi_\mu | \chi_\nu \rangle \). Because these basis sets will be finite, this introduces another source of error in addition to the neglect of correlation — basis set incompleteness. The most common choice of basis sets is the atomic orbital basis set, where the basis functions are based on the solutions to the hydrogen-like atom Schrödinger equation, though with parameters adjusted to serve better as basis functions for molecular orbitals. The exponential decay behavior is replaced with Gaussian functions for easier computation of integrals[8]. Basis functions are often the sum of multiple Gaussians to better approximate an exponential. Atomic orbital basis sets often allow convergence to close to the basis set limit with a reasonable number of basis functions[9].
1.2.4 The Hartree–Fock Equation

With this, the Hartree–Fock approximation can be defined as the variationally optimal single Slater determinant in a given finite basis set. The goal is to minimize

\[ E_0 = \langle \Psi_0 | H | \Psi_0 \rangle = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | ij \rangle - \langle ij | ji \rangle \]  

(1.6)

where \( \langle i | h | j \rangle = \int \phi_i^*(x) \left( \frac{1}{2} \nabla^2 + V_n(x) \right) \phi_j(x) dx \) and \( \langle ij | kl \rangle = \int \int \phi_i^*(x) \phi_j(x') \frac{1}{|x-x'|} \phi_k(x) \phi_l(x') dx dx' \). This energy ignores the nuclear repulsion energy which can be added back at the end. The sum over \( j > i \) has been replaced by half of the sum over \( i \neq j \) since each pair will occur twice. Also, the quantity summed over is zero when \( i = j \), so this has been replaced with a sum over all \( i \) and \( j \) for simplicity.

This is sometimes referred to as a mean-field equation because

\[ \sum_j \langle ij | ij \rangle = \int \int \phi_i^*(x) \phi_i(x) \frac{1}{|x-x'|} \sum_j (\phi_j^*(x') \phi_j(x')) dx dx' \]

can be interpreted as the interaction of electron \( i \) with the field generated by the average position of the other electrons. Meanwhile, \( \langle ij | ji \rangle \) is called the exchange term. It lacks a simple classical explanation, but arises from spin statistics and cancels the interaction of each electron with itself.

Lagrange multipliers can be used for the constrained optimization.

\[ \mathcal{L}(\phi_i) = \sum_i \langle i | h | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | ij \rangle - \langle ij | ji \rangle - \sum_{ij} \varepsilon_{ij} (\langle \phi_i | \phi_i \rangle - \delta_{ij}) \]  

(1.7)

Collecting the energy terms into a single operator known as the Fock operator,

\[ \langle \phi_i | F | \phi_k \rangle = \langle i | h | k \rangle + \frac{1}{2} \sum_j \langle ij | kj \rangle - \langle ij | jk \rangle \]  

(1.8)

the Lagrangian is extremized when \( F | \phi_i \rangle = \sum_j \varepsilon_{ij} | \phi_j \rangle \). Because any unitary transformation of the orbitals leaves the same Slater determinant, there is always a canonical solution where \( F | \phi_i \rangle = \varepsilon_i | \phi_i \rangle \).

In a finite basis set, this becomes a matrix equation

\[ \sum_\nu F_{\mu \nu} C_{\nu i} = \varepsilon_i \sum_\nu S_{\mu \nu} C_{\nu i} \]  

(1.9)

or \( FC = SC \varepsilon \), where \( \varepsilon \) is a diagonal matrix. This is the equivalent of diagonalizing \( F \) in a non-orthogonal basis. However, the procedure is not as simple as a diagonalization because the Fock matrix depends on the orbital coefficients. This means that iterative procedures must be used to solve the Hartree–Fock Equation. The simplest is to begin with some guess for the orbital coefficients, then use this guess to construct a Fock matrix, diagonalize the Fock matrix to get a new guess and then repeat. This procedure can be ended when it has converged to some threshold. The result is the Hartree–Fock wave function \( | \Psi_0 \rangle \) and gives its energy \( E_0 \). However, it is not accurate enough for practical purposes and must be corrected.
1.3 Correlation Methods

Hartree–Fock energies are very close to the correct numbers in absolute terms, generally achieving about 99% of the exact energy. However, it is relative energies that are important, and Hartree–Fock energies are not accurate enough to predict chemistry there, often failing to give even qualitatively correct answers. For example, the HF error in the bond dissociation energy of $H_2$ is approximately 1 eV. This is especially the case in intermolecular interactions, where the energy differences are small and dependent on dispersion which is a correlation effect. Some treatment of electron correlation is thus necessary for correct treatment of chemistry. Today, Hartree–Fock is better thought of as starting point for correction methods than as its own approximation method.

A converged Hartree–Fock procedure gives orbitals that diagonalize the Fock matrix. However, a good basis set has many more basis functions than there are electrons. We have focused on only the lowest $n$ orbitals – the occupied orbitals – which have electrons and show up in the Fock matrix. Diagonalizing the Fock matrix defines one molecular orbital for each linearly independent basis function. The remainder have no effect on the Fock matrix, but can used to define additional Slater determinants to use as a basis for corrections to the Hartree–Fock wave function. Linear combinations of Slater determinants are still antisymmetric functions, and can describe wave functions with correlations between the electrons. The set of all possible Slater determinants with any $n$ of the molecular orbitals form a basis for the whole space spanned by the basis set. The determinant that replaces orbital $i$ from the Hartree–Fock solution with virtual orbital $a$ is referred to as $|\Psi_i^a\rangle$. Those that replace more than one are called $|\Psi_{ij}^{ab}\rangle$ and so on. If the matrix of $H$ is computed for every possible Slater determinant, it can be diagonalized to solve the Schrödinger equation exactly in the basis. This is called full configuration interaction (FCI). However, the number of possible determinants grows as $\binom{N}{n}$ with $n$ electrons and $N$ basis functions, which is factorial in the size of the system, making this impossible to solve for all but the smallest systems. Much of the work in quantum chemistry is in finding intermediate methods that are more accurate than HF, but faster than FCI. The simplest idea would be truncating the CI expansion at a certain level of substitution. CI singles do not affect the ground state, since the definition of Hartree–Fock ensures that $\langle \Psi_i^a | H | \Psi_0 \rangle = 0$ for any singly excited determinant. Higher levels of truncation do define actual corrections to the Hartree–Fock solution, but have undesirable properties that make them unusable. At any intermediate truncation level, the CI energy is not size extensive, meaning that the energy of two infinitely separated systems is not the sum of the energies of the individual systems. This is a fatal flaw for chemistry and means that useful methods must take a different approach.

1.4 Perturbation Theory

The lowest scaling (and most important for this work) correlation method is second order Møller–Plesset perturbation theory[10, 11]. Perturbation theory is a technique where
the solution to a Hamiltonian that cannot be solved exactly is approximated using a simpler Hamiltonian that can be solved. With the exact Hamiltonian $H$, the simpler Hamiltonian $H_0$ and the difference, called the perturbation, $V$, the relation is $H = H_0 + \lambda V$. The parameter $\lambda$ makes the Hamiltonian exact when it is 1 and the simple one when it is 0. With the equation $(H_0 + \lambda V) |\psi\rangle = E |\psi\rangle$, the energy and wave function can be treated as a power series in $\lambda$:

\[(H_0 + \lambda V) (|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \cdots) = (E^{(0)} + \lambda E^{(1)} + \cdots) (|\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \cdots) \quad (1.10)\]

This allows the collection of terms with the same powers of $\lambda$. The $\lambda^0$ equation is just the equation for the approximate Hamiltonian $H_0 |\psi^{(0)}\rangle = E^{(0)} |\psi^{(0)}\rangle$, but the later equations are useful. For example, the first order equation looks like this

\[H_0 |\psi^{(1)}\rangle + V |\psi^{(0)}\rangle = E^{(0)} |\psi^{(1)}\rangle + E^{(1)} |\psi^{(0)}\rangle \quad (1.11)\]

and the rest are similar.

Some manipulation gives the results that

\[E^{(1)} = \langle \psi^{(1)} | V | \psi^{(1)} \rangle \quad (1.12)\]

and

\[|\psi^{(1)}\rangle = \sum_{n \neq 0} \frac{\langle \psi^{0}_{n} | V | \psi^{0}_{n} \rangle}{E^{(0)} - E^{(n)}} |\psi^{0}_{n}\rangle \quad (1.13)\]

where the sum is over the other eigenstates of $H_0$. The first order correction to the energy is simply the expectation value of the perturbation with the unperturbed solution. The correction to the wave function is a linear combination of all the other solutions to the unperturbed Hamiltonian. This allows the solution for the second order correction to the energy

\[E^{(2)} = \sum_{n \neq 0} \left| \frac{\langle \psi^{0}_{n} | V | \psi^{0}_{n} \rangle}{E^{(0)} - E^{(n)}} \right|^2 \quad (1.14)\]

This can be continued, but the equations become increasingly complicated. The expansion can be truncated at any point. For example, the energy can be approximated as $E^{(0)} + E^{(1)} + E^{(2)}$. If the series converges, it will converge to the exact answer, and early truncation will often lead to good results. Even if the series does not converge, low order truncation may still be useful.

1.4.1 Møller–Plesset Perturbation Theory

When perturbation theory is applied to electronic structure with Hartree–Fock as the unperturbed solution, it is called Møller–Plesset perturbation theory\[10, 11\]. The properties of Hartree–Fock make perturbation theory simple, especially at second order. Earlier, we
saw that the Hartree–Fock solution and excited determinants are eigenfunctions of the Fock operator. The Fock operator can be used as the unperturbed Hamiltonian for perturbation theory, and can be thought of as a Hamiltonian that ignores electron correlation. The perturbation is thus the correlation. Because the Hartree–Fock energy is not the eigenvalue of the Fock operator, it is best to define the unperturbed Hamiltonian as the shifted Fock operator $H_0 = F + \langle \Psi_0 | (H - F) | \Psi_0 \rangle$. The eigenstates are the same as the Fock operator, but the eigenvalues correspond to the correct energy. First, this makes it clear that $E^{(1)} = 0$, so that there is no first order correction to the energy. The lowest possible perturbative correction comes at second order. Looking back at equation 1.14, the second order energy will depend on all excited determinants whose $V$ matrix element is nonzero. As these are eigenstates of $H_0$, the matrix elements are the same as $H$ matrix elements off the diagonal. By the properties of Slater determinants, $\langle \Psi_{ijk}^{abc} | H | \Psi_0 \rangle = 0$ for triply and higher excited determinants, as $H$ is a two electron operator. Also, as mentioned earlier, $\langle \Psi_0^a | H | \Psi_0 \rangle = 0$ for the Hartree–Fock solution. Therefore only doubly excited determinants need to be considered. The equation becomes

$$E^{(2)} = \frac{1}{4} \sum_{ij} \sum_{a} \sum_{b} \frac{\langle \Psi_{ij}^{ab} | H | \Psi_0 \rangle^2}{E^{(0)} - E_{ij}^{ab}}$$

(1.15)

As above $\langle \Psi_{ij}^{ab} | H | \Psi_0 \rangle$ is equal to $\langle ij | ab \rangle - \langle ij | ba \rangle$ which can also be written as $\langle ij || ab \rangle$. The denominator is equal to $\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$. As the quantity being summed over is 0 when $i = j$ or $a = b$, the sums over pairs of distinct indices can be replaced with half of sums over all pairs, for a total factor of $\frac{1}{4}$. The final equation is

$$E^{(2)} = \frac{1}{4} \sum_{ijab} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

(1.16)

As virtual orbitals are higher in energy than occupied ones, this quantity is always negative, and the second order Møller–Plesset (MP2) energy is always lower than that of Hartree–Fock. The energy is not an expectation value of the Hamiltonian, so MP2 does not obey the variational principle and is capable of underestimating the true energy. However, unlike truncated CI, it is size extensive, which makes it much more useful than truncated CI. MP2 is much more accurate than Hartree–Fock, making it useful for many applications in chemistry. It is well suited for intermolecular interactions, but it known to overestimate dispersion in some systems, such as π-stacking complexes[12–14]. When greater accuracy is desired, there are slower, but more accurate methods such as coupled cluster[15]. From the point of view of intermolecular interactions, MP2 corrects Hartree–Fock’s overestimation of dipole moments, underestimation of polarizabilities and intermolecular charge transfer, and complete neglect of dispersion.

The majority of time of an MP2 calculation is spent calculating the integrals $\langle ij || ab \rangle$. There are $o^2v^2$ of them in a system with $o$ occupied orbitals and $v$ virtual orbitals, but the orbitals are linear combinations of basis functions and the integrals can only be calculated
in terms of them. Each orbital is a linear combination of $N$ basis functions, so each transformation takes time proportional to $N$, making the overall calculation scale as $O^{2}v^{2}N$ or fifth order in the size of the system. Attempts at speeding up MP2 therefore focus on the integrals. One very common approximation is resolution of the identity MP2, or RIMP2$^{[16]}$. This does not change the overall scaling of MP2, but leads to significant speed up with negligible loss of quality. The main innovation of RIMP2 is to use an auxiliary basis set to approximate pairs of functions from the original basis set for the purpose of the four center integrals. Remember that

$$\langle \mu \nu | \lambda \sigma \rangle = \int \int \phi_{\mu}^{*}(x)\phi_{\nu}^{*}(x')\frac{1}{|x-x'|}\phi_{\lambda}(x)\phi_{\sigma}(x')dx dx'$$

The product $\phi_{\mu}^{*}(x)\phi_{\lambda}(x)$ can be approximated by a linear combination of auxiliary basis functions $K$, so that the integral can be approximated as

$$\sum_{KL} C_{KL}^{\mu \lambda} \left( \int \int K(x)\frac{1}{|x-x'|}L(x')dx dx' \right) C_{\nu \sigma}^{L}$$

RIMP2 does not decrease the scaling of MP2 because the size of the auxiliary basis must be proportional to the size of the original basis. However, it is possible to achieve good results with auxiliary basis sets only about three times larger than the original basis set$^{[17]}$. The costly transformation to the molecular orbital basis can be done with the three center fit coefficients, which are much smaller in number than the four center integrals. This allows for large speed ups, often in range to 3 to 30 times. There are several different ways of producing fit coefficients, but all try to minimize the error in the approximate integrals. The most effective is the use of the Coulomb metric$^{[18]}$. With this, reasonable accurate binding energies can be calculated in small amounts of time.

### 1.5 Energy Decomposition

When used for intermolecular interactions, the most natural thing to do in electronic structure is compute the binding energies according to the supermolecule approach $\Delta E = E(AB) - E(A) - E(B)$. This gives the interaction energy for two molecules as a single number. But when considering the interactions between two molecules, people are used to thinking in terms of conceptually different forces. From the perspective of the math, the only force is the electrostatic interaction that appears in the Hamiltonian, but the binding energy can be thought of as coming from different sources. Already, the potential energy is divided into Coulomb, exchange, and correlation, but this division is based on the mathematical framework of the calculation, rather than a conceptual division. First year chemistry classes teach about such things as intermolecular charge transfer in hydrogen bonds, London
dispersion forces, and dipole–dipole interactions, but none of this is apparent in the binding energy. Energy decomposition analysis (EDA) is an attempt to divide the binding energy into conceptually meaningful multiple categories. The division must be to a certain extent arbitrary as the equations of quantum mechanics do not care about human intuition, but ideally an EDA can help chemists gain additional insight about a system beyond the simple binding energy that emerges from an electronic structure calculation. Many different EDAs have been defined, with various different components of the energy as well as different ways of assigning energy to those components.

The earliest EDA to become popular was developed by Kitaura and Morokuma for Hartree–Fock (HF) in 1976.[19] It divided the energy into electrostatic interaction, exchange, polarization, and charge transfer. Other than exchange, these became popular choices for future EDAs. It had flaws related to the invalidity of the intermediate wave functions, but later variations mitigated these flaws and extended it to apply to DFT as well. Today, two of the most popular families of EDAs are natural energy decomposition analysis schemes,[20] based on natural bond orbitals[21] (NBO), and symmetry-adapted perturbation theory[22] (SAPT). The NBO approach is an attempt to formalize the concept of Lewis structures by creating localized molecular orbitals similar to bonding orbitals and lone pairs. This allows the partitioning of intermolecular interactions based on these orbitals. NEDA tends to describe charge transfer as the most important contribution to binding, sometimes exceeding 100% of the total interaction (with the sum of the other forces opposing binding), so proponents of NBO theory tend to believe in a charge transfer-heavy theory of intermolecular interactions[23]. SAPT uses a noninteracting system as a base and treats the intermolecular interaction as a perturbation on top of that. Because of this, it comes up with its own binding energy and it cannot decompose the binding energies of accurate post-HF methods. Separation of charge transfer is not natural within the SAPT framework, and it is usually included in an induction term along with on-molecule polarization. Others have doubted whether charge transfer even meaningfully exists[24]. They usually believe in a description of intermolecular interactions where electrostatic effects are most important. The σ-hole theory[25] explains hydrogen and halogen bonds in terms of electrostatic phenomena. The approach described here is more agnostic, allowing either charge transfer or electrostatics as important in different (or sometimes the same) systems.

Previous approaches do not work well for post-HF methods. Most EDAs are defined only for HF and density functional theory, the latter of which is not systematically improvable. Some have simply called the contribution from post-HF methods correlation, but this is not physically meaningful. Others have tried to identify this as dispersion, but as we will see in chapter 2, this is not tenable. As post-HF methods are the most reliable for computing binding energies, it is desirable to have an EDA for them.

Because of the wide variety of possible EDAs that can be defined, it is useful to have some goals in mind when designing one. The first goal is the decomposition should partition the binding energy of a reliable electronic structure method exactly, and ideally be extensible to many such methods. Next, the terms of the decomposition should all be physically meaningful, lacking both terms to collect leftovers (such as exchange), and terms that contain
multiple distinct effects (such as SAPT induction). Ideally, all terms should have a well-defined basis set limit, though full achievement of the goal is beyond the scope of the current work. In the non-overlapping limit, when all terms have unambiguous definitions, the EDA should get the correct values, with correct asymptotic behavior, and these values should continue meaningfully into the interacting region. Finally, the decomposition should be based on intermediate wave functions which be understood as capturing the physics of the corresponding type of interaction.

Prior work at Berkeley on the Absolutely Localized Molecular Orbital EDA [26, 27] meets many of these goals, but is only defined for HF and DFT. It provides a good starting point for the definition of an EDA for post-HF methods, starting with MP2. As the MP2 energy is a correction to HF, an MP2 EDA should be a correction to a HF EDA. The ALMO EDA defines some intermediate sets of orbitals which can be used as a starting point for MP2 equivalents.

Finally, it's important to consider what components are included in the EDA. Here are the concepts included in the MP2 ALMO EDA.

1.5.1 Frozen Interaction

The frozen interaction is the interaction between two molecules whose wave functions are not allowed to relax in each other’s presence. This includes two conceptually different pieces, one that can be understood in terms of classical reasoning and one that is purely quantum, but the difference does not emerge naturally. The purely quantum effect is Pauli repulsion. It is the volume excluding effect that causes different atoms to repel each other at close distances. It is larger and faster growing than pure electron-electron repulsion would dictate. Pauli repulsion is largely a result of the antisymmetry of wave functions requiring that two electrons of the same spin be in different states. This forces electrons to be in higher energy states when they are close to each other. Pauli repulsion is a purely repulsive effect as the name suggests, and is often the only repulsive force balancing the others at equilibrium. Beyond short distances, it decays exponentially, so it is only important in the short range.

The other part of the frozen interaction is permanent electrostatics. In the limit on non-overlapping wave functions, this is well defined and equal to the classical electrostatic interaction of the charge distributions. It can be thought of in terms of the multipole expansion. Charge-charge interactions decay as slowly as $R^{-1}$, dipole-dipole as $R^{-3}$, quadrupole-quadrupole as $R^{-5}$, and so on. Two spherically symmetric systems, such as two atoms, can have no permanent electrostatic interaction in the non-overlapping limit. In cases where molecules have low non-zero moments, the permanent electrostatics will be the dominant long range interaction, and can be attractive or repulsive depending on the alignment of the molecules. As HF tends to overestimate the sizes of multipole moments, it will usually overestimate the magnitude of permanent electrostatics whether attractive or repulsive. These effects still apply in the overlapping region, but assignment of electrons to molecules becomes ambiguous and there is no one obviously correct definition. It is the job of an EDA to meaningfully extend the frozen energy into this region.
1.5.2 Polarization

In the presence of other molecules, each molecule will polarize, changing its charge distribution in response. This is always a favorable interaction. The strength of the induced electrostatics will depend on the polarizability of the molecule as well as the strength of the interactions with it. In the long range, the distance dependence is once again determined by the properties of the charge distribution, similar to classical electrostatics. Charge induced dipole interactions decay as $R^{-4}$ while dipole induced dipole interactions decay as $R^{-6}$. In the short range, polarization also includes a relaxation of the Pauli repulsion that is overestimated by the frozen reference.

1.5.3 Charge Transfer

Charge transfer is the donation of charge from one molecule to another. It is similar to covalent interactions in bonds, but between molecules and weaker. It decays exponentially with distance because it depends on orbital overlap, so it is expected to be important only in the short range. It is also highly direction dependent and can be the most important thing giving rise to the shape of hydrogen bonded complexes. In the range where charge transfer is important, it can be difficult to distinguish from polarization, as both are conceptually similar when the assignment of electrons to molecules is not clear.

1.5.4 Dispersion

Even in molecules without non-zero low permanent multipole moments, there is a slowly decaying intermolecular interaction arising from the correlations in fluctuations of the electron density. This is the London dispersion force, and in many weakly bound systems, this is the most important force holding the molecules together. Dispersion decays as $R^{-6}$ in the long range. It cannot be described at all by HF, because it is a result of correlation. Even most DFT methods cannot naturally describe dispersion unless a semi-empirical dispersion correction is added. Because of this MP2 is the simplest method that describes dispersion in an ab initio way, though it sometimes overestimates it. Therefore, a description of dispersion is one of the major goals of an MP2 EDA.

1.6 Outline

In this work, we first discuss the effects contained within the MP2 and CCSD(T) correlation contribution to the binding energy, and in particular why they cannot be understood purely as dispersion. Next we define an EDA for MP2 that properly accounts for all the different effects in the correlation energy, and describe how to implement it efficiently. Finally, it is applied to some important classes of intermolecular interactions to help understand them.
1.6.1 Chapter 2

The electron-electron correlation energy is negative, and attractive dispersion interactions are entirely a correlation effect, so the contribution of correlation to intermolecular binding is commonly assumed to be negative, or binding in nature. However, there are many cases where the long-range correlation binding energy is positive, and therefore anti-binding, with certain geometries of the water dimer as a prominent example. The correlation anti-binding has its origin in the systematic overestimation of dipole moments by Hartree-Fock theory, leading to a reduction in the calculated electrostatic attraction upon inclusion of correlation. Thus, energy decomposition analyses that include correlation but do not correct mean field electrostatic terms are sub-optimal, especially those that describe all of the correlation energy as dispersion. Furthermore, methods such as attenuated second order Møller-Plesset theory, which smoothly truncate long-range electron correlation effects to zero, can, paradoxically, have the correct long-range behavior for many intermolecular interactions. This work has been published in J. Phys. Chem. Lett.[28]

1.6.2 Chapter 3

An energy decomposition analysis (EDA) of intermolecular interactions is proposed for second-order Møller-Plesset perturbation theory (MP2) based on absolutely localized molecular orbitals (ALMOs), as an extension to a previous ALMO-based EDA for self-consistent field methods. It is based on dividing the double excitations that contribute to the MP2 wave function into classes based on how the excitations involve different molecules. The MP2 contribution to the binding energy is decomposed into four components: frozen interaction, polarization, charge transfer, and dispersion. Charge transfer is defined by excitations that change the number of electrons on a molecule, dispersion by intermolecular excitations that do not transfer charge, and polarization and frozen interactions by intra-molecular excitations. The final two are separated by evaluations of the frozen, isolated wave functions in the presence of the other molecules, with adjustments for orbital response. Unlike previous EDAs for electron correlation methods, this one includes components for the electrostatics, which is vital as adjustment to the electrostatic behavior of the system is in some cases the dominant effect of the treatment of electron correlation. The proposed EDA is then applied to a variety of different systems to demonstrate that all proposed components behave correctly. This includes systems with one molecule and an external electric perturbation to test the separation between polarization and frozen interactions and various bimolecular systems in the equilibrium range and beyond to test the rest of the EDA. We find that it performs well on these tests. We then apply the EDA to a halogen bonded system to investigate the nature of the halogen bond. This work has been published in J. Chem. Phys.[29]
1.6.3 Chapter 4

The absolutely localized molecular orbital (ALMO) EDA has been extended from the self-consistent field level to the second order Møller-Plesset (MP2) theory level. This chapter reports an efficient implementation of the MP2 ALMO-EDA that scales optimally, employs the resolution of the identity (RI) approximation for post-SCF matrix elements, and is shared-memory parallel. The algorithms necessary to achieve this implementation are described in detail. Performance tests using the aug-cc-pVTZ basis set for water clusters of up to 10 molecules are reported. The timings suggest that the MP2 ALMO-EDA is computationally feasible whenever MP2 energy calculations themselves are feasible, and the cost is dominated by the SCF itself in this size regime. The MP2 ALMO-EDA is applied to study the origin of substituent effects in anion-π interactions between chloride and benzene and mono through hexa-fluorobenzene. The effect of fluoro substituents was primarily to change the frozen interaction. Detailed analysis supports the interpretation that anion-π interactions are favorable because of electrostatic interaction with the substituents. This work has been published in *J. Phys. Chem. A* [30]

1.6.4 Chapter 5

The halogen bond is a class of non-covalent interaction that has attracted considerable attention recently. A widespread theory for describing them is the σ-hole picture, which predicts that the strength of the interaction is proportional to the size of the σ-hole, a region of positive electrostatic potential opposite a σ bond. Previous work shows that in the case of CX₃I, with X equal to F, Cl, Br, and I, the σ-hole trend is exactly opposite to the trend in binding energy with common electron pair donors. We propose that this is because the σ-hole is a purely electrostatic theory, which neglects the role of intermolecular charge transfer. While charge transfer and electrostatics usually have the same trend, they seem to be opposed here. Using energy decomposition analysis applied to a potential energy scan as well as the recent adiabatic EDA technique, we show that the observed trend is a result of charge transfer, and that therefore a picture of the halogen bond that excludes charge transfer cannot be complete.
Chapter 2

Electrostatics in intermolecular correlation

Ab initio wave function methods that include treatment of electron correlations are widely used for the accurate calculation of intermolecular interactions (e.g., for a bimolecular AB complex), using the supermolecule approach in which $\Delta E = E(AB) - E(A) - E(B)$. Correlation methods correct the mean field Hartree–Fock (HF) approximation for the effect of instantaneous electron–electron correlations: $E = E_{HF} + E_{corr}$. Common examples include high accuracy coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T))[31], and, for larger molecules, the more computationally efficient second order Möller–Plesset perturbation theory (MP2)[32].

The contribution of electron correlation, $E_{corr}$, to absolute molecular energies, $E$, is negative semi-definite and crucial for calculating accurate intermolecular interactions, though it is typically only about 1% of the total energy. CCSD(T) in particular[33–35] — and sometimes even MP2 theory (e.g., for hydrogen-bonded systems[36, 37]) — is more accurate than most widely used density functionals for intermolecular interactions[38, 39], despite continuing progress in functional development. With sufficiently large basis sets, both CCSD(T) and MP2 are tremendously successful, although MP2 is known to significantly overestimate the strength of stacking interactions[12–14], and the high cost of CCSD(T) prevents application to large molecules without additional approximations. Accordingly, modifications are sought to MP2 theory to improve its accuracy for intermolecular interactions without increasing cost, such as spin-component scaling[40–42] and electronic attenuation[43, 44].

Physically, the HF reference captures some key aspects of intermolecular interactions, such as permanent electrostatics (either attractive or repulsive) and Pauli repulsion associated with the frozen orbitals of isolated fragments, and the induced orbital interactions or mixings. To unravel these contributions, energy decomposition analysis (EDA) methods, such as the Kitaura–Morokuma method[19] and its many descendants[45–49], partition the HF binding energy, $E_{HF}$, into physically motivated components: $\Delta E_{HF} = \Delta E_{FRZ} + \Delta E_{IND}$. Some EDAs further partition the induced orbital interactions into terms associated with polarization (on a fragment) and donor–acceptor orbital interactions (between fragments)[26,
CHAPTER 2. ELECTROSTATICS IN INTERMOLECULAR CORRELATION

27, 50, 51].

How should an EDA be modified when electron correlation is included in the calculation? Inclusion of correlation accounts for purely attractive dispersion forces between molecules due to correlation in the temporary multipoles created by electron movements, an effect entirely absent in the HF reference. For neutral, non-polar molecules, dispersion is usually the most important long-range interaction, decaying as the inverse of the sixth power of the separation between molecules. Given that dispersion interactions are purely attractive, and the correlation energy itself is negative semi-definite, the simplest modification to such EDAs is to include the correlation binding energy (CBE) as an additional term[47, 49], labeled as dispersive: $\Delta E_{\text{DISP}} = \Delta E_{\text{corr}}$. There have been some additional attempts[52, 53] to further partition the correlation energy into a purely dispersive part, where there is no net transfer of electrons, a charge-transferring contribution, and intra-fragment correlation.

This letter will present some calculations which challenge the identification of $\Delta E_{\text{corr}}$ as dispersive by illustrating that for many intermolecular interactions, the long-range contribution of the correlation energy is, in fact, electrostatically dominated and can either be binding or anti-binding: $\Delta E_{\text{corr}} > 0$. This result appears surprising since it is intuitive that a supermolecule should have more correlation than the isolated sum of its parts. Thus one expects that the CBE should be negative semi-definite, consistent with it being primarily dispersive. While that is of course true for non-overlapping atoms, real systems often differ from this idealization in important ways. It can only be accurate in general if, despite those differences, none of the other effects captured by post HF methods are ever as important as dispersion. Though this fact has been previously described[54] in an analysis that was understood and mentioned in several papers over the following few years[55–58], especially among the symmetry-adapted perturbation theory community, it is not widely known in quantum chemistry (indeed we are grateful to a referee for pointing out these references to us). Because of intrinsic interest, and significance for EDAs, improvements to Hartree-Fock for dispersion, and the attenuation of MP2, it is useful and timely to explore the nature of the long-range CBE in detail, and examine the resulting implications.

In investigating the types of effects the correlation energy can describe, the water dimer will be used as an example system, though as we shall see, the results immediately generalize to many other systems. All calculations were performed with Q-Chem 4.0[59]. There are four geometries of interest. The first is the equilibrium geometry of the dimer where one molecule is rigidly translated along the axis between the centers of mass of the two molecules, as depicted in figure 2.1(a), which will be referred to as the stretched equilibrium geometry. Next is two aligned coplanar water molecules with oxygen atoms separated along the axis parallel to the molecules’ dipoles, which is depicted in figure 2.1(b) and will be referred to as the aligned geometry. This geometry was chosen to maximize favorable electrostatic interactions. The next is similar to the previous, but with one molecule flipped so the dipoles are antiparallel, and is depicted in figure 2.1(c) and will be referred to as the anti-aligned geometry. This geometry was chosen to maximize unfavorable electrostatic interactions. Last is the geometry with two water molecules arranged with perpendicular dipoles with oxygen atoms separated along the axis perpendicular to both molecules’ dipoles, which is depicted
in figure 2.1(d), and will be referred to as the perpendicular geometry. This geometry was chosen to minimize electrostatic interactions, by making the dipole–dipole interaction zero.

![Figure 2.1: Four different geometries of the water dimer. The stretched geometry is based on the S22 equilibrium geometry. The other three geometries each have equivalent monomers with bond length of 0.9584 Å and bond angle of 104.46°.](image)

The binding energy curves for the geometries with intermolecular separation beyond the equilibrium distance are shown below in figure 2.2. The calculations were done with resolution of the identity approximation MP2 (RIMP2) in the aug-cc-pVQZ basis set and the corresponding auxiliary basis set, without the frozen core approximation or counterpoise correction. There is nothing particularly surprising in this graph. The perpendicular and anti-aligned geometries are repulsive everywhere, though the perpendicular geometry has a local minimum in the short range. The stretched equilibrium geometry is lowest in energy in the short range, due to hydrogen bonding. And the aligned geometry is lowest in energy in the long range, where the dipole interaction is most important.

However, when focusing only on the correlation contribution to the binding energy, an unexpected effect is visible. As can be seen in figure 2.3, for the stretched equilibrium and the aligned geometries, the CBE is positive beyond the equilibrium separation, meaning that MP2 binds the dimer less strongly than HF. The maximum value here is small, less than 0.2 kJ/mol, but still large enough to be noticeable. It defines the entire long range interaction of
the dimers, all the way out to infinite separation. Furthermore, the CBE for the anti-aligned geometry decays much more slowly than the expected inverse sixth power of intermolecular separation. The positive CBE is not limited to MP2. The diamonds in figure 2.3 are the CBE values calculated with CCSD(T), and show the same effect as in MP2. Neither is this result basis set dependent. Figure 2.4 shows the curve for the stretched equilibrium geometry in other basis sets. The magnitude of the maximum is somewhat larger with aug-cc-pVTZ, and slightly larger still with aug-cc-pVDZ. However, differences are small and the effect is definitely present in the smaller basis sets, and the trend implies that it will be present even at the basis set limit.

Figure 2.2: RIMP2 binding energy curves for the water dimer in four different geometries.

Figure 2.3: RIMP2 correlation binding energy curves for the water dimer in four different geometries, along with a CCSD(T) value (the diamonds) at 5.5 Å for each.
The positive CBE observed here contradicts our previously mentioned intuition that the treatment of electron correlation should always contribute to binding. EDAs that define dispersion as the CBE implicitly make this assumption since physical dispersion is a purely attractive force. A positive CBE is potentially noticeable to anyone who performs post HF binding energy calculations, and was discussed in the late 1980s[54-58]. However, knowledge of positive CBE does not seem to be widespread in the general quantum chemistry community, and several recent methods do not properly account for its implications, as we shall see below. What, then, is the cause of the positive CBE? As has been shown, it is not related to the particular post HF method or basis used. Therefore, it would seem to be an actual effect rather than a computational artifact. The tails of the curves for the stretched equilibrium and aligned geometries both decay as the inverse of the cube of the separation between the molecules. Since this is the characteristic long range behavior of dipole–dipole interactions, it suggests that the explanation lies in the electrostatics.

Hartree–Fock has a tendency to overestimate the strength of dipoles of molecules[60–63]. This can be thought of as a result of the HF model being slightly too ionic in character due to neglect of correlation, or the fact that anti-bonding orbitals with opposite polarity to bonding orbitals acquire small occupation numbers when correlation is included. Thus, post HF methods calculate a smaller dipole as part of providing a more accurate description of the molecules. This difference can be seen in water. As shown in Table 1, the two nonequivalent water molecules in the stretched equilibrium geometry, when each considered as an isolated system, have dipole moments approximately 5% lower with MP2 and CCSD(T) than with
Table 2.1: Dipole moments (in debye) for the two water molecules in the stretched equilibrium geometry with three different methods.

<table>
<thead>
<tr>
<th></th>
<th>Water molecule 1</th>
<th>Water molecule 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>1.986</td>
<td>1.981</td>
</tr>
<tr>
<td>MP2</td>
<td>1.867</td>
<td>1.863</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.879</td>
<td>1.875</td>
</tr>
</tbody>
</table>

HF. Since HF overestimates the dipole moments, it will also overestimate the strength of the attraction between them. When post HF methods correct the dipoles downward, they will also calculate a correspondingly lower binding energy.

To test this numerically, the difference between the dipole-dipole interactions of HF and MP2, given the dipole strengths in table 2.1 and the orientation of the molecules, is equal to $38.035 \text{ (kJ/mol)} \cdot \text{Å}^3/R^3$. The plot of this function is depicted in figure 2.5 along with the CBE curve for the stretched equilibrium geometry in the long range. The two curves coincide almost perfectly beyond 10 Å of separation and diverge only in the short range, where other correlation effects such as dispersion and charge transfer become comparably important. Further support for this electrostatic explanation comes from the relative behaviors of the four geometries. The aligned geometry displays positive CBE to a greater extent than the stretched equilibrium geometry, as its greater dipole interaction would lead us to expect, while the perpendicular geometry does not display it at all, because of its lack of a dipole-dipole interaction. The anti-aligned geometry is discussed below.

Further confirmation can be obtained from the anti-aligned geometry. The situation for this geometry is the opposite of the aligned one: a large negative CBE instead of a large positive one, though the decay should still be as the inverse cube of intermolecular separation in the long range. To confirm this, the CBE was plotted against separation on a log-log plot, as seen in figure 2.6. As expected, the plot tends to a line with slope $-3$, indicating inverse cubic decay. The aligned geometry converges to a line parallel to that of the anti-aligned geometry. The fact that their signs are opposite is not visible on the log-log plot. That the two very different curves converge to something so similar indicates the same effect is behind the long range behavior for both geometries, and the slope being $-3$ confirms that this effect is electrostatic.

It seems safe to conclude that the positive correlation binding energy in the stretched equilibrium and aligned geometries of the water dimer is because of a post HF correction to the electrostatic interactions in the system. The electrostatic correction can be more important than dispersion in the long range, and causes the CBE to have two properties very different from dispersion: being anti-binding in nature and having a long-range decay as the inverse cube of separation, rather than the inverse sixth power.

While we have illustrated the effect for the water dimer, it will be widespread because the tendency for the HF method to overestimate dipole moments is fairly general. For example, taking the dipole–dipole bound small intermolecular complexes from the A24 data set, as
Figure 2.5: Correlation binding energy of the water dimer in the stretched equilibrium geometry vs. difference in dipole interaction from HF to MP2. As the center of the charge distribution does not affect the dipole moment, the centers of the charge distributions are chosen to be 0.35 Å farther apart than the O-O separation.

Figure 2.6: Log-log plot (natural logarithm) of absolute value of CBE for water in the aligned and anti-aligned geometries.

summarized in table 2.2 below, we see that the CBE is uniformly negative at the equilibrium geometry and uniformly positive at a sufficiently stretched geometry. For four of the systems, this occurs by 3 Å, though for the ammonia dimer, it happens only at a larger separation. In contrast, for the methane dimer, an example nonpolar system, the CBE is $-4.231$ kJ/mol at equilibrium and remains negative at all separations, being $-0.09984$ kJ/mol at 3 Å beyond
Table 2.2: Correlation contributions to the intermolecular interaction energies of small complexes from the A24 database, evaluated at the equilibrium geometry and at a geometry where the monomers are translated apart by 3/7 Å. RIMP2 is used with the aug-cc-pVQZ basis set and the corresponding auxiliary basis, without counterpoise correction and with the frozen core approximation. Values in parentheses are evaluated via attenuated RIMP2 with the aug-cc-pVTZ basis set: RIMP2(terfc, aTZ), also with the frozen core approximation.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta E_{\text{corr}} (R_e)$ (kJ/mol)</th>
<th>$\Delta E_{\text{corr}} (R_e + 3\text{Å})$ (kJ/mol)</th>
<th>$\Delta E_{\text{corr}} (R_e + 7\text{Å})$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water-ammonia</td>
<td>-9.041</td>
<td>0.01982</td>
<td>0.02448</td>
</tr>
<tr>
<td></td>
<td>(-9.119)</td>
<td>(0.08533)</td>
<td>(0.02679)</td>
</tr>
<tr>
<td>HF dimer</td>
<td>-3.212</td>
<td>0.1153</td>
<td>0.02821</td>
</tr>
<tr>
<td></td>
<td>(-3.656)</td>
<td>(0.1377)</td>
<td>(0.3046)</td>
</tr>
<tr>
<td>HCN dimer</td>
<td>-4.106</td>
<td>0.3424</td>
<td>0.1275</td>
</tr>
<tr>
<td></td>
<td>(-4.136)</td>
<td>(0.3614)</td>
<td>(0.1241)</td>
</tr>
<tr>
<td>ammonia dimer</td>
<td>-7.240</td>
<td>-0.06488</td>
<td>0.00541</td>
</tr>
<tr>
<td></td>
<td>(-6.827)</td>
<td>(0.00855)</td>
<td>(0.00774)</td>
</tr>
<tr>
<td>formaldehyde dimer</td>
<td>-9.054</td>
<td>0.4988</td>
<td>0.1260</td>
</tr>
<tr>
<td></td>
<td>(-7.909)</td>
<td>(0.6469)</td>
<td>(0.1296)</td>
</tr>
</tbody>
</table>

The general result of this work is that intermolecular interactions at long range are often reduced, rather than increased, by the inclusion of electron correlation as a consequence of correcting the overly large permanent dipole moments of the Hartree–Fock model. As a result, the long-range distance dependence of the correlation contribution to the binding energy is often much stronger than the $R^{-6}$ of true dispersion interactions: it may go instead as the leading contribution of electrostatic moments that are not correctly described by the HF reference. Hence the long-range contribution of correlation to intermolecular interactions has a leading distance dependence of $R^{-3}$ in the water dimer, and it can go as slowly as $R^{-2}$ for the case of an ion–dipole complex such as $\text{Na}^+...\text{H}_2\text{O}$.

Attenuated MP2 methods[43, 44, 64, 65] have recently attracted attention because smooth removal of long-range correlation can cancel basis set superposition errors and erroneous $C_6$ values in stacking complexes, and yield much more accurate intermolecular interaction energies than conventional MP2 in the same basis set. Since the correlation potential is damped to zero at long range, it may be reasonable to assume that the leading correlation contribution to intermolecular interactions is lost upon attenuation. We demonstrate, perhaps surprisingly, that this is often not true. As shown in table 2.2, the MP2(terfc, aTZ) results do correctly recover the long-range interaction energy in many intermolecular complexes,
because that interaction is not dispersive. The correlation correction to an A–B intermolecular electrostatic interactions is retained in attenuated MP2 because it implicitly enters the short-range correlation energy expression through changes in the orbital eigenvalues of molecule A (and B) due to the long-range electrostatic perturbation of molecule B (and A). In turn this changes the monomer correlation energies, even if the explicit intermolecular correlation terms (dispersive in nature) are damped to zero.

A different approach is used in Hartree–Fock plus dispersion (HFD) methods\cite{66}, which have lately been the subject of renewed interest\cite{67, 68}. These methods add an $R^{-6}$ dispersion term to the HF intermolecular interaction and stand in contrast to attenuated MP2. Whereas attenuated MP2 includes only short range correlation, HFD attempts to account for only long range correlation. However, most HFD methods only modify HF by the addition of dispersion and HF electrostatics unmodified. Therefore, unlike attenuated MP2, they cannot correctly describe the long range behavior of dipole-bound systems. An exception is the HFDc method\cite{67} of Szalewicz et. al., which also computes on-molecule correlation, allowing it to describe the electrostatics correctly. A more typical recent HFD approach is described by Iwata, which accounts for dispersion by including only intermolecular correlation\cite{68}. He observed that polar systems were over-bound; the results presented here show that the explanation is the overestimation of HF dipole moments, with the error growing more pronounced in the long range. His HFD method does not include the post-HF electrostatic corrections discussed here.

The same considerations also have implications for energy decomposition analysis (EDA) methods that partition an intermolecular interaction into physically motivated components. For any post-HF EDA that includes correlation to be fully satisfactory, it should include terms correcting the permanent — as well as induced — electrostatics of the mean field HF reference. Failure to do so\cite{19, 47, 53} means ignoring an effect that can be more important than dispersion in the long range, and that becomes increasingly significant (though no longer dominant) in the short range. We are currently working on an EDA for MP2 that partitions the correlation energy into terms including corrections to the HF electrostatics and polarization and hope to present results soon.
Chapter 3

An EDA for MP2 based on ALMOs

3.1 Introduction

Intermolecular interactions control the properties and behaviors of a wide variety of systems. Intuitively, the forces between molecules can be divided into several different categories, such as the London dispersion force, induced dipole forces, permanent dipole forces, and covalent-type interactions, each with their own characteristic strengths, properties, and decay rates. The standard supermolecule approach gives accurate binding energies, but combines all different intermolecular interactions into a single number. Energy decomposition analysis (EDA) methods exist to divide the total binding energy into its physically meaningful components. The earliest popular EDA is that of Kitaura and Morokuma for Hartree-Fock (HF).[19] It has components for electrostatic interaction, exchange, polarization, and charge transfer and is computed by zeroing corresponding blocks of the Fock matrix for each of these components. However, the intermediate wave functions for KMEDA are not antisymmetric, leading to explosions in certain terms when the basis is large.[69, 70] There are successful cousins of the KMEDA which have been developed for applications to density functional theory (DFT) calculations.[71–73]

There have been other variational approaches for both HF and DFT that address this issue. One has been the natural energy decomposition analysis,[20] which uses natural bond orbitals[21] to construct intermediate wave functions that obey the Pauli principle. Others include the related reduced variational space self-consistent field (RVS SCF)[46] and restricted constrained space orbital variations (CSOV)[45] methods. These methods compute the polarization due to each molecule by freezing its occupied orbitals and allowing the other molecules’ orbitals to relax in their field. This means that neither of these methods has a self consistent polarization energy, but rather treat it as the sum of separate calculations. The polarization energy was first separated in the block-localized wave function (BLW) EDA.[50, 51] The BLW-EDA imposes locality constraints on intermediate wave functions and solves the resulting non-orthogonal problem with the self consistent field for molecular interactions (SCF-MI) method.[74–77] A more recent approach, which this paper builds on, has been
the absolutely localized molecular orbital (ALMO) based method.\cite{26, 27} With ALMOs, the system is divided into fragments, usually representing molecules, and each atomic orbital basis function is assigned to the fragment that its atom belongs to. When the SCF procedure is performed, each molecular orbital is also assigned to a fragment and a constraint is imposed that allows a molecular orbital to be formed only out of basis functions that belong to its fragment. This forms an ALMO basis where each molecular orbital can be associated with a single fragment. The ALMO-EDA uses the same separation of frozen orbital and polarization energies as the BIW-EDA to divide either a DFT or HF energy into frozen electrostatics, polarization, and charge transfer. All basis set superposition error is contained in the charge transfer term, which can be well approximated by perturbation theory, allowing the approximation of a binding energy in less time than a standard SCF calculation, as well as separation of forward and back donation.

A parallel development has been symmetry-adapted perturbation theory,\cite{22} which avoids the supermolecule approach and instead treats intermolecular interactions as perturbations to the noninteracting system. SAPT is based on London’s use of perturbation theory,\cite{78} but constrains the expansion to have the correct exchange symmetry, addressing the major defects with the earlier theory. Interaction energy in SAPT is divided into four components, termed electrostatic, induction, dispersion, and exchange. The electrostatic and exchange terms are first order, with exchange being symmetry adapted and electrostatic not. Dispersion and induction are second order in the perturbation expansion and each has both an adapted and non-adapted piece. SAPT has been among the most widely used EDA methods, particularly with the development of efficient SAPT-DFT variants.\cite{79, 80} However, the perturbation approach can fail for strongly interacting systems. Furthermore, as SAPT eschews the supermolecule approach, the decompositions that it produces are not compatible with the most accurate available binding energies computed by post-HF correlation methods. This problem can become especially apparent in systems containing anions, which are well-described by MP2 and modern DFT functionals, but for which SAPT produces particularly poor results.\cite{81}

Ab initio wave function correlation methods are widely used for intermolecular interactions. These correct HF by treating electron correlation. While HF provides a reasonable first approximation to the Pauli repulsions, electrostatics, and induced polarizations, correlation methods can correct this approximation, as well as introduce phenomena not captured by HF, such as dispersion. Practical methods range from second-order Møller–Plesset perturbation theory (MP2)\cite{32} for large systems to coupled cluster with singles, doubles, and perturbative triples (CCSD(T))\cite{31} when highest accuracy is needed. These methods, especially CCSD(T),\cite{33–35} are generally more accurate for intermolecular interactions than most commonly used density functionals.\cite{38, 39} While MP2 is not as accurate as CCSD(T), it is widely used because of its much smaller computational cost, and has its own notable strengths, such as hydrogen bonding,\cite{36, 37} and weaknesses, such as stacking interactions.\cite{12–14} Weaknesses of MP2 for dispersion-dominated interactions can be understood\cite{82}, and even corrected.\cite{83, 84}

Despite the accuracy of correlation methods, there has been limited development in
variational EDAs for them. (MP2 is not usually thought of as a variational method, but the Hylleraas formalism\[85\], commonly used for MP2 analytical derivative theory\[86\] allows the MP2 excitation amplitudes to be thought of as parameters minimizing a Lagrangian function equivalent to the correlation energy.) The simplest such method declares the whole correlation binding energy to be dispersion\[47\]. As it is clear that correlation is not entirely dispersion, there have since been others that treat charge transfer separately\[52, 53\]. However, as we showed in a previous paper, the correlation energy includes other effects than these, such as corrections to electrostatics\[28\]. It, in fact, includes the whole range of intermolecular forces, any of which may be more important than dispersion. Therefore, it is vital for any correlation EDA to describe all these forces. In this paper, we will present such an EDA for MP2.

### 3.2 Theory

Presented here is an MP2 extension to the absolutely localized molecular orbital (ALMO) based SCF EDA\[26\], or its variations. The SCF EDA decomposes the interaction energy into a frozen interaction term, a polarization term, and a charge transfer term. The MP2 EDA includes a correction to each of the SCF terms, and introduces dispersion, which is inherently a phenomenon of correlation and cannot be described by mean field theories. For the MP2 corrections, intermediate energies are evaluated variationally as optimized MP2 energies subject to locality constraints using intermediate orbitals produced by the HF EDA. This allows the terms other than dispersion to be simply added as corrections to their HF counterparts.

MP2 is a perturbation theory that corrects the Hartree–Fock reference by mixing it with excited Slater determinants. Single excitations do not mix with the HF solution by Brillouin’s Theorem, and triple and higher excitation do not do so because of the Slater–Condon rules\[4\]. Therefore, the MP2 correction to HF is a linear combination of of doubly-excited Slater determinants, and the MP2 correlation energy is the sum of negative-definite energies associated with each double excitation.

In decomposing interactions between molecules, then, we can define three types of double excitations, as shown in figure 3.1. One is where all orbitals are on one molecule; another is where one occupied and virtual orbital each are on two different molecules, such that the excitation preserves the number of electrons associated with each molecule; and a third transfers charge between two or more molecules, potentially involving three or four different molecules. However, it is impossible to draw this distinction with the canonical orbitals that are the result of the standard HF procedure, as these orbitals are not localized to any particular molecule. It does become possible when localized orbitals are used\[87\] and the ALMOs are a natural choice for an EDA. Accordingly, they are also used by the SCF EDA to compute the polarized energy.
3.2.1 Strong orthogonality

For MP2 to be well-defined, the virtual space must be orthogonal to the occupied space over the entire system. However, simply taking the union of the ALMOs of the different fragments results in occupied and virtual orbitals that are only orthogonal within a fragment. To meet this condition, the virtual orbitals are projected into the orthogonal complement of the occupied space.[87] The resulting virtual orbitals are not quite absolutely localized, nor do they lie entirely within the original virtual space, but these are necessary compromises. As a last step, the occupied orbitals are symmetrically orthogonalized between fragments. Occupied orbitals are compact with relatively small overlap between separate molecular fragments, so this can be achieved with minimal loss of locality and significant gains in computational simplicity. These localized orbitals allow the double excitations to be divided as above.

3.2.2 Non-orthogonal MP2

For simplicity we shall treat the spin-restricted case, using indexes \( i, j, \ldots \) to refer to doubly occupied levels, and \( a, b, \ldots \) to refer to virtual levels. For MP2 performed in the ALMO basis, orbitals on different fragments are not orthogonal and the Fock matrix is not diagonal. Therefore, the standard MP2 energy expression

\[
E = -\frac{1}{4} \sum_{ijab} \frac{(ia|jb)(2(ia|jb) - (ib|ja))}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}
\]  

(3.1)
is not valid. The generalized form of the MP2 energy is

\[ E = -\frac{1}{4} \sum_{ijab} t_{ij}^a (ia|jb) \]  

(3.2)

where \( t \) is the solution to the following linear equation, which is derived from the previous expression by basis transformation and is subject only to the requirement that the occupied and virtual spaces be orthogonal.[88]

\[ \sum_{ijab} \Delta_{ijij'}^a b' \cdot t_{ij}^a = (2 (i'a'|j'b') - (i'b'|j'a')) \]  

(3.3)

Here, \( \Delta \) is an eighth-rank tensor defined as

\[ \Delta_{ijij'}^a b' = F_{ii'}^{aa'} C_{jj'}^{bb'} - C_{ii'}^{aa'} F_{jj'}^{bb'} \]  

(3.4)

where

\[ F_{ii'}^{aa'} = f_{aa'} g_{ii'} - f_{ii'} g_{aa'} \]  

(3.5)

and

\[ C_{ii'}^{aa'} = g_{ii'} g_{aa'} \]  

(3.6)

where \( f \) and \( g \) are the Fock and overlap matrices respectively. When \( f \) is diagonal and \( g \) the identity matrix (the canonical orbitals), this formulation is equivalent to the standard MP2 expression.

### 3.2.3 Charge conserving correlations

MP2 allowing only charge conserving correlations (CCC), or CCCMP2, is a variant of MP2 defined here to allow the separation of the correlation energy into excitations that are charge transfer-like and those that are not. This additional constraint on MP2 only permits double excitations that do not change the total number of electrons associated with each fragment. In other words, it excludes the third type of excitation described above. To help impose this constraint, an excitation basis is defined where indices are over occupied-virtual pairs. The tensors \( \Delta, F, \) and \( G \) are naturally expressed in this basis, as their indices are in occupied-virtual pairs. \( \Delta_{ijij'}^{a b'} \) becomes \( \Delta_{KK'LL'} \) where \( K = \{i, a\} \) and so on. It is straightforward to impose the CCC constraint in this basis by only including the indices \( K \) where \( i \) and \( a \) are on the same fragment. Solving the \( t \) equation subject to this constraint produces an energy associated with electron correlation effects that do not yield net charge transfer between fragments. Properties of these tensors have previously been exploited in defining fully non-orthogonal local MP2 methods.[89, 90]
3.2.4 Notation

The main type of energy discussed here will be the MP2 correlation energy. Therefore, \( E \) refers to MP2 correlation energy and \( \Delta E \) a binding energy. Subscripts on \( \Delta E \) indicate components of the EDA. Parenthesis after \( E \) indicate details of the calculation. The first value in the parentheses will be either “sys” or “frag”, indicating whether the system as a whole is being considered or just a single fragment. Fragment energies will usually be summed over all fragments. There may also be a slash followed by another word in the parenthesis, indicating the molecular orbital basis and Fock matrix used. When omitted, in the case of a sys energy, it means the correlation energy for the whole system with canonical orbitals, and in the case of a frag energy, it means the correlation energy of the fragment as an isolated system, without any influence from the other fragments. The two variants will be discussed as they are used.

In this notation, the correlation binding energy, which is the quantity that the EDA describes by decomposition, is expressed as

\[
\Delta E = E_{\text{sys}} - \sum_{\text{frag}} E_{\text{frag}}
\]  

which by construction is equal to the sum of the four components of the EDA

\[
\Delta E = \Delta E_{\text{CT}} + \Delta E_{\text{disp}} + \Delta E_{\text{pol}} + \Delta E_{\text{frz}}
\]  

3.2.5 Charge transfer

Charge transfer, or \( \Delta E_{\text{CT}} \), is the energy change associated with the transfer of electron density from one fragment to another, such as in a dative interaction. Charge transfer exists at the HF level, but as MP2 alters the HF orbital occupations and electron density, there is a correction to the charge transfer energy associated with MP2. Charge transfer should be negative as should the MP2 correction to it. It straightforward to define \( \Delta E_{\text{CT}} \) with the formalism already developed. The CCC energy excludes charge transferring excitations, so \( \Delta E_{\text{CT}} \) can be defined as

\[
\Delta E_{\text{CT}} = E_{\text{sys}} - E_{\text{ccc}}(\text{sys}/\text{ALMO})
\]  

\( E_{\text{ccc}} \) denotes the imposition of the CCC constraint, and \( /\text{ALMO} \) indicates that the calculation is done in the ALMO basis with fragments being influenced by all other fragments through the Fock matrix.

As in the SCF EDA, MP2 charge transfer may be further decomposed into forward and back donation between pairs of fragments and system-wide non-additive piece. However, a procedure to do so is beyond the scope of this paper.

3.2.6 Dispersion

Dispersion, or \( \Delta E_{\text{disp}} \) is the intermolecular force associated with the favoring of correlation of aligned polarizations of electron densities on different fragments in the probability
CHAPTER 3. AN EDA FOR MP2 BASED ON ALMOS

distribution of the system’s wave function over unaligned or anti-aligned polarizations.[91]
As it is a purely correlation effect, it cannot be described by HF, and no term for it appears
in the SCF EDA. Dispersion is a purely attractive force, and its decay as a function of intermolecular separation limits to $R^{-6}$ in the long range, which MP2 recovers qualitatively correctly.[82] For non-polar systems, dispersion is usually the most important intermolecular force at long range. $\Delta E_{\text{disp}}$ can also be defined simply in terms of what has already been discussed. The CCC energy includes dispersion-like correlation, as well as correlation confined to a single fragment. $\Delta E_{\text{disp}}$ can be defined as their difference, or

$$\Delta E_{\text{disp}} = E_{\text{ccc}}(\text{sys}/\text{ALMO}) - \sum_{\text{frag}} E(\text{frag}/\text{ALMO})$$  \hspace{1cm} (3.10)

The subtrahend on the right side of the above equation is expressed as the sum of the individual fragment’s ALMO energies. However, due to the orthogonality of the occupied orbitals between fragments, this is equal to the optimized MP2 energy for the entire system with the constraint that each double excitation be entirely constrained to a single fragment. With this substitution the equation becomes the difference of two equally optimal MP2 energies with differing levels of constraint.

Dispersion can be further decomposed in n-body terms. The dispersion between two fragments can be defined as

$$\Delta E_{\text{disp}}(1, 2) = E_{\text{ccc}}(\text{frag}_1 \cup \text{frag}_2)/\text{ALMO}) - \sum_{n=1,2} E(\text{frag}_n)/\text{ALMO})$$  \hspace{1cm} (3.11)

where $\text{frag}_1 \cup \text{frag}_2$ means that only charge conserving excitations only involving fragments 1 and 2 are allowed. Though dispersion is nearly pairwise additive, the sum of all the two-body dispersion energies will not be exactly equal to the total energy. Though these corrections will be small, it is possible to define the n-body dispersion energy recursively as

$$\Delta E_{\text{disp}}(S) = E_{\text{ccc}} \left( \bigcup_{n \in S} \text{frag}_n/\text{ALMO} \right) - \sum_{n \in S} E(\text{frag}_n)/\text{ALMO}) - \sum_{T \subset S} \Delta E_{\text{disp}}(T)$$  \hspace{1cm} (3.12)

where $S$ is some subset of the fragments of the system, $T$ sums over every non-empty strict subset of $S$, and the one-body dispersion is defined to be zero. The sum of every n-body dispersion energy will equal the total dispersion energy.

Let us offer a final clarification about our definition of the dispersion energy. As already discussed, our $\Delta E_{\text{disp}}$ will in general correctly recover the long-range $R^{-6}$ behavior of the dispersion energy of non-overlapping molecules, in contrast to the full correlation binding energy itself.[28] In the long-range regime, $\Delta E_{\text{disp}}$ should agree qualitatively with the magnitude of dispersion evaluated by corrections to DFT, based either on damped intermolecular potentials[92, 93], or Van der Waals density functionals[94, 95], or SAPT-type methods[22]. By contrast, the dispersion energy is not uniquely defined in the overlapping regime, and therefore different definitions will lead to different results. The dispersion corrections to DFT
usually damp to zero at short interatomic distances, to avoid double-counting problems with the semi-local treatment of electron correlation in the XC functional. Our $\Delta E_{\text{disp}}$, by contrast, does not damp to zero as two molecules approach each other, but instead captures that part of correlation which is “dispersive” in character, based on figure 3.1.

### 3.2.7 Frozen and polarization interaction

The remaining correlation binding energy consists of double excitations localized to one fragment. Other fragments can only influence these excitations through the Fock matrix. Therefore, this correlation is electrostatic in nature. Following the SCF EDA, this electrostatic correlation should be split into $\Delta E_{\text{pol}} + \Delta E_{\text{frz}}$.

As in the SCF EDA, frozen interaction refers to the energy difference of the interacting fragments when their wave functions are not allowed to change — a combination of classical electrostatics of the charge distributions and of quantum effects associated with the Pauli principle. Polarization is energy change associated with the polarization of the two systems in reaction to each other. It includes the unfavorable energy of the systems polarizing as well as the favorable interaction of the polarized systems.

The frozen interaction as a whole (HF + correlation) can be either attractive or repulsive, and its long range behavior can range from $R^{-1}$ for ion-ion systems to $R^{-5}$ quadrupole-quadrupole interactions in nonpolar systems to exponential decay in noble gas-noble gas interactions. For most systems, the MP2 frozen component will have the same long range behavior but opposite sign of its HF counterpart. This is because HF tends to overestimate multipole moments[60–63] — a tendency that is corrected by MP2. Polarization, on the other hand, is strictly attractive. However, the MP2 polarization can have either sign. HF tends to underestimate the polarizability of molecules relative to MP2, which pushes towards a negative MP2 polarization energy. On the other hand, the multipoles inducing these polarizations will be weaker, so the overall sign depends on which of these is stronger. The long range behavior will again depend on the specifics of the system.

However, the frozen/polarized distinction is not particularly natural in MP2, which does not satisfy the Hellman–Feynman theorem. It will be accomplished by creating a new term and defining

$$\Delta E_{\text{pol}} = \sum_{\text{frag}} E(\text{frag}/\text{ALMO}) - E(\text{frag}/\text{frz}) \quad (3.13)$$

and

$$\Delta E_{\text{frz}} = \sum_{\text{frag}} E(\text{frag}/\text{frz}) - E(\text{frag}) \quad (3.14)$$

**Definition of $E(\text{frag}/\text{frz})$**

Defining $E(\text{frag}/\text{frz})$ to separate the frozen and polarization interaction is complicated. At the HF level, it is possible to freeze the orbitals and calculate the energy in the presence of the other fragments. However, the same procedure does not work for MP2. If only the
orbitals were frozen, the wave function would still polarize when modified to first order. Therefore, it is necessary to freeze the entire wave function. The standard expression for the second order perturbation theory energy is

$$\langle \Psi^{(1)} | V | \Psi^{(0)} \rangle = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \langle \Phi_{ij}^{ab} | V | \Phi \rangle$$

(3.15)

When the perturbation is electron correlation, this is equal to the standard MP2 energy expression from above. However, this expression will not work for the frozen energy as it assumes the energy is being evaluated in the same potential that the \( t \) amplitudes form the MP2 solution to, but we are also including the potential due to the other fragments. In fact, since the effect of the other fragments (\( X \)) is a one-electron operator, \( \langle \Phi_{ij}^{ab} | X | \Phi \rangle = 0 \) by the Slater–Condon rules and this expression would lead to a frozen energy equal to the isolated fragment energy.

Energy with an external potential  
It is then necessary to use the Hylleraas expression\[85\] for the MP2 energy, which is valid for \( t \) amplitudes other than the MP2 solution. It takes the form

$$\mathcal{L} = 2 \langle \Psi^{(1)} | \hat{H} - E_0 | \Psi^{(0)} \rangle - \langle \Psi^{(1)} | \hat{H}_0 - E_0 | \Psi^{(1)} \rangle$$

(3.16)

which in the language of \( t \) amplitudes becomes

$$\mathcal{L} = 2 \left( -\frac{1}{4} \sum_{ijab} t_{ij}^{ab} (ia|jb) \right) - \left( \sum_{pq} P_{pq} F_{pq} \right)$$

(3.17)

The left term is the normal expression for the isolated fragment energy, and unaffected by the presence of the other fragments. The right term is the contraction of the MP2 response density matrix\[96\] with the Fock matrix that contains the influence of the other fragments. For the MP2 solution, the two terms are equal and this is equal to the standard expression. In this case, however, it allows the calculation of the energy associated with the isolated wave function in the presence of the other fragments.

The MP2 response density matrix is defined according to its occupied-occupied and virtual-virtual blocks

$$P_{ij} = -\frac{1}{2} \sum_{kab} t_{ij}^{ab} t_{jk}^{ab}$$

(3.18a)

$$P_{ab} = \frac{1}{2} \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc}$$

(3.18b)

This form follows from the right term in the Hylleraas expression. Note that from a perturbation theory perspective, the only perturbation is still electron correlation, as in ordinary MP2 theory. The frozen wave function is evaluated in presence of the external field due to the other fragments. Though this is similar to first order perturbation theory, we are not attempting to approximate the solution to the Hamiltonian in the presence of the field as SAPT and related methods do.
Relaxed density matrix  This expression will still not lead to the correct frozen energy because MP2 does not obey the Hellmann–Feynman theorem, which states that

$$\frac{dE}{d\lambda} = \left\langle \Psi(\lambda) \left| \frac{d\hat{H}}{d\lambda} \right| \Psi(\lambda) \right\rangle$$  \hspace{1cm} (3.19)$$

for some external parameter $\lambda$ for wave functions that are variationally optimized for all relevant parameters.\[97\] MP2 is not optimized in terms of orbital rotations, so this theorem will not hold. This is relevant as many electrostatic values are actually derivatives, such as the electric dipole

$$\frac{dE}{dE} \neq \left\langle \Psi(E) | \hat{\mu} | \Psi(E) \right\rangle$$  \hspace{1cm} (3.20)$$

If the expression from the previous section were used, the frozen energy would only account for dipole moments calculated by $\left\langle \Psi(E) | \hat{\mu} | \Psi(E) \right\rangle$, or equivalently, $P(E)_{pq}\mu_{pq}$, rather than the true MP2 dipole moment. To solve this issue, the same method that is used to calculate the dipole moment and other properties for MP2\[98\] can be applied here. This method produces an occupied-virtual matrix that is contracted with the occupied-virtual block of the property’s matrix. Because it is applied the same way as the missing block of the response density matrix would be, they are added together. The result is called the relaxed density matrix.\[96\]

As the breaking of the Hellman–Feynman theorem comes from the fact that MP2 is not optimized in terms of the orbitals, the correction is related to the derivative of the MP2 energy with respect to orbital rotations. Orbital rotations are defined relative to the HF orbitals. There is one rotation angle $\theta_{ia}$ for each occupied virtual pair, such that

$$\begin{bmatrix} i' \\ a' \end{bmatrix} = \begin{bmatrix} \cos \theta_{ia} & -\sin \theta_{ia} \\ \sin \theta_{ia} & \cos \theta_{ia} \end{bmatrix} \begin{bmatrix} i \\ a \end{bmatrix}$$  \hspace{1cm} (3.21)$$

Extending this to an occupied×virtual $\theta$ matrix, we can define

$$C(\theta) = C_0 e^{-\theta^i 0}$$  \hspace{1cm} (3.22)$$

where $C_0$ is the HF MO coefficient matrix that will give the same result as the previous formula for any given occupied-virtual pair. Occupied-occupied and virtual-virtual mixings do not affect energy, so there is no need to define rotations for them. Thus, for each possible partitioning of the occupied and virtual subspaces, there is some set of orbital rotations that define it while keeping the orbitals orthonormal. HF is variationally optimized with regard to these parameters (they are defined so that the minimum is achieved when $\theta = 0$), but MP2 is not.

The expression $P_{uv}\mu_{uv}$ takes the form of an energy derivative with respect to some parameter affected by some perturbation contracted with that perturbation. The response density matrix is the derivative of the MP2 energy with respect to one electron integrals
and the part of the Fock matrix affected by the external perturbation is the one electron integrals. A similar expression for orbital rotations will correct the values calculated by the energy expression. The other parameters for MP2 are either variationally optimized \((t)\) or are not affected by this perturbation (the overlap matrix and the two electron integrals). Therefore, the additional correction to the energy will take the form

\[
\sum_{ia} L_{ia} \Theta_{ia} \tag{3.23}
\]

where

\[
L_{ia} = \frac{\partial E}{\partial \theta_{ia}} \tag{3.24}
\]

and \(\Theta\) is the orbital response. Rather than calculate the orbital response directly, we can apply the coupled perturbed Hartree–Fock (CPHF) equation\[99\], which comes from the fact that the derivative of the HF energy is zero. In this case, where the perturbation does not affect the overlap matrix or the two electron integrals, it takes the form

\[
\mathcal{E}^{\theta\theta} \Theta = -\frac{\partial^2 \mathcal{E}}{\partial \theta \partial F} F \tag{3.25}
\]

where \(\mathcal{E}\) is the HF energy and \(\mathcal{E}^{\theta\theta}\) is its second derivative with respect to orbital rotations. \(-\frac{\partial \mathcal{E}}{\partial \theta}\) is merely the off-diagonal block of the Fock matrix, so \(\frac{\partial^2 \mathcal{E}}{\partial \theta \partial F}\) becomes a delta function. We can take our contraction over \(L\Theta\) and insert \(\mathcal{E}^{\theta\theta}\) and its inverse to get \(L(\mathcal{E}^{\theta\theta})^{-1} \mathcal{E}^{\theta\theta} \Theta\). Defining \(z^T = L(\mathcal{E}^{\theta\theta})^{-1}\) and making the CPHF substitution yields

\[
-2 \sum_{ia} z_{ia} F_{ia} \tag{3.26}
\]

which is the orbital correction to the MP2 response. The factor of two arises because the contraction is over both occupied-virtual blocks of the Fock matrix.

This \(z\) vector can be subtracted from both (previously zero) occupied-virtual blocks of the density matrix to yield the so-called relaxed density matrix \(P'\). Contracting with \(P'\) includes the \(z\) vector correction and yields the true MP2 response to the presence of the other fragments.

Now, expressions for \(L\) and \(\mathcal{E}^{\theta\theta}\) are needed. For \(\mathcal{E}^{\theta\theta}\), the expression for restricted HF is not too complicated assuming orthonormal, but not necessarily canonical, orbitals

\[
\mathcal{E}^{\theta\theta}_{iajb} = \frac{\partial^2 E}{\partial \theta_{ia} \partial \theta_{jb}} = \delta_{ij} F_{ab} - \delta_{ab} F_{ij} + 4(ia|jb) - (ib|ja) - (ij|ab) \tag{3.27}
\]
The expression for $L$ is more complicated

$$L_{ia} = -\sum_{jk} t_{jk}^{ab}(jb|ik) + \sum_{jbc} t_{ij}^{bc}(jb|ac) + \sum_{bc} P_{bc}^{2} (\delta_{ab} F_{ic} + \delta_{ac} F_{bi} - (4(bc|ia) - (ib|ca) - (ba|ic)))$$

$$-\sum_{jk} P_{jk}^{2} (\delta_{ij} F_{ck} + \delta_{ik} F_{jc} + (4(jk|ia) - (ij|ka) - (ja|ik)))$$

(3.28)

These two expressions allow the calculations of the $z$ vector which will allow $E(\text{frag}/\text{frz})$ to correctly capture frozen-level effects.

This all provides a method for separating frozen and polarization interactions in the non-overlapping regime, but does not extend obviously to when the fragments overlap and the virtual space of one fragment is not orthogonal to the occupied spaces of the others. For excitations to be well-defined, it seems that the virtual orbitals should be projected into the orthogonal complement of the total occupied space. However, to keep the wave function the same as in the isolated fragments, it is necessary to use the unprojected orbitals. The solution is to do both. The $t$ amplitudes are calculated with unprojected orbitals, as required, but are interpreted as excitations in the projected basis. That is, the relaxed density matrix is computed exactly as normal for an isolated fragment, but multiplied with a Fock matrix including the effects of the other fragments and in a projected basis. This compromise lets $E(\text{frag}/\text{frz})$ function in the overlapping regime.

### 3.2.8 Counterpoise correction

Like most calculations with finite basis sets, this EDA is subject to basis set superposition error (BSSE), as it decomposes supermolecule binding energies that are themselves subject to BSSE. The most common countermeasure is counterpoise correction,[100] which introduces ghost atoms with associated basis functions to the calculation of the monomer single point energies. When decomposing a counterpoise corrected binding energy, the BSSE should be subtracted from $\Delta E_{CT}$. That is to say, counterpoise correction should be thought of as modifying the energy of the whole system rather than the energy of the fragments. BSSE takes the form of erroneous transfer of electron density from one fragment’s orbitals to another, so conceptually it should be described as charge transfer by any EDA. This is the same procedure used by the SCF EDA, and it applies here for the same reason. When counterpoise corrected, $\Delta E_{CT}$ can be positive. This is a result of counterpoise corrected binding energies being too weak in finite basis sets,[101] and can usually be avoided by performing half counterpoise correction,[102] virtual counterpoise correction,[103] or some other less zealous procedure to combat BSSE. One important exception to the identification of BSSE as charge transfer is discussed next.
3.2.9 Auxiliary basis set superposition error

This EDA is primarily intended to be used with resolution of the identity MP2 (RIMP2),\cite{[16]} which is a fairly transparent approximation whose use does not usually require any special considerations. However, there is one such case that is relevant here. Standard RI fitting methods can have fit coefficients that decay slowly as a function of the distance between the orbitals and the auxiliary basis function.\cite{[104]} This leads to cases where auxiliary functions on one fragment can have significant effects on approximate integrals entirely on another fragment. This type of basis set superposition error is different from the standard kind and cannot be considered a type of erroneous charge transfer, and therefore must be treated differently by the EDA. Standard counterpoise correction solves this issue for normal binding energy calculations, however this option is not available here, as cross-fragment integrals are necessary for $E_{ccc}$ which is not susceptible to regular BSSE. Unless special care is taken, auxiliary basis set superposition error (ABSSE) will contaminate one of the terms of the EDA, depending on when the auxiliary functions of the whole system are introduced. Charge transfer will be contaminated an equal and opposite amount as ABSSE is subtracted from it along with BSSE.

There are two main ways to solve this problem. One is to ensure that fit coefficients decay quickly enough to prevent ABSSE from becoming an issue. The other is to explicitly correct for ABSSE in a scheme similar to counterpoise correction.

For simplicity, the EDA currently uses the latter. $\Delta E_{frz}$ is calculated as the difference between $E(frag/frz)$ and $E(frag)$, where $E(frag)$ is calculated with the auxiliary functions of the whole system. The difference between the energies with and without the fragments’ functions is the ABSSE. To ensure that all components of the EDA sum to the total binding energy, this same ABSSE is added to $\Delta E_{CT}$, where it cancels the ABSSE present in the total BSSE that was already subtracted from $\Delta E_{CT}$.

3.2.10 Final form of the EDA

In addition to the normal calculations for a counterpoise corrected binding energy ($E(sys)$ and $E(frag)$ for each fragment as well as its equivalent with ghost atoms), the pieces needed for the EDA are $E_{ccc}(sys/ALMO)$ for the system and $E(frag/ALMO)$, $E(frag/frz)$, and the full system auxiliary function version of $E(frag)$ for each fragment.

Putting this all together, we get

\[
\begin{align*}
\Delta E_{CT} &= E(sys) - E_{ccc}(sys/ALMO) - (BSSE - ABSSE) \\
\Delta E_{disp} &= E_{ccc}(sys/ALMO) - \sum_{\text{frag}} E(frag/ALMO) \\
\Delta E_{pol} &= \sum_{\text{frag}} E(frag/ALMO) - E(frag/frz) \\
\Delta E_{frz} &= \sum_{\text{frag}} E(frag/frz) - E(frag) - ABSSE
\end{align*}
\]
where BSSE is the difference between the energies of the fragments with and without ghost atoms and ABSSE is the difference with and without only the auxiliary functions of those ghost atoms.

\[ \Delta E_{CT}, \Delta E_{pol}, \text{and} \Delta E_{frz} \]
can then be added to their SCF ALMO-EDA equivalents and, along with \( \Delta E_{disp} \), this forms the MP2 ALMO-EDA.

### 3.2.11 Implementation

A pilot implementation of the MP2 ALMO-EDA has been completed within a development version of the Q-Chem electronic structure program.[59, 105] This version is closed shell only, and is not by any means fully optimized. Such a task awaits successful testing of the theory, which will be the topic of the remainder of this report. Exact 4-center 2-electron integrals are used for the HF energy evaluation, and auxiliary basis sets are used to expand the two-electron integrals needed for the MP2 correlation energy (i.e. RI-MP2).

### 3.3 Results

#### 3.3.1 Single fragment cases

As the most complicated definitions of the EDA relate to the separation of \( \Delta E_{pol} \) and \( \Delta E_{frz} \), it is illustrative to begin with examples with only a single fragment in the presence of some external electrostatic perturbation. With only a single fragment, \( \Delta E_{CT} \) and \( \Delta E_{disp} \) are both zero by definition as the ALMOs are equivalent to the ordinary MOs and the ccc and fragment constraints do nothing. Additionally, issues of basis orthogonality between fragments do not complicate things. This leaves only three calculations to do: the energy of system in the absence of the perturbation, the energy of system in the presence of the perturbation, and the frozen energy, where the Fock matrix includes the perturbation, but the wave function is frozen as it was without it. There are two interesting single fragment cases: a dipole in an electric field to demonstrate that \( \Delta E_{frz} \) is correct, and a noble gas with an external point charge to demonstrate that \( \Delta E_{pol} \) is correct.

**Hydrogen chloride in a external field**

The first example is a hydrogen chloride molecule in a uniform electric field along the axis of the molecule. If correct, the frozen energy will be equal to the dipole moment of the molecule multiplied by the strength of the field. The MP2 frozen energy should be equal to the field strength times the difference in dipole moments. The graph of the two EDA components vs field strength is below in figure 3.2a. The calculations were performed in the aug-cc-pVQZ basis using the rimp2-aug-cc-pVQZ auxiliary basis.

As can be seen in figure 3.2a, \( \Delta E_{frz} \) forms a straight line with slope of 0.0292 atomic units of dipole moment. This matches the difference between the Hartree-Fock dipole moment of 0.4674 au and the MP2 dipole moment of 0.4382 au. \( \Delta E_{pol} \) is quadratic and negative as
expected, as HF underestimates polarizabilities. The leading coefficient of the best fit for $\Delta E_{\text{pol}}$ cannot be directly matched to the difference in polarizability between the two methods as it includes the energy penalty for changing the wave function as well as energy benefit from the polarized system interacting with the field.

This case confirms the necessity of using the relaxed density matrix. The equivalent calculation without the correction is displayed in figure 3.2b. Without the correction, the slope for the $\Delta E_{\text{frz}}$ fit is only 0.00692 au, which corresponds to a dipole moment of 0.4605 au calculated by using the unrelaxed MP2 density matrix. This error gives $\Delta E_{\text{pol}}$ a large linear component as the EDA has nowhere else to put this missed frozen interaction. Therefore, the EDA can correctly describe electrostatic interactions, but only as a direct result of using the relaxed density matrix.

**Helium atom with an external point charge**

Another useful test case is a spherically symmetric atom interacting with a point charge of -1 elementary charge. The only interaction at long range should be from the polarization of the atom, so $\Delta E_{\text{frz}}$ should quickly go to zero as the point charge is moved further away. This
will verify that the EDA does not misclassify any polarization as frozen interaction. The graph is shown in figure 3.3. The calculations were performed in the aug-cc-pVQZ basis using the rimp2-aug-cc-pVQZ auxiliary basis. As can be seen, \( \Delta E_{\text{pol}} \) has long range decay as \( R^{-4} \).

Figure 3.3: log-log plot of the MP2 part (i.e. the correlation contribution) of the EDA for He interacting with a point charge at varying distances

This is characteristic of charge-induced dipole interactions. It is negative (which cannot be seen on the graph), meaning MP2 revised the HF polarizability upwards as is typical. The polarizability calculated with MP2 (by finite differences) is 1.36 au, while the HF value is 1.32 au. Exponential decay of \( \Delta E_{\text{frz}} \) with distance is consistent with expectations. Its lack of slower decaying behavior indicates that the EDA did not misidentify any polarization as frozen interaction, as would be the case if only the orbitals were frozen and not the wave function. However, \( \Delta E_{\text{frz}} \) is significant in the close range and it is less obvious how the frozen interaction of a point charge and an atom should behave.

The effect of the point charge at \( r_c \) on a frozen wave function is to add a \( \frac{1}{|r-r_c|} \) term to the Hamiltonian. The energy change due to this is

\[
\int \frac{\Psi^*(r)\Psi(r)}{|r-r_c|} \, dr = \int \frac{p(r)}{|r-r_c|} \, dr \tag{3.30}
\]

meaning it is simply a classical electrostatic interaction with the charge distribution corresponding to the wave function. The helium atom is spherically symmetric. Gauss’s law allows easy calculation of the electric field due to a spherically symmetric charge distribution — charge closer to the center of the distribution than the test charge acts as a point charge at the center, and charge farther from the center has no effect. The field is then

\[
E(r_c) = \frac{Z - \int_0^{r_c} 4\pi p(r)r^2 \, dr}{r_c^2} \tag{3.31}
\]

towards the nucleus, where \( Z \) is the nuclear charge. The electric potential is

\[
\phi(r_c) = \int_{\infty}^{r_c} -E(r) \, dr = \int_{\infty}^{r_c} \frac{Z + \int_0^r 4\pi p(r')r'^2 \, dr'}{r^2} \, dr \tag{3.32}
\]
and the energy is the potential times the magnitude of the external charge. $\Delta E_{\text{frz}}$ is then the difference between this value for the HF density and the MP2 density. It is possible to verify this value for $\Delta E_{\text{frz}}$ by comparing to the value computed from integrating the density. A plot of the radial part of the difference between the HF and MP2 densities is shown in figure 3.4a. As the difference is too small to see even on a logarithmic plot, the plot instead shows the difference as a percentage of the MP2 density. A comparison of the value of $\Delta E_{\text{frz}}$ computed from this and the value from the EDA is shown in figure 3.4b. The calculations were done with the aug-cc-pVQZ basis set and, for MP2, the rimp2-aug-cc-pVQZ auxiliary basis set. The close agreement indicates that this interpretation of the frozen energy is correct and

![Figure 3.4](image-url)

Figure 3.4: (a) Percentage difference between the HF and MP2 densities (b) log-lin plot of $\Delta E_{\text{frz}}$ from density and from EDA

that no other effects are contaminating the frozen term.

The negative value for $\Delta E_{\text{frz}}$ corresponds to the fact that the MP2 helium atom is more diffuse than the HF helium atom, as is typical for the two methods. This indicates another effect captured by $\Delta E_{\text{frz}}$: at close range, it will include significant amounts of Pauli repulsion as the distributions of neighboring fragments get more diffuse and overlap each other more. This will tend to overestimate the true repulsion, which will be corrected by $\Delta E_{\text{pol}}$ as the distributions deform to overlap less.
3.3.2 Helium dimer

As a first multi-fragment system, the helium dimer is a good choice because of its simplicity. In the close range, the atoms repel, which falls under the frozen term for both the HF and MP2 EDA. The weak binding is entirely a result of dispersion. We expect $\Delta E_{\text{frz}}$ to be positive in the short range to account for the increased repulsion between the more diffuse atoms and decay exponentially, $\Delta E_{\text{pol}}$ to be negative in the short range to correct the overestimation of repulsion and also decay exponentially, $\Delta E_{\text{CT}}$ to be smaller and also decay exponentially, and $\Delta E_{\text{disp}}$ to have $R^{-6}$ decay and therefore be the only significant component in the long range. The HF and MP2 EDAs are shown in figures 3.5a and 3.5b respectively. The calculations were done with the aug-cc-pVQZ basis set and, for MP2, the

![EDA energy (kJ/mol) vs Interatomic distance (Å) for Helium dimer](image)

Figure 3.5: (a) HF EDA and (b) MP2 EDA (including the HF contribution) for the He dimer as a function of separation.
rmp2-aug-cc-pVQZ auxiliary basis set.

The HF case is simple. Pauli repulsion (classified as frz) dominates the whole interaction and the system is unbound. The repulsion grows exponentially in the short range, and is 400 kJ/mol at 1 Å separation (not shown). Polarization and charge transfer contribute little to the overall picture. Adding in correlation leaves the overall trend for the first three components the same, though they all increase in magnitude somewhat, as the atoms are more diffuse with MP2. The major difference is the addition of the relatively large, slowly decaying dispersion. Because it is the only sub-exponentially decaying component, dispersion dominates the long range of the interaction, and is enough to make the dimer (very weakly) bound. Plotting only dispersion on a log-log scale as in figure 3.6 and fitting a power function to the long range part of the curve confirms that the long range behavior is indeed $R^{-6}$. Thus the EDA confirms the intuition that dispersion should be an $R^{-6}$ attractive force that is the only reason the helium dimer is bound. In this case, dispersion was the sole important contribution of MP2, though as we shall see, this is often not the case.

3.3.3 Chloride-argon

Another good example system is the interaction between a chloride ion and an argon atom, providing a two fragment version of the atom-external charge example above. We still expect to see $\Delta E_{\text{pol}}$ go as $R^{-4}$ and $\Delta E_{\text{frz}}$ to decay exponentially, but now there will also be $\Delta E_{\text{disp}}$ and $\Delta E_{\text{CT}}$. The former should once again have $R^{-6}$ long-range decay while the latter should be small and decay exponentially. The HF version of the EDA is shown in figure 3.7a, MP2 in figure 3.7b, and log-log plot of the correlation part only in figure 3.7c. The calculations were done with the aug-cc-pVQZ basis set and, for MP2, the rmp2-aug-cc-pVQZ auxiliary basis set. The results confirm all of these expectations. At the HF level, the binding is due to polarization. Adding in correlation changes all the EDA components, but the biggest change is from the addition of dispersion. This makes the binding more

Figure 3.6: log-log plot for dispersion component of He dimer EDA
than twice as strong and moves the energy minimum in by about 0.5 Å. As can be seen on the log-log plot, dispersion is not just the qualitatively main effect of correlation, but also once again quantitatively the largest over most of the range. However, in the long range, the more slowly decaying $\Delta E_{\text{pol}}$ becomes larger. Closer than 4.5 Å, $\Delta E_{\text{pol}}$ grows faster than the extrapolation of the $R^{-4}$ trend. This is the overlapping regime where $\Delta E_{\text{pol}}$ includes not only the electrostatic effect of the greater argon polarizability, but also the increased polarization of the more diffuse electron clouds in response to each other. A similar bump is seen on $\Delta E_{\text{frz}}$ plots when there is a long range frozen interaction.

### 3.3.4 Stretched water dimer

A final asymptotic example is the water dimer, stretched from the S22 equilibrium geometry along the axis connecting the molecules’ centers of mass. Equilibrium for this system is 2.909 Å on the chosen axis. The results are shown in the following graphs. The calculations were done with the aug-cc-pVTZ basis set and, for MP2, the rimp2-aug-cc-pVQZ auxiliary basis set. Both the HF EDA in figure 3.8a and the MP2 EDA in figure 3.8b show the attractive frozen interaction dominating the long range behavior, with the short range
behavior more controlled by the other components. This difference in the short range can be attributed to the hydrogen bond. According to the MP2 EDA, the water dimer is bound twice as strongly and 0.5 Å closer than it would be from only the frozen interaction. However, the frozen interaction also dominates the repulsive region. Therefore, in this case, the frozen interaction controls the very close and the very far.

Turning to the log-log plot of the MP2 part only in figure 3.8c, the major contribution in the long range is from the positive, $R^{-3} \Delta E_{\text{frz}}$. The prefactor on this in the long range is about 40. $(\text{kJ/mol}) \text{Å}^3$, depending on how it is calculated. This value can also be predicted from the dipole moments. MP2 shrinks the dipole moment of the first water molecule from 1.9882 D to 1.8592 D and the second from 1.9831 D to 1.8550 D. Given the orientation of the molecules, this corresponds to a prefactor of 41.135 $(\text{kJ/mol}) \text{Å}^3$, or 0.125 times the SCF EDA. This matches the results of the EDA. The $\Delta E_{\text{frz}}$ is large enough that the correlation binding energy is positive in the medium and long range, as seen by the dip in the total

Figure 3.8: (a) HF EDA, (b) MP2 EDA, and (c) log-log plot of the correlation part of the MP2 EDA for the water dimer as a function of center of mass separation.
energy line (since the log-log plot does not show sign, all that can be seen the curve passing through zero, which is $-\infty$ on the plot). In a previous paper, we argued that the long range behavior of the correlation binding energy in cases like this was due to MP2's correction of the electrostatics.[28] The results here provide further support for that argument. Additionally, unlike most correlation EDAs, this one is capable of recognizing this effect as electrostatic, rather than declaring it to be dispersion or another force.

Turning to $\Delta E_{\text{pol}}$, at the maximum distance of these calculations, it has not converged to some simple $R^{-N}$ behavior (for integer $N$). At the right edge of the graph, the behavior is approximately $R^{-6.6}$. The correct long range behavior of $\Delta E_{\text{pol}}$ is harder to reason about than $\Delta E_{\text{Hz}}$. There are two effects here: first is that the dipoles causing the polarization are weaker, and second is that the molecules themselves are more polarizable. These trends are opposite in direction, and the overall value is negative, meaning the increase in polarizability is more important. Both should be linear in the size of the HF polarization energy in the long range. Therefore, if they are approximately the same size, they may continue to cancel out for a long distance, and let higher scaling effects control the behavior of $\Delta E_{\text{pol}}$ over the ranges we can compute. In fact, the slope is still decreasing further to the right, and may converge to $R^{-6}$ in the long range.

$\Delta E_{\text{disp}}$ displays its typical $R^{-6}$ behavior, and $\Delta E_{\text{CT}}$ becomes significant in the close range where the hydrogen bond is significant. The line on the plot ends when the counterpoise corrected $\Delta E_{\text{CT}}$ becomes positive from the overzealousness of standard counterpoise correction.

### 3.3.5 Rotated water dimer

Now that the asymptotics have been established, it is time to look at the equilibrium range. Returning to the water dimer, we will compare the equilibrium geometry to one where the dipoles are aligned (which might be predicted as the equilibrium geometry if electrostatics were the only factor). For ease of comparison, the molecules have the same internal configuration between the two geometries. They are also separated by 3.2 Å when aligned, which is closer to the energy minimum for that geometry. figures 3.9a and 3.9b show the HF and MP2 EDA for a path connecting those geometries by simultaneously rotating the two molecules and translating them farther apart. The calculations plotted in the figures used the aug-cc-pVTZ/rimp2-aug-cc-pVQZ basis sets, while the numbers in table 3.1 used aug-cc-pVQZ/rimp2-aug-cc-pVQZ.

The greater accuracy of MP2 for this interaction is apparent, as HF puts the energy minimum somewhat distant from the true equilibrium geometry. Compared to HF, MP2 has greater binding due to charge transfer and polarization. Both are fairly orientation dependent and together make the hydrogen bond, particularly charge transfer, which is negligible in the aligned geometry. Dispersion changes much less with the orientation. Most

---

*aTotal MP2 energy is $-152.773793$ Hartree in the equilibrium geometry and $-152.770195$ Hartree in the aligned geometry*
Figure 3.9: (a) HF EDA and (b) MP2 EDA for water dimer rotated between two orientations: equilibrium on the left and aligned on the right. The x axes are both the dimensionless coordinate of transformation.

of the difference is caused by molecules being farther apart in the second geometry. The frozen interaction differs from the others. It has the opposite trend from the components, and is lower in energy in the aligned geometry, as the alignment of the dipoles is the most important effect it describes. The MP2 contribution is strictly positive, as it lowers the strength of the dipoles, as previously discussed. In the equilibrium geometry, it makes the total value repulsive, meaning that the Pauli repulsion overwhelms the attraction of the poorly aligned dipoles. Overall, the MP2 EDA strengthens the HF picture of a hydrogen bond as a combination of charge transfer and polarization effects.

**Basis set effects**

MP2 is known to converge to the basis set limit more slowly than HF. For the above case, the HF binding energy is nearly converged at aug-cc-pVDZ, while MP2 does not reach the limit even with aug-cc-pVQZ. A known issue with the HF EDA is that charge transfer does not have a non-trivial basis set limit.[106] This case is no exception — as the basis size
CHAPTER 3. AN EDA FOR MP2 BASED ON ALMOS

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium</th>
<th>Aligned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>MP2</td>
</tr>
<tr>
<td>$\Delta E_{\text{frz}}$</td>
<td>-5.285</td>
<td>3.782</td>
</tr>
<tr>
<td>$\Delta E_{\text{pol}}$</td>
<td>-5.756</td>
<td>-9.358</td>
</tr>
<tr>
<td>$\Delta E_{\text{CT}}$</td>
<td>-3.956</td>
<td>-7.137</td>
</tr>
<tr>
<td>$\Delta E_{\text{disp}}$</td>
<td>-15.001</td>
<td>-20.452</td>
</tr>
</tbody>
</table>

Table 3.1: HF and MP2 EDA for water dimer in two geometries (in kJ/mol)

is increased from aug-cc-pVDZ to aug-cc-pVQZ, charge transfer decreases and polarization increases. The MP2 EDA should share this issue for the same reason. $\Delta E_{\text{frz}}$ has a well-defined limit, as it uses the same wave function as the isolated fragments, which have a limit. $\Delta E_{\text{disp}}$ is not strongly affected by this as it cares mostly about which occupied orbitals the excitations are from, and the occupied orbitals can be local even in an overcomplete basis set. However, it will absorb some charge transfer. The last two terms will be affected the most. A double excitation is assigned to $\Delta E_{\text{pol}}$ if all its orbitals are on the same fragment. As the basis set becomes very large, virtual orbitals assigned to one fragment will describe the virtual space of the other fragments. This means it will grow to include interactions that should be part of $\Delta E_{\text{CT}}$. However, as MP2 converges more slowly, it will be less of an issue for practical basis sets.

The graphs below in figure 3.10 show the correlation part only for the four EDA components with three different basis sets between the same two orientations as before. All use rimp2-aug-cc-pVQZ as the auxiliary basis set.

Dispersion increases with increasing basis set size, and is slowing and approaching convergence. Going from aug-cc-pVDZ to aug-cc-pVQZ causes a factor of 1.5 increase, but the total correlation binding energy increases faster, and roughly doubles. Charge transfer lacks a consistent trend. The aug-cc-pVTZ and aug-cc-pVQZ lines are both smaller than aug-cc-pVDZ, but cross each other. This may be because charge transfer lacks a basis set limit. Another explanation is that charge transfer is where the effects of BSSE are expressed, so it is the least rigorous for small basis sets. While the counterpoise corrected values for aug-cc-pVTZ and aug-cc-pVQZ are very similar, the size of the corrections are very different. There is more than twice as much BSSE with aug-cc-pVTZ compared to aug-cc-pVQZ. This makes it hard to directly compare the numbers for the two.

Meanwhile, the frozen energy changes little with basis set as expected because it measures properties that are relatively stable between basis sets. The difference between aug-cc-pVDZ and aug-cc-pVQZ is less than 10%. Polarization, on the other hand, has the largest increase of any component and more than doubles from aug-cc-pVDZ to aug-cc-pVQZ. Part of this may be simply describing charge transfer more accurately, but much is because it absorbs charge transfer-like terms as the basis grows. Therefore, it seems that the lack of a non-trivial basis set limit is an issue for the MP2 ALMO-EDA for practical basis sets, just as it is
Figure 3.10: (a) $\Delta E$, (b) $\Delta E_{\text{pol}}$, (c) $\Delta E_{\text{frz}}$, (d) $\Delta E_{\text{CT}}$, and (e) $\Delta E_{\text{disp}}$ for water dimer rotated between two orientations, in three different basis sets. All x axes are the dimensionless coordinate of transformation.

with the HF EDA, though it takes a somewhat larger basis set before it becomes noticeable. In practice, the use of aug-cc-pVQZ when feasible, and aug-cc-pVTZ otherwise seems to be reasonably satisfactory.

3.3.6 Halogen bonding

As a first application of the MP2 ALMO EDA to a system whose nature is still not settled, we turn our attention to the halogen bond. Halogen bonds are noncovalent interactions between positive halogen atoms on one molecule and negative sites on another,[107, 108] and have been subject of renewed theoretical interest lately.[109–111] Explanations for the nature of the halogen bond range from a traditional view of domination by charge transfer[112, 113] to a purely electrostatic picture[24, 114] that has been proposed more recently. The
electrostatic view relies on the notion of the $\sigma$-hole,[25] wherein a covalently bonded halogen or other atom has a region of positive potential opposite its bond. According to this view, the halogen bond is an electrostatic interaction between the $\sigma$-hole on the halogen atom, and a locally negative site on on another molecule, such as a lone pair or a pi bond. This interpretation suggests that a halogen bond should be highly directional[108] and similar in nature to a hydrogen bond,[111] which may also be considered a $\sigma$-hole interaction. While a full application of the MP2 ALMO EDA to halogen bonding is outside the scope of this paper, the halogen bond between chlorine monofluoride and water provides a good start. The system is analogous to the water dimer, with the electron receptor water molecule replaced with a chlorine monofluoride molecule. Both have the electron donating water molecules bent out of line with the intermolecular bond, which means than in both cases the dipole moments of the two molecules are not fully aligned. This system also has a similar interaction strength to the water dimer. As a final advantage, it is not described even qualitatively correctly by HF, making it an ideal case for an MP2 EDA.

The $\text{H}_2\text{O}-\text{ClF}$ geometries used are the global minimum halogen bonded structure and a planar structure that serves as the transition structure between the minimum and its equivalent structure reflected through the plane. This second structure is also what one might predict as the minimum based purely on the dipole moments. A path between them was found using the growing string method–intrinsic reaction coordinate (GSM-IRC).[115] These geometry calculations, along with the subsequent EDA calculations, were performed in the aug-cc-pVQZ basis using the rimp2-aug-cc-pVQZ auxiliary basis. This path allows us to examine the directionality of the halogen bond in this system. There are two symmetric minima. If the barrier between them is low, then in practice, the system would exhibit high amplitude vibration between the two minima rather than stay in a fixed configuration as the term bond would imply. As seen above in figure 3.9, the water dimer loses more than 40% of its binding energy in the dipole aligned geometry. The results for $\text{H}_2\text{O}-\text{ClF}$ are below in figure 3.11. These numbers are not counterpoise corrected, but the BSSE at this level ranges between 2.10 kJ/mol and 2.30 kJ/mol and so does not affect the overall picture much. Instead, a geometry distortion term is included.

Some things are apparent before looking at the EDA numbers. First, unlike with the water dimer, HF is not even qualitatively correct, underestimating the binding energy by more than half and missing the relative energies of the two configurations. Second, and also in contrast to the water dimer is how weakly directional the halogen bond is along this coordinate. While in the water dimer, the dipole aligned configuration lost about 40% of the binding energy, here it loses less than 10%. The difference is just 1.98 kJ/mol. As this configuration is also the transition state between the halogen bonded minimum and its mirror image, this low barrier would allow the water molecule to undergo high amplitude vibration rather than the relatively small implied by the term "bond". Turning to the EDA can help explain why. The most striking feature is how strongly the frozen electrostatics prefer the dipole aligned configuration. Both configurations are in the range where Pauli repulsion dominates the frozen term, but the favorable alignment helps overcome some of it. Dispersion is nearly independent of direction. The dip in the aligned configuration is
due to slightly larger intermolecular distance. The Cl-O distance is 2.52 Å vs 2.48 Å at equilibrium. While not much impacting the relative energy of the configurations, this large contribution is responsible for much of the increase in binding predicted by MP2 over HF. The directionality comes from the remaining two components, which together are able to overcome the 11 kJ/mol electrostatic preference for the aligned configuration. Of polarization and charge transfer, the latter is more important in this respect. It is the greatest contributor to binding and is strongly directional. If it were slightly weaker, the aligned geometry would be preferred and there would be no halogen bond. This supports the idea that charge transfer is the driving force of the halogen bond. The importance of this configuration is that the lone pairs of the water molecule are aligned properly to donate charge to the chlorine atom. Therefore, we conclude that this particular halogen bond is driven by charge transfer and not particularly directional.
3.4 Conclusions

The ALMO MP2 EDA successfully captures physical intuition about the simple systems to which it is applied here. $\Delta E_{\text{CT}}$ decays exponentially, as it must. It is always negative, consistent with MP2 allowing excitations from one molecule’s occupied space to another’s virtual space. It is large in systems where partial covalent interactions are expected, such as the hydrogen bonded water dimer, and small in systems without such an interaction, such as the helium dimer. $\Delta E_{\text{disp}}$ captures dispersion’s $R^{-6}$ long range separation dependence. It acts almost exactly like that beyond a few ångströms of separation, and behaves smoothly in the close range. Dispersion contributes essentially all the binding for the helium dimer and controls the long range behavior of any system without an electrostatic interaction. $\Delta E_{\text{pol}}$ is the only MP2 correction whose sign is not obvious. MP2 tends to calculate a greater polarizability than HF, which tends to cause a negative correction. This is seen in the case of argon-chloride. However, for systems without isolated charges, polarization is induced by multipoles which are weaker with MP2. As seen for the water dimer, the greater polarizability wins out and the correction is negative, but there may be systems where the reverse is true. $\Delta E_{\text{frz}}$ is the most complicated term to describe, but the simplest to evaluate. It is exact in one molecule systems, and behaves well for two or more molecule systems. In the long range, it is controlled by the MP2 correction to the dipole moment, as seen in the water dimer, where it has a positive $R^{-3}$ tail that dominates the long range of the correlation binding energy. In the close range, it is controlled by the MP2 correction to Pauli repulsions, which can be seen in every system studied. Thus, for many systems, the frozen interaction dominates both the close and long range, with the other components only becoming important around equilibrium. In general, there is a cancellation of errors observed with HF, where overestimation of the binding of the frozen interaction is more than offset by underestimation of polarization and charge transfer and omission of dispersion.

The EDA was applied to the chlorine monofluoride–water system as the beginning of an investigation into halogen bonding. It was found that while frozen electrostatics strongly favored a planar geometry, charge transfer effects were able to overcome it and make a geometry where the FCI molecule is in line with a water lone pair more favorable. Thus, the EDA supports the traditional view over one that says electrostatic effects are the cause of the halogen bond. This opposition of forces leads to a weakly directional bond, with a less than 10% difference between the two geometries.

By using the same orbitals as the SCF ALMO EDA, this EDA can be added to it directly as its MP2 correction. This means that it inherits many of the previous work’s strengths and weaknesses. It is a variational method and can be applied to strong as well as weakly interacting systems. BSSE is confined entirely to $\Delta E_{\text{CT}}$, with the exception of ABSSE. It is also of comparable cost to a simple MP2 binding energy. However, like its parent method, it requires disjoint fragments with integer numbers of electrons and lacks a true basis set limit. The first is a fundamental attribute of the EDA, while the second may be improved in a future version. For now, none of the energies are too unstable with respect to basis sets, but when comparing EDA results, the same basis set should be used throughout.
The simplest future direction for this work is an efficient implementation. This may include an approximation to the full charge transfer energy, eliminating the need for the total system energy. As a consequence, this would allow an efficient approximation to the MP2 binding energy that scales better than MP2 in the case of a growing number of molecules of a fixed size. Additional extensions would be to treat open shell systems using unrestricted orbitals, and to extend this method to modifications of MP2, such as attenuated MP2, orbital optimized MP2, and double hybrid DFT functionals. A longer term goal is to apply these principles to CCSD and CCSD(T).

Finally, this work is the first EDA for a post-HF method that distinguishes all types of intermolecular forces. We hope that future EDAs for correlation methods, as well as all discussion of the effect of electron correlation on intermolecular binding, will account for the fact that electrostatic forces play a key role.
Chapter 4

Efficient Implementation of MP2 EDA and Application to Anion-\(\pi\) Interactions

4.1 Introduction

Second order Møller-Plesset (MP2) theory[32] is perhaps the simplest wave-function theory that includes the effects of dynamic electron correlation[119]. MP2 thus corrects the self-consistent field (SCF) Hartree-Fock (HF) molecular orbital model with missing physics that includes reduced ionic character in the electron density and thus reduced dipole moments[60–63], and dispersion interactions[22, 120] that provide a universal long-range attraction. Both of these effects are important for intermolecular interactions, and therefore MP2 theory provides a great improvement over HF theory in the accuracy obtained for ion-water interactions[37], hydrogen bonds[36], electrostatically bound complexes[13, 28], and dispersion-bound systems[13]. MP2 tends to overestimate dispersion interactions, particularly in stacking interactions of aromatic systems, as is well known[12–14]. However, despite its simplicity, MP2 theory often matches more expensive methods such as coupled cluster singles and doubles (CCSD) for hydrogen-bonded systems such as water clusters[121]. Triples corrections, such as CCSD(T) are needed to reliably outperform MP2 theory on such systems, although spin-component scaling is a successful semi-empirical alternative[40, 41, 122, 123], and even attenuated MP2[43, 44] is valuable in smaller basis sets. MP2 theory also outperforms almost all density functionals for ion-water interactions, particularly for multiply charged ions[124].

Because of their usefulness, as well as their low computational cost compared to CCSD, CCSD(T), etc, it is desirable to be able to analyze the results of MP2 calculations of intermolecular interactions. This is the task of an energy decomposition analysis (EDA). An EDA takes a calculated intermolecular binding energy and ascribes portions of it to different physical contributions such as permanent and induced electrostatics, dispersion, Pauli repulsions, and charge transfer.[51, 125–127] Most EDAs that have been proposed and widely used to date apply to SCF wavefunctions, such as HF and/or Kohn-Sham DFT.[72]
While it is beyond our scope to review them in any detail, it is worth mentioning that the Kitaura-Morokuma (KM) decomposition \cite{19} is perhaps the seminal method, followed soon afterwards by the Ziegler-Rauk approach. \cite{71} More recent significant developments have been the separation of polarization from charge transfer using fragment-blocked molecular orbital coefficients, \cite{26, 27, 50, 51, 128} the development of density-based EDA approaches for DFT, \cite{129–132} and very recent efforts to obtain stable basis set limits for polarization and charge transfer. \cite{106, 133, 134} It is noteworthy that application of the KM EDA \cite{48} has helped to inform the development of advanced force field approaches, such as the effective fragment potential method \cite{135–137}.

There has been much less effort devoted to developing EDAs that unravel the contributions to post-HF binding energies, as given by MP2 or CC methods. The very simplest model is to ascribe the post-HF correlation binding in an intermolecular interaction to dispersion, as has sometimes been advocated. \cite{47} However, since MP2 reduces the ionicity of HF charge distributions, the electrostatics are also affected, and thus the correlation contribution can even be net repulsive. \cite{28} Local correlation models \cite{87, 89} are a good basis for identifying correlation contributions to specific intermolecular interactions \cite{52, 138}, with efforts along these lines continuing to the present day \cite{139}. Local correlation models are quite naturally able to separate intermolecular correlation effects that are associated with dispersion from those that correspond to charge transfer. Difficulty arises in distinguishing post-HF contributions to polarization from charge transfer.

Nonetheless, we feel that an important criterion for a successful post-HF EDA is to organize the correlation contributions to an intermolecular interaction so as to correspond directly to the terms that are well-accepted at the SCF level. We recently presented \cite{29} the theory and a pilot implementation for an MP2 EDA that meets this criterion for the first time, to our knowledge. This approach employs the fragment-blocked absolutely localized molecular orbitals (ALMOs) that were used in the earlier HF-level ALMO-EDA \cite{26, 27}, rather than the virtual orbitals derived from linear response \cite{133} to electric fields and gradients that are used in the recent second generation ALMO-EDA \cite{134} to ensure a valid complete basis set limit for polarization. The MP2 ALMO-EDA identifies the correlation contributions to the so-called frozen interaction (permanent electrostatics + Pauli repulsion), induced electrostatics, and charge transfer. In addition, using local correlation arguments \cite{89}, a dispersion term is defined. The main purpose of this paper is to report an efficient production-level implementation of the MP2 ALMO-EDA, which will enable its application to any system for which MP2 calculations are themselves feasible.

The outline of the remainder of the paper is as follows. In Sec. 4.2, the theory defining the MP2 ALMO-EDA is briefly reviewed, to clearly define all relevant terms. In Sec. 4.3, we then address the critical issues needed to achieve an efficient implementation, and discuss the way in which we have chosen to address them. To assess the success of the implementation, a series of benchmark timing tests are reported in Sec. 4.4, including the question of how well our OpenMP parallelization performs. We then turn to an example of the application of the new MP2 ALMO-EDA implementation in Sec. 4.5, which is the question of the origin of substituent effects in anion-π interactions. Anion-π interactions \cite{140}
have become a topic of considerable interest over recent years, as it has become evident that such interactions are not weak, and are relevant in systems ranging from biomolecules to supramolecular complexes.[141–144] Wheeler and Houk have previously analyzed substituent effects in halide-aryl interactions[145], and using high level calculations together with calculated electrostatic potentials, they concluded that direct through-space interactions of the anion with the substituents are the dominant factor controlling substituent effects.

4.2 Brief review of the MP2 EDA

The MP2 EDA is an extension of the HF version of the ALMO-EDA. At the HF level, the EDA uses ALMOs to create two constrained intermediate Slater determinants and defines its three components as the differences between these, the isolated system energies, and the full system energy. The first intermediate is the initial wave function. It is simply the HF solutions for the individual molecules as isolated systems joined into a single Slater determinant. The difference between its energy and the sum of the energies of isolated systems is the frozen term, describing the permanent electrostatics and Pauli repulsion. The second intermediate is the SCF for molecular interactions (SCF-MI) solution.[74–77] This is produced by finding the minimum energy solution subject to the constraint that molecular orbitals belonging to one molecule do not include any atomic orbital basis functions belonging to any other molecule. This produces the ALMOs that are key to the method. The difference between the SCF-MI energy and the initial energy is the polarization term, which describes induced electrostatics. Finally, the difference between the full system HF energy and the SCF-MI energy is the charge transfer term. Therefore, the three terms sum to the supermolecule binding energy by construction.

The MP2 version of the ALMO-EDA also decomposes the correlation contribution to the binding energy, by defining a MP2 to correction to each of the HF components and adding another one for dispersion. It does so through the definition an MP2 version of each energy, along with one additional intermediate to describe dispersion. The equivalent of the initial energy is referred to as $E_{\text{frag/froz}}$. It is complicated by the need for all virtual orbitals to be orthogonal to all occupied orbitals. This requires a projection scheme. The MP2 amplitudes from the isolated systems are frozen and used for the energy in the presence of the full system. The standard MP2 energy formula only applies to the MP2 solution. Since the presence of the other molecules is a one-electron perturbation, it is necessary to use the Hylleraas functional[85] for the MP2 energy. Additionally, the fact that the amplitudes of the MP2 solution are not variationally optimized parameters means that MP2 does not meet the criteria for the Hellmann–Feynman theorem[97], so the relaxed density matrix[96] must be used in the Hylleraas functional in place of the ordinary “unrelaxed” MP2 response density matrix.

Both of the remaining intermediates are calculated by constrained MP2 using the ALMO basis. The ALMO basis allows each occupied and virtual orbital to be assigned to a particular molecule (though the ALMO virtuals must be projected into the complement of the
occupied space). The first ALMO intermediate, $E_{\text{frag/ALMO}}$ is analogous to the SCF-MI energy. It is the MP2 solution when constrained to only allow double excitations entirely on one molecule. This allows the system to polarize at the correlation level, but does not allow dispersion-like excitations. The second ALMO intermediate is $E_{\text{ccc(sys/ALMO)}}$, or the charge conserving correlation energy. This is the MP2 solution when constrained to allow double excitations involving two molecules, but only if they do not change the number of electrons associated with each molecule. This allows dispersion-like excitations, but not transfer of charge. The difference between the two ALMO intermediates is the dispersion term of the EDA. The other three terms are also the differences between successive energies, the same as their HF counterparts. For the final energy decomposition, the HF and MP2 contributions to each term are summed together to produce four terms that decompose the MP2 binding energy.

### 4.3 Implementation

The terms of the EDA to be calculated are as follows.

\[ \Delta E_{\text{CT}} = E_{\text{sys}} - E_{\text{ccc(sys/ALMO)}} - (\text{BSSE} - \text{ABSSE}) \]  
\[ \Delta E_{\text{disp}} = E_{\text{ccc(sys/ALMO)}} - \sum_{\text{frag}} E_{\text{frag/ALMO}} \]  
\[ \Delta E_{\text{pol}} = \sum_{\text{frag}} E_{\text{frag/ALMO}} - E_{\text{frag/froz}} \]  
\[ \Delta E_{\text{frz}} = \sum_{\text{frag}} E_{\text{frag/froz}} - E_{\text{frag}} - \text{ABSSE} \]

Several terms, $E_{\text{sys}}$, $E_{\text{frag}}$, and BSSE are calculated exactly as in a standard counterpoise corrected binding energy job, and need not be discussed here. (If decomposing a binding energy that is not counterpoise corrected, the BSSE term is simply omitted, but ABSSE must still be included.) The remaining terms can be broken into two groups based on which molecular orbital basis is used. The first uses the modified ALMO basis and includes $E_{\text{ccc(sys/ALMO)}}$ and $E_{\text{frag/ALMO}}$, while the second uses the isolated fragment basis and includes $E_{\text{frag/froz}}$ and ABSSE. ABSSE is the difference between $E_{\text{frag}}$ calculated with the full system’s auxiliary functions and calculated with only the particular fragment’s auxiliary functions. The latter is computed as part of a normal binding energy calculation, but the former must also be computed for the EDA.

#### 4.3.1 ALMO terms

Calculation begins by preparing the common basis for the two ALMO terms. As input, the calculation requires the polarized ALMO solution for the system as well as the corresponding Fock matrix. However, the ALMO basis is modified to be suitable for MP2. The full
CHAPTER 4. EFFICIENT IMPLEMENTATION AND ANION-II INTERACTIONS

The system occupied space is symmetrically orthogonalized. The new occupied orbitals are used to create an orthogonal projector and each virtual orbital is projected into the orthogonal complement of the occupied space. Then, the resulting virtual orbitals are orthonormalized within each fragment’s virtual space, but not between fragments. The Fock matrix is transformed to this basis. As a final transformation, the system is canonicalized on each fragment. To do so, on each fragment, both the occupied-occupied and virtual-virtual blocks of the Fock matrix are diagonalized and the resulting eigenvectors are used to transform the corresponding ALMOs. This results in a new basis where the Fock matrix is diagonal within the fragment o-o and v-v blocks. These preparation steps take a negligible amount of time (both practically and asymptotically) compared to later steps, so further detail is not necessary.

The new ALMO basis has the required property of strong orthogonality between the full system occupied and virtual spaces as well as a desirable amount of sparsity in both the overlap and Fock matrices. The overlap matrix is identity in the o-o block, zero in the o-v block, and identity in each fragment’s v-v block, but it has no special properties in the cross-fragment parts of the v-v block. The Fock matrix is diagonal on each fragment’s o-o block and v-v block, but has no special properties in the cross-fragment parts of the blocks. The o-v part is not relevant to MP2. This sparsity allows faster calculation of $E_{ccc}^{\text{sys}/\text{ALMO}}$.

The three-center resolution-of-the-identity integrals must also be transformed. This step is the only one that scales as $N^4$ with an increasing number of identical fragments, so it is asymptotically dominant, though for most practical systems the actual construction of the four center electron repulsion integrals will take longer despite scaling as $N^3$. Calculation proceeds the same as in standard RIMP2, through the creation of a B matrix such that $\sum_B B_{ia}^P B_{jb}^P \approx (ia|jb)$. Unfortunately, the locality of CCCMP2 (MP2 with only charge conserving correlation) is not enough to allow creation of a smaller B matrix. Integrals of the form $(ia|jb)$ and $(ib|ja)$ are needed where $i$ and $a$ share a fragment as do $j$ and $b$. For the first type of integral, only the entries in the on-fragment blocks of the B matrix are required. However, the second type has no such restriction and requires the construction of the entire B matrix. There are two steps to transforming the AO basis three center integrals into the B matrix. The first is transforming from the atomic orbital basis $(mn|P)$ to the ALMO basis $(ia|P)$. This can be done in two BLAS calls per auxiliary function. Without taking advantage of sparsity, this requires time $O(n^2oxN^4)$ where $n$ is the number of basis functions, $o$ is the number of occupied orbitals, $v$ is the number of virtual orbitals, and $x$ is the number of auxiliary functions on a fragment and $N$ is the number of fragments. However, for a sufficiently large system, many integrals are zero. The next step is the multiplication by the $(P|Q)^{-\frac{1}{2}}$ matrix, which can be done in a single BLAS call and takes time $O(ouvx^2N^4)$. As $x > n$ for the RI approximation to be accurate, this is the slower of the two steps. In addition to the normal B matrix, a fragment blocked B matrix is created where only entries $(ia|P)$ with $i$ and $a$ on the same fragment are included.

With this, the preliminary work is complete. The first thing to calculate is $E(\text{frag}/\text{ALMO})$ for each fragment. Since the basis is orthonormal and canonical on each fragment, this proceeds exactly as in normal RIMP2 with the only exception being that the $t$ amplitudes are saved. The required integrals can be constructed easily from the fragment blocked B matrix.
The most complex step is the calculation of $E_{ccc}(\text{sys/ALMO})$. The basis is neither globally orthonormal nor canonical, so the standard MP2 methods cannot be used. While we may use the energy equation,

$$E = -\sum_{ijab} t_{ij}^{ab} (ia|jb) \quad (4.2)$$

to get $t_{ij}^{ab}$ we must solve the linear system

$$\sum_{ijab} \Delta_{ij}^{ab} t_{ij}^{ab} = 2 (i'a'|j'b') - (i'b'|j'a') \quad (4.3)$$

with $\Delta$ as an eighth-rank tensor defined as

$$\Delta_{ij}^{ab} = -f_{ii} g_{aa} g_{bb} + g_{ii} f_{aa} g_{jj} g_{bb} - g_{ii} f_{aa} f_{jj} g_{bb} + g_{ii} g_{aa} f_{jj} f_{bb} \quad (4.4)$$

Equation (4.2) is simple to compute as $(ia|jb)$ can be formed from the fragment blocked B matrix with a single BLAS call in time $O(v^2xN^3)$. Equation (4.3) is more interesting and has two challenging pieces. One is calculating the right hand side and the other is solving the equation.

**Electron repulsion integrals**

Calculating the right hand side is challenging because of the $(ib|ja)$ term. This presents more of a challenge here than in ordinary MP2 because the fragment locality does not directly help. In ordinary MP2, every $(ib|ja)$ integral is also a $(ia|jb)$ integral, so they do not need to be calculated separately. However, when $i/a$ are on a different fragment from $j/b$, $(ib|ja)$ does not appear as a $(ia|jb)$ integral in CCCMP2. Though calculating them has the same $O(v^2xN^3)$ scaling as the other integrals, poor locality means that they cannot be computed as efficiently. Calculating the $(ib|ja)$ integrals involves all $ovN^2$ entries of the B matrix each used in $ov$ different integrals, while the $(ia|jb)$ integrals involve only $ovN$ entries of the B matrix used in each $ovN$ different integrals.

The simplest way to compute these integrals is best, with some modifications to prevent duplicated work. A procedure to compute $I_{ij}^{ab} = 2 (ia|jb) - (ib|ja)$ appears in figure 4.1 (this is specific to the restricted, closed-shell case). OpenMP parallelism can be exploited to speed up the process considerably.

The algorithm ensures that only one out of each pair of equivalent entries in $I$ need be calculated. Each duplicate value can then be copied at the end. The looping order $P$, $i$, $a$ is the same as the order of the indices in $B$, taking advantage of as much locality as possible. The choice of which of $I_{ij}^{ba}$ and $I_{ij}^{ab}$ to assign to in the main loop is also significant, as the right indices of $I$ are the fast ones, so this helps increase locality of references to $I$. 
Allocate space for a temporary \( I \) for each thread and set all entries to 0

Compute the upper triangle:

Loop over all auxiliary basis functions \( P \)
using OpenMP to divide the work among different threads

Loop over all occupied orbitals \( i \)

Loop over virtual orbitals \( a \) that share a fragment with \( i \)

\[
I_{ii}^{a} = B_{ia}^P B_{ia}^P
\]

Loop over virtual orbitals \( b > a \) that share a fragment with \( i \)

\[
I_{ii}^{b} = B_{ib}^P B_{ia}^P
\]

Loop over occupied orbitals \( j > i \)

Loop over virtual orbitals \( b \) that share a fragment with \( j \)

\[
I_{ji}^{b} = 2B_{jb}^P B_{ja}^P - B_{jb}^P B_{ja}^P
\]

Combine the temporary copies of \( I \):

Loop over the temporary copies of \( I \) for each thread beyond the first

Loop over all entries in \( I \)

Add the thread’s temporary \( I \) to the main \( I \)

Free the temporary \( I \)

Copy to lower triangle:

Loop over all occupied orbitals \( i \)

Loop over virtual orbitals \( a \) that share a fragment with \( i \)

\[
I_{ii}^{ab} = I_{ii}^{ba}
\]

Loop over occupied orbitals \( j > i \)

Loop over virtual orbitals \( b \) that share a fragment with \( j \)

\[
I_{ij}^{ab} = I_{ij}^{ba}
\]

Figure 4.1: Algorithm for \( I \)

Solving the linear equation

With the right-hand side of equation (4.3), the task becomes solving the linear system. Since \( \Delta \) is a fourth-rank tensor over occupied-virtual pairs with side length \( ovN \), the system can be solved in time \( O(o^4v^4N^4) \) without taking advantage of any of its internal structure. However, this has unacceptable eight-order scaling with respect to the size of the fragments and undesirable fourth-order scaling with respect to the number of fragments. Taking advantage of some internal structure allows the application of an explicit inverse of \( \Delta \) in time \( O(o^3v^3N^3) \). This achieves the desired third-order scaling with respect to the number of fragments, but still has less-than-ideal sixth-order scaling with respect to the size of the fragments, when MP2 scales as fifth-order. While \( \Delta \) cannot easily be inverted, forward application is possible in time \( O(o^3v^3N^3) \), matching MP2’s scaling. Since this is much faster
than inversion and $\Delta$ is a symmetric, positive definite operator, the iterative conjugate gradients method can be used to solve the system. The one requirement for conjugate gradients is a fast forward application of the operator. It can be significantly sped up with a good initial guess for the solution to the system and a simple approximate inverse of the operator as a preconditioner.

While the zero vector may be used as the initial guess for iteration, convergence can be significantly faster with a better guess. A reasonable guess is available from the calculation of $E(\text{frag}/\text{ALMO})$. The $t$ amplitudes can be combined into an initial guess for the solution to the system and a simple approximate inverse of the operator as a preconditioner.

As the convergence of conjugate gradients depends on the condition number of the system, preconditioning can drastically improve convergence. This can be thought of as an approximate inverse, as it brings the operator closer to the identity. The preconditioner must be fast to apply, as it is used each iteration of the method. The fastest preconditioner is a diagonal one. We will use the inverse of the diagonal elements of $\Delta$, as this can be applied with one division per double excitation, which is negligible time compared to the full forward application of $\Delta$. This is same as the inverse of $\Delta$ in the limit where overlap between virtual orbitals on different fragments is 0. In large or weakly interacting systems, most of these overlaps will be 0 and most of the remaining ones will be small, making this is a good preconditioner.

The only remaining piece is an efficient application of $\Delta$. Remember that $\Delta$ is defined as

$$\Delta_{ijj'j''} = -f_{ii'}g_{aa'}g_{jj'}g_{bb'} + g_{ii'}f_{aa'}g_{jj'}g_{bb'} - g_{ii'}g_{aa'}f_{jj'}g_{bb'} + g_{ii'}g_{aa'}g_{jj'}f_{bb'}$$

subject to the constraint that each pair $i/a$, $j/b$, $i'/a'$, and $j'/b'$ shares a fragment. Since this is a linear operator, the four pieces can be applied separately. Furthermore the last two are the same as the first two, but with different indices. This leaves two pieces to consider. The second piece, $g_{ii'}f_{aa'}g_{jj'}g_{bb'}$ is the simpler one. Because of the global orthogonalization of the occupied orbitals, $g_{jj'} = \delta_{jj'}$. This along with the fragment constraint ensures that $b$ and $b'$ share a fragment. As each fragment’s virtual space is orthonormal, $g_{bb'} = \delta_{bb'}$. A similar argument applies to $g_{ii'}$ and $f_{aa'}$, so taking advantage of the sparsity placed in $f$ an $g$ during the basis set-up, the second piece of $\Delta$ becomes $f_{ii'}\delta_{aa'}\delta_{jj'}\delta_{bb'}$. As this is diagonal, it is trivial to apply.

The first piece, $f_{ii'}g_{aa'}g_{jj'}g_{bb'}$, is more complicated. It is the same, except $f$ and $g$ switch places. The argument for $g_{jj'}g_{bb'} = \delta_{jj'}\delta_{bb'}$ still holds, but the argument for the first two terms does not. The virtual-virtual overlap matrix $g_{aa'}$ does not have any special properties, so it doesn’t require that $i$ and $i'$ share a fragment. The between fragments part of $f_{ii'}$ also lacks any special properties. Therefore, the two matrices will actually have to be applied. Keeping the fragment constraint is tricky and requires two separate matrix multiplications per pair of fragments. Luckily, these are standard matrix multiplications and can be performed
CHAPTE R 4. EFFICIENT IMPLEMENTATION AND ANION-II INTERACTIONS 63

by BLAS. The first and third pieces can also be combined, cutting in half the number of matrix multiplications. The procedure for computing \( r = \Delta t \) appears in figure 4.2. It also parallelizable with OpenMP. The structure of \( f \) and \( g \) allow considerable time savings. The

Loop over all fragments \( n \)

Loop over all pairs \( j \) and \( b \) such that \( j \) and \( b \) share a fragment

using OpenMP to divide the work among different threads

Loop over all fragments \( n' \)

Set the temporary matrix “block” to zero

If \( n = n' \)

On a fragment, \( f \) and \( g \) are diagonal

Loop over pairs of \( i \) and \( a \) on fragment \( n \)

\[
\text{block}_i^a - = f_{ii}t_{ij}^{ab} \\
\text{block}_i^a + = f_{aa}t_{ij}^{ab}
\]

Otherwise

With BLAS, compute \( \text{temp}_i^a = g_{aa'}t_{ij}^{a'b} \)

(with \( a \) constrained to fragment \( n \) and \( a' \) and \( i' \) constrained to fragment \( n' \))

With BLAS, compute \( \text{block}_i^a = f_{ii'}\text{temp}_i^a' \)

(with \( a \) and \( i \) constrained to fragment \( n \) and \( i' \) constrained to fragment \( n' \))

Loop over pairs of \( i \) and \( a \) on fragment \( n \)

Atomically, \( r_{ij}^{ab} += \text{block}_i^a \)

Atomically, \( r_{ji}^{ba} += \text{block}_i^a \)

Figure 4.2: Algorithm for multiplication by \( \Delta \)

bulk of the time will be spent on the BLAS calls. The slower of the two requires time \( O(ov^2) \), and is done \( N^2 \) times for each of the \( ovN \) \( j/b \) pairs, for a total time complexity of \( O(o^2v^3N^3) \).

This structure minimizes the number of writes to the \( r \) matrix, which cannot be local for both \( r_{ij}^{ab} \) and \( r_{ji}^{ba} \). Within the final loop, adding to \( r_{ij}^{ab} \) takes care of the \(-f_{ii'}g_{aa'}g_{jj'}g_{bb'} \) and \( g_{ii'}f_{aa'}g_{jj'}g_{bb'} \) pieces of \( \Delta \), while adding to \( r_{ji}^{ba} \) takes care of \(-g_{ii'}g_{aa'}f_{jj'}g_{bb'} \) and \( g_{ii'}g_{aa'}g_{jj'}f_{bb'} \) without recomputing the identical blocks of the update matrix.

With this, all the ingredients for conjugate gradients are in place and the CCCMP2 equation can be set up and solved.

4.3.2 Isolated terms

The remaining terms use the isolated fragment orbital basis. Since they do not involve any global calculations like \( E_{ccc}(\text{sys/ALMO}) \), they are simpler to compute. The total amount of work associated with them scales only linearly with the number of fragments. The first step is \( E(\text{frag}) \). This is the same as the canonical MP2 energy of each isolated fragment,
but with the auxiliary functions from all fragments included. However, the $z$ vector must be computed to be used for $E(\text{frag}/\text{frz})$. In addition, the $t$ amplitudes are saved. For computing $E(\text{frag}/\text{frz})$, projected basis versions of the Fock matrix and the B matrix are required. The Hylleraas functional is used for energy. This includes the normal MP2 energy evaluation and one using the relaxed response density matrix of the isolated fragment $t$ amplitudes and $z$ vector. These steps are not substantially different in implementation than ordinary MP2 and do not need to be described in further detail.

4.4 Performance

The algorithms described above have been implemented in a development version of the Q-Chem quantum chemistry program package\[105\]. The only two subcalculations that scale both as fifth order in the size of the fragments and third order in the number of fragments are the calculation of the right hand side of equation (4.3) and finding its solution. Therefore, these are the most important to benchmark.

4.4.1 Benchmarking solving the linear equation

Because of the iterative nature of the conjugate gradients algorithm, the two factors determining the speed of solving the system are the number of iterations and the time taken for each iteration. The number of iterations should grow very slowly or not at all with the size of the system. This was tested by performing test calculations with water clusters from two to ten molecules. The main and auxiliary basis sets used were aug-cc-pVTZ and rimp2-aug-cc-pVTZ, which have 92 main and 198 auxiliary basis functions per molecule. This system was also used as a test of the initial guess and the preconditioning for reducing the number of iterations. As can be seen in table 4.1, with any of the algorithms, the number of iterations roughly stabilizes after about 6 water molecules. The preconditioner leads to a greater than factor of ten reduction in the number of iterations, reducing conjugate gradients from taking the large majority of overall computational time to being merely one of several roughly equally sized steps. The initial guess is less important, but is worthwhile if it can save even one iteration as it is trivial to compute. Between the two of them, conjugate gradients takes at most 11 iterations for up to 10 water molecules. This is with fairly stringent convergence criteria ($\|r\|_{\infty} \leq 10^{-15}$, where $r$ is the residual). A few more iterations could be saved with looser criteria, but this would come at the expense of precision.

The other factor is the time taken per iteration. There should be roughly cubic scaling in the number of identical fragments. This behavior is seen in figure 4.3, as predicted.

The quality of the parallelization can also be benchmarked. Ideally, speed would grow in direct proportion to the number of threads, but this is not feasible for many problems. In any case, speed should still increase significantly with the number of threads. The behavior is graphed in figure 4.4 for a varying number of threads. The graph shows an increase of speed with every additional thread, but with a slowing increase after 4 threads.
CHAPTER 4. EFFICIENT IMPLEMENTATION AND ANION-II INTERACTIONS

Table 4.1: Number of conjugate gradient iterations vs number of water molecules, for four different algorithms. G denotes using the isolated fragment excitations as an initial guess, P denotes preconditioning with the diagonal elements of $\Delta$, GP both, and $\emptyset$ neither.

<table>
<thead>
<tr>
<th>n</th>
<th>GP</th>
<th>P</th>
<th>G</th>
<th>$\emptyset$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>117</td>
<td>130</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>117</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>11</td>
<td>117</td>
<td>128</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>11</td>
<td>119</td>
<td>129</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>12</td>
<td>125</td>
<td>133</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>12</td>
<td>122</td>
<td>135</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td>12</td>
<td>123</td>
<td>131</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>12</td>
<td>123</td>
<td>133</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>12</td>
<td>122</td>
<td>132</td>
</tr>
</tbody>
</table>

Figure 4.3: A log-log plot of time per conjugate gradient iteration vs. number of water molecules, with a cubic fit line.

4.4.2 Benchmarking integral calculation

The same timing concerns apply to the calculation of $\mathbb{I}$. It should also be cubic for an increasing number of fragments. This is verified by the plot in figure 4.5. Behavior when parallelized is also important, as this calculation is primarily memory bound and cannot rely on BLAS calls, unlike the multiplication by $\Delta$. Because of this, calculation of $\mathbb{I}$ shows a more modest improvement with additional threads when compared to the conjugate gradient iterations. This is shown in figure 4.6.
Figure 4.4: A plot of time per conjugate gradient iteration vs. number of threads

Figure 4.5: A log-log plot of time to compute $I$ vs. number of water molecules, with a cubic fit line

### 4.4.3 Overall benchmarks

While those are the two most important steps for most systems, the transformation of the RI integrals into the molecular orbital basis can be significant when there is a large number of fragments. It is worth comparing the overall time for all of the EDA to the necessary standard calculations: HF plus RIMP2 energy. The times given for the EDA do not include calculating the three center, atomic orbital basis RI integrals, as those are identical between the EDA and standard RIMP2. For the EDA, the two described steps are the most important. However, the transformation of the RI integrals to the molecular orbital basis B matrix is also significant. As expected, it grows in importance for greater numbers of fragments. For small numbers of molecules, the transformation (including the two fragment blocked B matrices needed for the frozen energy) takes about one quarter of
the overall running time. With 10 molecules, it is about one third. Everything other than transformation of the B matrices and the CCC energy takes less than 2% of the overall time with 10 molecules. This includes all basis transformations and the single-fragment polarized, frozen, and isolated energies for all 10 molecules.

In comparing the EDA with standard RIMP2, Q-Chem 4.3 was used with eight threads on the same computer as the EDA benchmarks. The comparison is shown in figure 4.7. The graph compares the running time of the EDA to the HF calculation as well as the additional time for the RIMP2 portion of the calculation. In all cases with three or more molecules, the SCF time was 40 or 50 times larger than the RIMP2 time. As can be seen, the standard RIMP2 calculation is slightly faster for four or fewer molecules. However, thanks to better scaling, the EDA takes less time for five or more molecules, despite also having to calculate the single fragment energies. With ten molecules, the EDA takes about 1.6 times less time. The CCC energy involves less interaction than standard MP2. However, it requires a less efficient formulation of the MP2 energy. This means that greater speed is not seen until a relatively large number of molecules. However, the benchmarks show that even for as few as two molecules, the EDA is not particularly expensive to do in addition to a standard MP2 binding energy calculation. When counterpoise correction is applied, this will be true to an even greater extent, as the EDA requires no change in algorithm to work with the counterpoise corrected binding energy.

This trend continues in systems with larger numbers of atoms. To demonstrate this, the same benchmark was performed on ammonia-water clusters with a single ammonia molecule surrounded by 5-30 water molecules, using the cc-pVDZ basis set. The result is shown in figure 4.8. The efficiency gains of fragment blocking can be seen more strongly here, as there is a factor of 4 speedup in the largest system. As the system becomes larger, the additional computing time required for the EDA becomes negligible compared to the that for binding energy.
4.5 Application: anion-\(\pi\) interactions

To demonstrate the use of the efficient implementation of the EDA, we will apply to larger systems than we have previously done. The system is the anion-\(\pi\) interaction between the chloride anion and the \(\pi\) system of substituted benzene rings. Anion-\(\pi\) interactions have become the subject of much interest recently in part because of potential uses in biological systems or for molecule recognition.\[142\] They are similar to the better known cation-\(\pi\) interactions. However, the negative charge of the ion means that quadrupole moment of an unsubstituted benzene ring is repulsive rather than attractive. Therefore, attractive anion-\(\pi\) interactions are found only in systems where the aromatic ring has strongly electron withdrawing substituents. Therefore, there has been considerable interest in understanding the nature and origin of anion-\(\pi\) bonds. One such explanation comes from Wheeler and
Houk, who argue[145] that the anion-π interaction can be understood as weak, repulsive anion-benzene interaction plus a purely electrostatic interaction between the ion and the dipole moments of the substituents. They say that higher order effects, such as substituents modifying the interaction between the ion and the π system are not important and that the interactions with each of the individual substituents can simply be summed together. Others, meanwhile, have claimed that charge transfer[146] or “multi-center covalency”[147] is the key force in the bonds. These claims are evaluated here through the EDA. Structures for the substituted benzene rings were obtained from Wheeler and Houk’s supplementary information.

4.5.1 Perpendicular path

The test system is a chloride ion moved along a perpendicular path from the center of a benzene ring with a varying number of substituted fluorine atoms. PhF₂ is in the para isomer, PhF₃ is in the sym (1,3,5) isomer, and PhF₄ is in the 1,2,4,5 isomer. Therefore, other than PhF, no molecule studied here has a net dipole moment. The results support a picture where the influence of the additional fluorine atoms on the anion-π interaction is an electrostatic effect and the overall interaction only become attractive when there are enough fluorine atoms to reverse the overall quadrupole moment of a benzene molecule. As can be seen in figure 4.9, the interaction between benzene and a chloride ion is not attractive, though there is a shallow local minimum. Every additional fluorine atom to the benzene ring makes the interaction more favorable. The long range behavior of each curve is the $R^{-3}$ decay characteristic of ion-quadrupole interactions (though even at 10 Å, not all curves are yet close to their asymptotic behavior). For 2 or fewer fluorine atoms, the long range interaction is repulsive, and for 3 or more, it is attractive. Each additional fluorine atom adds nearly the same amount of favorable effect to the overall interaction.

![Figure 4.9: Binding energy of six different anion-π interactions](image)
Applying the EDA to these binding energy curves shows that the difference between the different π systems is an electrostatic one. Figure 4.10a shows the frozen interaction for the different systems and figure 4.10b shows the sum of the other components. As can be seen, in the frozen interaction, each fluorine atom makes the interaction more favorable. However, the other components show almost no change between the systems. The difference is barely visible on the graph. This is not a cancellation of larger differences – each individual component shows a similarly small change.

Figure 4.10: (a) Frozen interaction and (b) sum of polarization, charge transfer, and dispersion for six different anion-π interactions

The frozen term can be understood in terms of Pauli repulsion and electrostatics. The close range part is dominated by Pauli repulsion, which should be similarly sized in each of these systems. Every additional fluorine adds a favorable interaction, which is similarly sized and shaped each time. This is the electrostatic interaction between the dipole of the carbon-fluorine bonds and the charge of the chloride ion. Other than PhF, the molecules have no net dipole, so the interaction can be understood in terms of the higher multipole moments. Even in the case of PhF, the path of the ion is perpendicular to the plane of the benzene ring and therefore also to the dipole. This means the leading term of the interaction decays as a quadrupole’s characteristic $R^{-3}$ in the long range rather than $R^{-2}$. Since the different in-plane components of the dipoles do not effect the energy, so there is no cancellation effect as the second fluorine atom added, even though it cancels the net dipole of the first. This makes it possible to closely approximate the effect of an additional fluorine atom by simply adding the scalar energy of the interaction.

The insignificant changes in the non-frozen components of the EDA strongly supports Wheeler and Houk’s argument that the substituents primarily affect the interaction through electrostatics. We see that despite the electron withdrawing effect of the fluorine atoms, there is no significant increase in charge transfer from the chloride ion to the π system. Neither is there any noticeable change in polarization. Even dispersion changes little with the increasing number of electrons as more fluorine atoms are added.
Therefore, the non-electrostatic parts of the interaction are not changed significantly with the addition of substituents. Accordingly, studying the interaction with benzene is sufficient to understand these effects for all of the systems considered here. The full EDA for that system is shown in figure 4.11. At the distance of the interaction, charge transfer is not significant as expected from the fact that both systems are electron rich. The local minimum that this interaction displays is primarily due to polarization and dispersion. The local minimum is a result of its faster $R^{-4}$ decay compared to the dominant frozen interaction. In the case of PhF$_3$, where the quadrupole moment and thus the electrostatic interaction are nearly zero, polarization and dispersion are the two significant forces and do make a fairly strong favorable interaction. It is worth noting the importance of electron correlation for this interaction. Figure 4.12 shows the EDA for only Hartree-Fock. The major difference is the lack of dispersion, which is significant in the interacting region. Also, the HF graph shows the characteristic overestimation of multipole moments, and the repulsive frozen interaction is significantly overestimated in the medium to long range. These two errors prevent HF from describing the local minimum in the binding energy. It also because of this that HF describes the PhF system as unbound and gets the long range behavior of all systems wrong.

![Figure 4.11: EDA for chloride-benzene interaction](image)

The frozen term can be analyzed further by looking at the multipole moments of the substituted benzene molecules. Beyond the range of Pauli repulsion, the frozen term is dominated by electrostatic interactions. The changes in multipole moments are due to the greater electronegativity of fluorine relative to hydrogen, so this could be viewed as interaction with the substituents even though the moments belong the overall molecule. Since we are only concerned with the z axis, the traceless Cartesian multipole moment $Q_{z\ell}$ and the real and pure spherical multipole moments $Q_{\ell0}$ and $Q_{0\ell}$ are all equal and we do not have to be concerned with a choice of convention. For every molecule except PhF and PhF$_3$, the odd moments are zero as they have even dihedral symmetry with a horizontal mirror plane about the chosen origin (which causes them to have even symmetry with respect to
CHAPTER 4. EFFICIENT IMPLEMENTATION AND ANION-II INTERACTIONS

Figure 4.12: Hartree-Fock EDA for chloride-benzene interaction

reflection about all three coordinate planes, while each odd multipole moment has terms that have odd symmetry with respect to at least one coordinate. For PhF and PhF₃, these moments are nonzero, but they do not interact with a charge moving along the z axis, as \( Y_0^0 \) is the only spherical harmonics that is nonzero there. As for \( Q_\ell^0 \), it must be zero for odd \( \ell \) in the presence of a horizontal plane of symmetry through the origin (as for all terms in \( Y_0^0 \), \( z \) and \( \ell \) have the same parity).

In many situations, the long range electrostatic interaction can be closely approximated by its leading term — the lowest nonzero multipole moment. However, that is not sufficiently accurate in the case of the chloride-benzene interaction. As can be seen on the quadrupole line in figure 4.13, the quadrupole does not match the frozen term particularly well, even at 10 Å of separation. Adding in the hexadecapole moment makes the curves match much more closely, but are still visibly different in the region closer than 6 Å. Evidently, even higher multipole moments are needed. Figure 4.13 also shows the addition of the sixth (hexacta-tetrapole) and eighth (hecatonicosaoctapole) moments. With all of those multipole moments the expression for the approximation becomes \( V(z) = -\frac{Q_2^0}{z^3} - \frac{Q_4^0}{z^5} - \frac{Q_6^0}{z^7} - \frac{Q_8^0}{z^9}. \) The sixth order approximation is closer to the frozen curve than the eighth order one is. However, the frozen term also includes Pauli repulsion at close range, so the electrostatic curve should not necessarily match the frozen one at distances of a few angstroms. We can confirm the correct order of truncation by looking at the difference between the two curves. This is plotted in a lin-log plot in figure 4.14. This curve shows Pauli repulsion’s characteristic exponential decay until about 7 Å and then slows down. However, due to limitations with finite basis sets and subtractive calculation of Pauli repulsion, this is about as far as we should expect an accurate decomposition to go. With truncation at sixth order, deviation from exponential decay is clear, and the multipole approximation becomes less repulsive than the frozen energy beyond about 5 Å. Therefore, eighth order is the correct truncation for analyzing the electrostatics.
Therefore, the effect of the additional fluorine substituents on the frozen interaction can be analyzed by looking at changes in the first several multipoles of the substituted benzene molecule. They are shown in table 4.2. To show that these accurately describe the interaction, the difference for all of them is plotted in figure 4.15. The plot only goes to 7 Å for reasons described above. Even at this distance, it can be seen that the PhF₆ and PhF₃ curves decay too quickly. However, in the short range, all curves show exponential decay. Differences are small, but not negligible. The remainder at 3 Å ranges from 70 kJ/mol for benzene to 95 kJ/mol for PhF₆. The size of repulsion is the order of increasing amount of fluorine atoms, but rather than being evenly spaced, differences get larger as more atoms are added. Regardless, this shows that the electrostatic portion of the frozen interaction is
well described by the truncated multipole expansion.

Table 4.2: Significant multipole moments for substituted benzenes. Units are D·Å⁻¹

<table>
<thead>
<tr>
<th></th>
<th>benzene</th>
<th>PhF</th>
<th>PhF₂</th>
<th>PhF₃</th>
<th>PhF₄</th>
<th>PhF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_0)</td>
<td>-7.9807</td>
<td>-5.0545</td>
<td>-2.1191</td>
<td>0.4191</td>
<td>3.2045</td>
<td>8.1383</td>
</tr>
<tr>
<td>(Q_4)</td>
<td>65.7708</td>
<td>40.0664</td>
<td>14.5271</td>
<td>-6.7322</td>
<td>-31.0507</td>
<td>-72.0979</td>
</tr>
<tr>
<td>(Q_6)</td>
<td>-435.886</td>
<td>-295.645</td>
<td>-159.343</td>
<td>-49.5916</td>
<td>68.7468</td>
<td>253.124</td>
</tr>
<tr>
<td>(Q_8)</td>
<td>2907.83</td>
<td>2587.72</td>
<td>2312.83</td>
<td>2118.02</td>
<td>2101.59</td>
<td>2269.89</td>
</tr>
</tbody>
</table>

Figure 4.15: Lin-log plot of differences between frozen interactions and multipoles approximation to classical electrostatic interaction

The table of multipole moments reveals that changes are not quite the same for each additional fluorine atom. The quadrupole moment increases by 2.93 D·Å for the first atom, but only an average of 2.47 D·Å for the fifth and sixth. The hexadecapole moment changes are similarly inconsistent. However, the sixth order moment changes vary by factor of 1.5 between the smallest and the largest. The eighth order moment is much more erratic. Adding the first fluorine atom decreases it by 320 D·Å⁷, and the next few also lead to decreases. However, the fifth and the sixth actually increase it by an average of 84 D·Å⁷. These differences are reflected in the frozen energy and therefore also the overall interaction energy. Accordingly, the interactions between the chlorine atom and each of the fluorine substituents is not quite the same. Adding the same interaction potential is a good first order approximation, but can get the successive differences wrong by as much as 15%.

The EDA has shown that the favorability of the anion-π interaction when the benzene ring is highly substituted is a result of electrostatic interactions with the anion, agreeing with the argument of Wheeler and Houk. However, the effects are not quite additive, as different fluorine atoms cause somewhat different changes to the multipole moments of the
system. Furthermore, as was described earlier, the even this level of additivity is a result of perpendicular path over which the ion was translated.

### 4.5.2 Angled path

To demonstrate this, the same calculations can be repeated where the anion is instead moved at a $30^\circ$ angle instead. Only benzene, PhF, and PhF$_2$ are included here, so as to show the difference between a polar and nonpolar system when the ion’s path is not perpendicular to the dipole. The binding energy is shown in figure 4.16. As can be seen, the first fluorine atom makes the interaction more favorable, but the second one cancels the dipole effect and makes the overall interaction less favorable than the unsubstituted benzene. This shows that the simple additive nature of the interaction with the substituents depends on that path of the ion being perpendicular to the dipole. Otherwise, the in-plane components affect the energy and the interactions must be considered as vectors. Once again, the main change in the EDA components between systems is found in the frozen term, though PhF$_2$ does have a somewhat larger dispersion interaction in the short range due to the proximity of the ion and the second fluorine atom.

![Graph showing binding energy of three different anion-π interactions, with an angled path](image)

Figure 4.16: Binding energy of three different anion-π interactions, with an angled path

To make this clearer, the differences in the frozen energy between benzene and PhF as well as between PhF and PhF$_2$ are shown in figure 4.17. As can be seen, the two curves do not resemble each other. The benzene to PhF difference is dominated by the interaction with the molecular dipole. The long range of the PhF to PhF$_2$ is opposite and roughly equal as the dipole is canceled by the second fluorine atom. However, in the close range, the added interaction is attractive. This happens because the second fluorine atom (like the first) increases the favorability of the quadrupole and of some higher moments. Therefore, simply adding the interaction energy with each atom is not sufficient, as the quadrupole is reinforced and the dipole is canceled. However, the situation is somewhat more complicated
than this. The dipole moment is not the only one that is canceled with the addition of the second fluorine atom. At the quadrupole level, in the x-z plane, $Q_{z2}$ is not the only important moment. $Q_{x^2-y^2}$ also contributes. As shown earlier, $Q_{z2}$ is approximately doubled from PhF to PhF$_2$ because the two C-F bonds reinforce each other. However, $Q_{x^2-y^2}$ is 0 for benzene and PhF$_2$ by symmetry, but $-6.6$ D·Å for PhF. It is another example of a multipole moment that is canceled rather than reinforced, so even at the quadrupole level, the interaction energies cannot simply be added.

This continues for higher moments. Symmetry also requires benzene and PhF$_2$ to have no octopole moment, but PhF has nonzero $Q_{xz2}$ and $Q_{x(x^2-3y^2)}$ moments. At the hexadecapole level, all moments reinforce. Beyond that, the pattern continues. This could be ignored for the perpendicular path, since none of the canceling moments contribute to the energy along the z axis. This left only reinforcing moments, allowing the total interaction energy with several fluorine atoms to be approximated as the sum of several identical interactions. However, along any other path, the interaction must be considered as described here. If the second fluorine atom were not in the para position, then the interactions would not exactly cancel or double, but would be somewhere in between. Therefore, the simple, linear changes in interaction energy with additional substituents is a result of the path examined and not a property of anion-π interactions in general.

![Figure 4.17: Frozen energy differences between three different anion-π interactions, with an angled path](image)

### 4.6 Conclusions

The MP2 ALMO EDA has been implemented at a production quality level. Performance is comparable to full RIMP2 for a small number of molecules, and scales better with respect to an increasing number of molecules. The implementation supports BLAS for matrix operations and OpenMP for parallelism. With this level of performance, it is practical to
apply to the EDA to systems where RIMP2 is useful. Performance is aided by the problem being naturally amenable to preconditioned conjugate gradients. This implementation can also be readily applied to modifications of MP2 theory such as spin-component scaling[40, 41] and attenuated MP2[43, 44] that improve over standard MP2 theory. We are also very interested in extending this MP2 EDA to double hybrid density functionals that offer even more significant improvements in accuracy[148–152].

The MP2 ALMO-EDA was then applied to an anion-π system. Results show that polarization, charge transfer, and dispersion were nearly unaffected by the presence of substituents, and that all of change was in the frozen interaction. This supports the idea that favorable anion-π interactions are favorable because of electrostatic interaction with the substituents, rather than because the substituents cause the π system to become electron deficient, or any other more complicated explanation.
Chapter 5

Probing the Interplay Between Electrostatics and Charge Transfer in Halogen Bonding

5.1 Introduction

Non-covalent interactions have been the subject of considerable theoretical interest in recent years for their importance in a wide variety of molecular systems[33, 38]. One type that has been especially interesting recently is halogen bonding[29, 109–111]. While the halogen bonding interactions has been known for a long time[153], it was traditionally considered to be a type of charge transfer complex[112, 113, 154], analogous to a hydrogen bond but with a halogen rather than hydrogen atom as the electron pair acceptor. More recently, there has risen an attempt to describe the interaction as being controlled by electrostatics[24, 114]. This approach is known as the σ-hole concept[25], and has been applied to a wide variety of non-covalent interactions. Proponents of the σ-hole believe in the importance of electrostatic phenomena in explaining non-covalent interactions at the expense of charge transfer, with similar theories in cases such as hydrogen bonding[111]. Some have gone as far as to doubt the validity of the concept of charge transfer[24], viewing it as a misunderstanding of polarization.

What, then, is the physical content of the σ-hole picture? The σ-hole is defined as an area of positive electrostatic potential near a potential electron pair acceptor. The electrostatic potential of a molecule is computed on an electron density isosurface – traditionally at the arbitrary value of 0.001 electrons per cubic Bohr radius. There is generally a positive potential on this surface at the point opposite the σ bond between the acceptor halogen atom and the central carbon atom. The σ-hole picture states that halogen bond is an electrostatic interaction between the area of positive potential on the acceptor and the negative potential of the donor. This is intended as a explanation for why C–X⋯B interactions are linear. Meanwhile, halogen atoms can also act as electron pair donors in C–X⋯H–A hydrogen
bonds, with the explanation that the interaction is with the region of more negative potential on the halogen atom along the line halfway in between the bond and the \( \sigma \)-hole. Looking for the \( \sigma \)-hole on hydrogen atoms participating in hydrogen bonds finds that the entire atom is of positive potential, which is put forward as an explanation for why hydrogen bonds are often bent rather than linear. A charge transfer based explanation of the linearity of halogen bonds would instead describe the interaction as donation from the donor lone pair into the \( \sigma^* \) antibonding orbital. This orbital has its highest value in-line with the bond, but in the region beyond both of the bonded atoms, which is to say that the accessible lobe of the \( \sigma^* \) orbital is in the same place as the \( \sigma \)-hole. Furthermore, a halogen atom acting as an electron pair donor would donate from a lone pair orbital, which are centered about 75° from the point opposite the bond. Proponents of the charge transfer picture would argue that donation into the \( \sigma^* \) orbital would tend to lengthen, weaken, and red-shift the bond, all of which are experimentally observed in halogen bonds. The \( \sigma \)-hole response to this objection would be that these observations are the result of polarization in response to the presence of the donor\[155-157\]. Because of this consideration, some advocate calculating the \( \sigma \)-hole in the presence of a point charge when the donor is an anion, in order to account for polarization[158].

One of the major arguments deployed in favor of the \( \sigma \)-hole explanation is that the strength of interactions tend to correlate linearly with the size of the \( \sigma \)-hole[114, 159-161]. This has been the trend in several different sets of related molecules. This is often taken as proof for the key importance of the \( \sigma \)-hole in understanding halogen bonding. But there is almost necessarily a high level of concordance between these two pictures as they both attempt to describe the same phenomena. The \( \sigma \)-hole and the lobe of the \( \sigma^* \) orbital are in the same place because most the local electron density is concentrated in the \( \sigma \) orbital, and the \( \sigma^* \) must be orthogonal to that. There is high electrostatic potential between the bond and the \( \sigma \)-hole in the same place as the lone pair orbitals because the electrons are in the non-bonded sp\(^3\) orbitals. Polarization and charge transfer leading to similar behavior in the \( \sigma \) bond is not surprising because both are favorable in the same situations. And the correlation of the binding energy with the \( \sigma \)-hole strength may be because electrostatics, but that does not mean that electrostatics plays the sole role in the interaction. All but the most strident proponents of a charge transfer picture also recognize that electrostatic effects are also important in hydrogen and halogen bonds. While the bonds are not always perfectly in the direction of the dipole moments, there are usually close and are almost never observed opposing the dipole moments (and when they are, it is in large molecules with far away dipoles — the local electrostatics are still favorable). In addition to a purely electrostatic explanation, this arrangement also makes charge transfer more favorable, as it allows the charge density to move to an area of more positive potential. The \( \sigma \)-hole may be good proxy for the overall classical electrostatic interaction — a simpler alternative to considering every multipole moment of the two molecules. In large molecules, lower moments give more information about the whole molecule. Information about the local electrostatics is contained in the higher moments, but in a way that is opaque to understanding. Part of the value may come from providing a good heuristic to the local electrostatic environment
in complicated systems. But that doesn’t make it a unique or uniquely good parameter. In small, symmetrical molecules like the ones that will be discussed here, the dipole moment should be at least as good of an electrostatic parameter. The question is then whether this is enough, or whether the $\sigma$-hole can only explain electrostatics, and it is also necessary to consider strength of charge transfer in cases where the two are not correlated (though there is good reason to think that they usually will be).

Recent work by Stefan Huber and colleagues demonstrate a simple family of halogen bond complexes where the trend in binding strength is exactly opposite the trend in $\sigma$-hole size[162]. With an acceptor molecule of CX$_3$I (where Y is any of F, Cl, Br, and I) and donors as a halide ion or trimethylamine molecule, iodine as a substituent leads to the strongest interaction, and fluorine the weakest in the order of the periodic table. Of course, the electronegativity trend in halogens goes the opposite direction. This makes CF$_3$I have the strongest favorable dipole moment, while CI$_4$ has no dipole at all. The $\sigma$-hole trend is the same as the electronegativity one. That means both measures of electrostatics predict the opposite of the observed trend. This remains the case when varying the halide donor or when changing the acceptor atom from I to Br or Cl. The most straightforward explanation is that CI$_4$ is the strongest charge acceptor and that this is enough to overcome the more favorable electrostatic properties of CF$_3$I. They propose the explanation that CI$_4$ has the lowest energy $\sigma^*$ orbital, which allows for stronger charge transfer (according to a charge donation point of view, the interaction strength should go up with $|\langle \sigma^* | H | n \rangle|^2$ and go down with $E_{\sigma^*} - E_n$. The limit is $|\langle \sigma^* | H | n \rangle|^2$ when the denominator is large compared to the numerator). If this point of view is accepted it seems a perspective must be taken that is richer than $\sigma$-hole allows, where electrostatics and charge transfer must be considered as separate forces at play in non-covalent interactions. In this work, we will examine some of these systems more closely and try to determine the necessity of charge transfer in the picture of halogen bonding.

5.2 Methods

The energy decomposition analysis (EDA) methods used here are the SCF absolutely localized molecular orbitals (ALMO) EDA[26, 27] and its MP2 extension[29, 30]. The SCF version can be applied to either Hartree–Fock or DFT and the MP2 version decomposes the electron correlation contribution to the binding energy in a way compatible with the HF EDA. By construction, each version of the EDA exactly decomposes the supermolecule binding energy — the difference between the energy of the complex and the energies of the isolated monomers. Intermediate energies are defined and EDA components are successive differences between these energies. Three components appear in both the SCF and MP2 EDAs, and a fourth is specific to the MP2 version. The first component is the frozen electrostatic term. It describes the interaction between the monomers when their wave functions are not allowed to relax in response to each other and includes Pauli repulsion and permanent electrostatics. The next is polarization. It permits relaxation, but not transfer of charge between molecules, and it describes induced electrostatics. Third is charge transfer,
which allows the exchange of electron density between molecules and describes intermolecular covalent-like interactions. The final component, which only appears in the MP2 EDA is dispersion, which is not described at all by HF and only poorly by density functionals that do not contain empirical dispersion corrections or a van der Waals density functional.

For each intermediate energy, there are corresponding definitions for SCF methods and for the MP2 correlation energy. The MP2 intermediate is the sum of the HF intermediate and the MP2 correlation intermediate. The first intermediate is the frozen energy. For SCF, the wave functions of each isolated molecule are combined into one spanning the entire system, and its energy is evaluated. The MP2 equivalent is defined similarly, though the procedure is more complicated. The MP2 solutions for the isolated molecules are used, though they must be evaluated through the Hylleraas functional rather than the normal MP2 energy expression. Additionally, an orbital relaxation correction must be applied because MP2 is not a variational method. The difference between this energy and the energy of the isolated molecules is the frozen term. The second intermediate is the polarized energy. The SCF version is the SCF for molecular interactions (SCF-MI) solution. This is the minimum energy wave function subject to the constraint that molecular orbitals belonging to one molecule do not include any atomic orbital basis functions belonging to any other molecule. These orbitals are the ALMOs for which the method is named. Their importance is that they, unlike canonical molecular orbitals, allow each orbital to be associated with a particular molecule. The corresponding polarized MP2 intermediate is the MP2 energy using the ALMOs as a basis, but only allowing double excitations completely local to one molecule. The difference between the polarized and frozen energies is the polarization term of the EDA. The final intermediate exists only for MP2. It is the charge conserving correlation energy. The is the MP2 energy again using the ALMOs as the one-particle basis, but with the constraint relaxed to allow double excitations between two molecules as long they do not change the number of electrons associated with each molecule. The difference between this and the polarized MP2 correlation energy is the dispersion term. Finally, the difference between the full energy of the supersystem and the previous intermediate (polarized for SCF and charge conserving correlation for MP2) is the charge transfer term of the EDA.

The most common way to apply an EDA traditionally has been by applying it to a single structure for each system (most commonly the minimum energy geometry) and decomposing that binding energy. However, an alternative method that has recently been proposed is the adiabatic EDA[163]. In it, instead of there being only a single structure, the system geometry is optimized at each successive level of the EDA: first the isolated molecules, then the system with only the frozen component allowed (this will include dispersion for dispersion corrected density functionals), next with both the frozen and polarization terms, and finally also allowing charge transfer, which means optimizing the overall energy. This way, the effect of each component can be seen on the geometry of the system and, for example, the charge transfer energy can defined as the difference in energy between the optimum structures with and without charge transfer. As analytical gradient code is not yet available for the MP2 EDA, the adiabatic EDA in this paper was be done using Powell's method[164] on the internal coordinates, which does not require derivatives.
CHAPTER 5. INVESTIGATION OF HALOGEN BONDING

The calculations were performed in a development version of the Q-Chem quantum chemistry program package[105]. RI-MP2 was used for all calculations with the def2-TZVPP basis set using the rimp2-aug-cc-pVTZ auxiliary basis set. The def2-TZVPP set includes an ECP on the iodine atom. For EDA calculations, H functions were removed from the auxiliary basis set because of code limitations. Energy differences resulting from this change were negligible. Counterpoise correction was used for all energies. All geometries were optimized with the same method and basis sets, with no constraints for the minima and with the I-Y\(^-\) distance constrained for the potential energy scan.

5.3 Results

In halogen bonds between the acceptor molecule CX\(_3\)I and the donor ion Y\(^-\), the trend in binding energy across different halogen substituents (X=F, Cl, Br, I) has been shown to be opposite of that which is predicted by the \(\sigma\)-hole theory. Fluorine is the most electronegative atom, and so causes the highest potential in the \(\sigma\)-hole on the acceptor iodine atom. However, iodine is the substituent that leads to the strongest binding. This remains the case with several different halogen ions as the donor (Y=F\(^-\), Cl\(^-\), Br\(^-\)), as well as with other donors. The trend is also opposed to the electrostatic one. CF\(_3\)I has a strong favorable charge-dipole interaction with the ion, while Cl\(_4\) has none. The different binding energies are shown in Figure 5.1.

![Figure 5.1: Binding energy of CX\(_3\)I-Y\(^-\), for X=F, Cl, Br, I and Y=F, Cl, Br](image)

This shows the previously discovered unexpected trend. Changing the donor ion changes the strength of the interaction, but leaves the overall trend nearly the same. This raises the question of why the observed trend occurs, given that it contradicts the simple electrostatic prediction and a widely held theory. EDA will now be used to attempt to answer this question. First, the binding energies are decomposed into charge transfer in Figure 5.2 and frozen+polarization (which includes electrostatic and Pauli repulsion) in Figure 5.3. The dispersion interaction is similar enough in all cases to not affect the overall picture.
CHAPTER 5. INVESTIGATION OF HALOGEN BONDING

The decomposition attributes the substituent trend to increased charge transfer going down the periodic table. The electrostatic terms show the opposite trend, but makes less of a difference to the overall binding energy changes. This is at least partially because of the weakening dipole moment. On the other hand, most of the donor ion difference arises from electrostatics. One interesting point is that Cl⁻ complexes have weaker contributions from charge transfer than F⁻ complexes do, and have more repulsive frozen interactions. The first is odd because a Cl⁻ ion would seem like a better electron donor than F⁻. The second suggests the Pauli repulsion plays a role. As this must be resolved before examining other cases in detail, the EDA must be examined over other geometries.

One way of exploring more of the configuration space is to scan over the potential energy surface. This is done by constraining the I⁻Y⁻ separation to various distances and performing a geometry optimization at each point. From there, the binding energy can be decomposed for each optimized geometry. The results of this are shown in Figure 5.4(a) for Cl₄⁻F⁻ and Figure 5.4(b) for Cl₁⁻Cl⁻. The total energy curve also includes geometrical distortion, which
is the energy difference between Cl$_4$ and its minimum geometry energy. It is not included in any of the EDA components, but is too small to be visible in an interesting way on the graphs and so not shown.

![Figure 5.4: (a) EDA for Cl$_4$F$^-$ (b) EDA for Cl$_4$Cl$^-$. The geometry is fully optimized at each I-Y$^-$ distance](image)

As can be seen, CT is actually significantly greater for Cl$^-$ than for F$^-$ over the entire range observed. The difference is factor of two or three, confirming the common-sense intuition that Cl$^-$ is a better donor for charge transfer. However, this was masked in the equilibrium structure EDA because of the different I-Y$^-$ distances. The point in each curve that is not at a multiple of 0.5 Å is the minimum energy structure. Because the F$^-$ minimum is over 0.5 Å closer, the CT when compared at the points of equilibrium is greater. The reason for the Cl$^-$ being significantly farther out despite stronger charge transfer is the much greater Pauli repulsion. At 2.5 Å, the frozen term for Cl$^-$ is over 200 kJ/mol more repulsive than for F$^-$ (and off the plotted axes). Beyond 5 Å or so, the two frozen terms coincide within a few percent, as the electrostatics of both systems are a −1 ion interacting with the same dipole. The difference in the close range is due to the much greater Pauli repulsion resulting from the bulkier nature of the Cl$^-$ ion. Most of the polarization difference is also due to Pauli repulsion, as it includes a correction to the frozen overestimation of it. In the long range, the two terms are similar because the main contribution is the charged induced dipole on the Cl$_4$ molecule. Dispersion would also favor Cl$^-$, but the difference is not major. The fact that the equilibrium EDA obscured that Cl$^-$ is a better electron donor than F$^-$ shows the importance of EDA methods that look beyond a single structure.

An alternative approach is the adiabatic EDA[163]. The results are shown in table 5.1.

In that framework, the binding energy difference comes at the electrostatic level. The energy of the polarized geometry is −105 kJ/mol for F$^-$, but only −54 kJ/mol for Cl$^-$. From there, charge transfer adds 98 kJ/mol for F$^-$ and 72 kJ/mol for Cl$^-$ when the systems are relaxed to their full minimum. The adiabatic EDA describes charge transfer as being stronger with F$^-$. However the two numbers are close, which is impressive for Cl$^-$ because
the interaction occurs at more than 0.5 Å greater distance. Looking at the adiabatic picture makes the importance of the greater distance clear because of the focus on the different geometries. Therefore, the three different ways of applying the EDA give three different pictures. At equilibrium only, the EDA shows CT and pol being weaker, and frz less repulsive, for \( \text{Cl}^- \) without providing much insight as to why that is. The potential energy scan EDA instead shows that CT at any given I-Y\(^-\) distance is significantly stronger for \( \text{Cl}^- \), and the electrostatic parts of frz and pol roughly the same, but the much greater Pauli repulsion pushes the interaction to a larger distance where the interaction is weaker. And the adiabatic EDA says that the electrostatics alone make \( \text{Cl}^- \) bind much weaker and farther than \( \text{F}^- \), but that charge transfer plays a similarly sized role in both systems despite the larger distance. The latter two tackle the problem from different directions and provide complementary insights, but the first alone is not very enlightening.

With that settled, we can now turn back to the original question of the trend as substituents change. A similar analysis is necessary to tell which effects are genuinely weakened from \( \text{Cl}_4 \) to \( \text{CF}_3 \text{I} \) and which appear lower due to the greater interaction distances. To start, the results of the relaxed potential energy scan EDA are shown in Figure 5.5(a) for \( \text{CF}_3 \text{I}-\text{F}^- \) and Figure 5.5(b) for \( \text{Cl}_4-\text{F}^- \) (repeated from Figure 5.4(a) for ease of comparison).

Comparing, we see that \( \text{Cl}_4 \) has the greater charge transfer everywhere, by about 20 kJ/mol in the equilibrium range. This is about half the difference between the two binding energies. Much of the rest of the difference comes from the fact that \( \text{Cl}_4 \) binds the fluoride closer, with equilibrium interaction distance of 2.11 Å, vs 2.20 Å for \( \text{CF}_3 \text{I} \). This happens because the greater CT is enough to overcome the frozen repulsion to a greater extent, even though it is more repulsive for \( \text{Cl}_4 \). The large dipole moment of \( \text{CF}_3 \text{I} \) shows up in the frozen term and is the main reason that it is less repulsive. However, the greater charge transfer is enough to compensate for the increase in the barrier, which is why the trend in these systems is opposite that predicted by electrostatics. While the EDA shows polarization as

### Table 5.1: Adiabatic EDA. All energies in kJ/mol. Dipole moment is of \( \text{Cl}_4 \).

<table>
<thead>
<tr>
<th></th>
<th>( \text{Cl}_4-\text{F}^- )</th>
<th></th>
<th>( \text{Cl}_4-\text{Cl}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sep</td>
<td>FRZ</td>
<td>POL</td>
</tr>
<tr>
<td>( E_{rel} )</td>
<td>0.000</td>
<td>-30.167</td>
<td>-105.670</td>
</tr>
<tr>
<td>( GD )</td>
<td>0.000</td>
<td>1.572</td>
<td>2.065</td>
</tr>
<tr>
<td>( \text{frz} )</td>
<td>-27.255</td>
<td>4.917</td>
<td>173.846</td>
</tr>
<tr>
<td>( \text{ct} )</td>
<td>-150.944</td>
<td>-142.210</td>
<td></td>
</tr>
<tr>
<td>( r(\text{C-X}) ) (Å)</td>
<td>2.132</td>
<td>2.147</td>
<td>2.151</td>
</tr>
<tr>
<td>( \angle(\text{X-C-X}) ) (°)</td>
<td>109.47</td>
<td>111.02</td>
<td>111.24</td>
</tr>
<tr>
<td>( r(\text{C-I}) ) (Å)</td>
<td>2.132</td>
<td>2.102</td>
<td>2.125</td>
</tr>
<tr>
<td>( r(\text{I-Y}) ) (Å)</td>
<td>-2.989</td>
<td>2.506</td>
<td>2.113</td>
</tr>
<tr>
<td>Dipole (D)</td>
<td>0.000</td>
<td>0.105</td>
<td>0.073</td>
</tr>
</tbody>
</table>
larger than charge transfer, in the short range the frozen and polarization terms have to be considered together as they both describe the Pauli effect to some extent. Looking at the difference between the two polarization terms, we see that polarization is more favorable for Cl by about the same amount as charge transfer. This is because Cl is more polarizable than CF3I. However, this alone would only be enough to make the interactions roughly equal in strength. Charge transfer is necessary to account for the Cl binding being significantly stronger.

The rest comes from the one body energies (once again, dispersion is essentially the same between the two systems). The Cl at equilibrium is 12 kJ/mol above its minimum geometry energy, while for CF3I the number is 20 kJ/mol even though the interaction is weaker and therefore likely to have less of an effect on the geometry. This difference is significant on the scale of the difference between the interactions, suggesting that part of the stronger interaction with Cl may be because it is more easily able to deform into the ideal geometry for charge transfer.

The same question can also be tackled with the adiabatic EDA, which can indicate how the different intermolecular forces influence the geometry of the system and allow the addition of each force to be considered separately. The CX3I−Y− system is simple enough that geometries can be specified by four parameters: C−X bond length, X−C−X bond angle, C−I bond length, and I−Y− distance. The relative energies and geometry parameters for each system are shown in table 5.2. To match the procedure used with the DFT version of the adiabatic EDA, dispersion is included along with the frozen interaction.

The adiabatic EDA confirms that charge transfer is significantly stronger with iodine as the substituent atoms. While the polarized structures have roughly similar energies, Cl has 40 kJ/mol more gain in binding energy with the introduction of charge transfer than CF3I. Most of the difference in polarization goes to overcoming the 15 kJ/mol that the frozen interaction favors CF3I by. The adiabatic EDA confirms that polarization is only enough to make the two interactions roughly equal in strength, and charge transfer explains the large
Aside the from the shrinking I–F distance, a notable trend is in the C–I bond length. The frozen geometries have a shorter bond than the isolated geometries, while the fully minimized geometries have a significantly longer one. As is typical, charge transfer into the acceptor bond weakens it and increases the length. On the other hand, a shorter C–I bond apparently leads to more favorable electrostatics, so the C–I bond length provides a measure of the relative importance of charge transfer and electrostatics. Interestingly, this leads to opposite trends in the dipole moment of the acceptor molecule. For CF$_3$I, dipole moment increases at every successive stage. With Cl$_4$F, this is not the case. The isolated molecule has no dipole by symmetry, but the presence of the fluoride ion causes the molecule to shift to a slightly polar geometry at the frozen level. However, the polarized geometry reduces this, and the final geometry reverses it, leading to a moderate dipole moment away from the ion. This is further evidence that the halogen bond is not a primarily electrostatic phenomenon.

Incidentally, this means Cl$_4$F has a long range favorable frozen interaction despite being nonpolar. It shows up in the potential energy scan because each point is an optimization with a constrained I–F distance. In the long range, where charge transfer in unimportant, the molecule can deform to be slightly polar and have a small favorable charge-dipole interaction with the ion. This supports the conclusion from the adiabatic EDA and explains it in terms of the dipole moment. Figure 5.6 shows the dipole moment for CX$_3$I at each point of the scan.

In the long range Cl$_4$F does have a slight dipole moment for the reasons described above, and it increases until 4 Å. The CF$_3$I dipole also increases over this range. But while the CF$_3$I dipole continues to increase over the whole range, to nearly double its original value, the Cl$_4$F reverses and actually becomes unfavorable in the interaction region. This mirrors the trend in the adiabatic EDA. The trends suggest that electrostatic effects are very important
for the CF₃I geometries, as the presence of the ion pushes the dipole moment significantly higher, but that electrostatics and charge transfer have opposing roles in determining the Cl₄ geometry and charge transfer wins out. One of the most important geometrical parameters is the C–I bond length, which is plotted at the different points of the scan in Figure 5.7. The dotted lines are bond lengths at the monomers’ minimum energy geometries, which are the right asymptotes of the graphs. In both cases, the bonds are lengthened in the interaction region, though the effect is larger for Cl₄ as expected from its greater charge transfer. But in Cl₄ the bond lengthening is accompanied by an unfavorable dipole moment, while in CF₃I it is not. This suggests that, at least in Cl₄, the C–I bond length can be used as a measure of the relative importance of electrostatics and charge transfer.

The conclusion supported by both EDA views is that electrostatics and charge transfer both play a role in the two examined halogen bonds. Electrostatics favors CF₃I while charge transfer favors Cl₄ strongly enough that it is the significantly stronger interaction despite
the electrostatics. Furthermore, the analysis seems to suggest that the CF$_3$I interaction is in some ways electrostatically dominated, with the geometry deforming to one favored by electrostatics. On the other hand, Cl$_4$ seems charge transfer dominated, deforming to geometries against what is electrostatically favorable.

If those are examples of halogen bonds, one with good electrostatics but poor charge transfer and one with good charge transfer but poor electrostatics, it is useful to examine a case that is good on both counts. It is necessary to use a somewhat contrived example to accomplish this, but the nitro group is more electrostatic than fluorine and about as conducive to charge transfer as iodine. The molecule C(NO$_2$)$_3$I forms an incredibly strong bond with F$^-$ of about 260 kJ/mol, which is in the range of some covalent bonds. A potential energy scan of this system is shown in Figure 5.8.

![Figure 5.8: EDA for C(NO$_2$)$_3$I–F$^-$](image)

The most noticeable difference on the graph is how much more favorable the frozen interaction is. At 2.5 Å, it is about 45 kJ/mol more favorable than even CF$_3$I, largely because of its huge dipole moment of 3.2 D (compared to 0.91 D). But unlike CF$_3$I which has a large increase in dipole moment as the ion gets closer, C(NO$_2$)$_3$I shows more moderate behavior. The dipole moment increases slightly to a maximum of about 3.4 D at around 3 Å, but it drops back down to 3.3 D at equilibrium. This suggests that despite the dipole, the nature of the system is more similar to Cl$_4$. Turning to charge transfer, we see behavior very similar to Cl$_4$. In the range of 2–3 Å, it is about 10% stronger in C(NO$_2$)$_3$I. In the longer range, the charge transfer appears to be more slowly decaying, reaching twice the strength of Cl$_4$ by 7 Å, but genuine charge transfer is difficult to distinguish from basis set superposition error at this distance. It seems that the properties of Cl$_4$ that make it favorable to charge transfer are matched or slightly exceeded by C(NO$_2$)$_3$I. Finally (ignoring dispersion once again), there is polarization. The value for C(NO$_2$)$_3$I falls halfway in between CF$_3$I and Cl$_4$ along the whole curve. While the polarization term contains some correction to Pauli repulsion in the short range, the differences between these three seem to be electrostatic in nature, as all three systems have the same strength of Pauli repulsion. The charge induced
dipole of the acceptor molecule should be much stronger than the dipole induced dipole on
the $\text{F}^-$ ion, so it is the main contributor to the polarization term. The polarizability of
$\text{C(NO}_2\text{)}_3\text{I}$ is in between that of the other two acceptor molecules. That means these systems
provide an example of a case where the trend in polarizability is different from the trend in
charge transfer. Therefore, a picture of halogen bonding that replaces charge transfer with
polarization would be unable to explain the strength of the $\text{C(NO}_2\text{)}_3\text{I}--\text{F}^-$. With the dipole
moment greater than in $\text{CF}_3\text{I}$, but the polarizability lower than in $\text{Cl}_4$, a purely electrostatic
model should not predict the extremely strong halogen bond observed.

The comparison between $\text{CF}_3\text{I}$, $\text{Cl}_4$, and $\text{C(NO}_2\text{)}_3\text{I}$ shows that electrostatics and charge
transfer act separately as forces in the halogen bond. They can be present in different
strength in different systems, and either one alone would be insufficient to understanding
the interaction. In $\text{CF}_3\text{I}$ there is a favorable dipole moment, in $\text{Cl}_4$ there is strong charge
transfer, and in $\text{C(NO}_2\text{)}_3\text{I}$ there is both. It is important to examine more than just the
equilibrium geometry when analyzing the interaction as the geometry is determined by the
balance of frozen electrostatics, induced electrostatics, dispersion, and intermolecular charge
transfer working against the wall of Pauli repulsion, so looking only at one geometry conflates
the influences of all these forces. All of them are important for determining the overall
interaction (though dispersion is very similar across the different systems, and so is not
important for comparisons), so each needs to be considered separately.

5.4 Conclusions

For the systems $\text{CX}_3\text{I}$, it has been previously shown that the $\sigma$-hole theory predicts the
incorrect trend in binding energy strength. It has been suggested that this is because the
$\sigma$-hole is a purely electrostatic descriptor, and some treatment of charge transfer is necessary
to fully describe halogen bonding as the two do not always coincide. Using energy decompo-
sition analysis, it was shown that charge transfer is indeed the differentiator between these
systems. While the electrostatic trends are in the direction predicted by the $\sigma$-hole strength
(and the dipole moment), the charge transfer trend is in the opposite direction and strong
enough to overcome this deficit. The adiabatic EDA and EDA over the relaxed potential
energy scan showed that only looking at the equilibrium is not enough, as the equilibrium
graphomy is determined by the balance between electrostatics, Pauli repulsion, charge trans-
fer, and other effects, which all have different length scales. The analysis implies that the
trend in binding energy is due to iodine substituents making the molecule a better acceptor
for charge transfer. Comparison to another system showed that electrostatic favorability
and charge transfer can vary separately. Because of this, it seems that no picture of the
halogen bond can be complete without accounting for charge transfer and for the Lewis
acid’s suitability as an electron pair acceptor as well as its electrostatic properties. We hope
to follow this work with an analysis of different parameters for estimating charge transfer
strength across a wide variety of halogen bonded systems and propose a suitable measure to
augment the $\sigma$-hole as a second parameter in a heuristic for estimating the strength of these
non-covalent interactions.
References


(42) Grabowski, I.; Fabiano, E.; Sala, F. D. A simple non-empirical procedure for spin-component-scaled MP2 methods applied to the calculation of the dissociation energy curve of noncovalently-interacting systems. *Physical Chemistry Chemical Physics* 2013, 15, 15485.


REFERENCES


REFERENCES


(111) Grabowski, S. J. Hydrogen and halogen bonds are ruled by the same mechanisms. *Physical Chemistry Chemical Physics* 2013, *15*, 7249.


REFERENCES


