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**New Theoretical Developments in Exploring Electronically Excited States:
Including Localized Configuration Interaction Singles
and Application to Large Helium Clusters**

by

Kristina Danielle Closser

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 Head-Gordon, Chair
Professor William H. Miller
Professor Jeffrey Neaton

Fall 2014

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and Application to Large Helium Clusters**

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Kristina Danielle Closser

Abstract

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This thesis presents new developments in excited state electronic structure theory. Contrasted with the ground state, the electronically excited states of atoms and molecules often are unstable and have short lifetimes, exhibit a greater diversity of character and are generally less well understood.

The very unusual excited states of helium clusters motivated much of this work. These clusters consist of large numbers of atoms (experimentally $10^3 - 10^9$ atoms) and bands of nearly degenerate excited states. For an isolated atom the lowest energy excitation energies are from $1s \rightarrow 2s$ and $1s \rightarrow 2p$ transitions, and in clusters describing the lowest energy band minimally requires four states per atom. In the ground state the clusters are weakly bound by van der Waals interactions, however in the excited state they can form well-defined covalent bonds.

The computational cost of quantum chemical calculations rapidly becomes prohibitive as the size of the systems increase. Standard excited-state methods such as configuration interaction singles (CIS) and time-dependent density functional theory (TD-DFT) can be used with ≈ 100 atoms, and are optimized to treat only a few states. Thus, one of our primary aims is to develop a method which can treat these large systems with large numbers of nearly degenerate excited states. Additionally, excited states are generally formed far from their equilibrium structures. Vertical excitations from the ground state induce dynamics in the excited states. Thus, another focus of this work is to explore the results of these forces and the fate of the excited states.

Very little was known about helium cluster excited states when this work began, thus we first investigated the excitations in small helium clusters consisting of 7 or 25 atoms using CIS. The character of these excited states was determined using attachment/detachment density analysis and we found that in the $n = 2$ manifold the excitations could generally be interpreted as superpositions of atomic states with surface states appearing close to the atomic excitation energies and interior states being blue shifted by up to ≈ 2 eV.

The dynamics resulting from excitation of He_7 were subsequently explored using ab initio molecular dynamics (AIMD). These simulations were performed with classical adiabatic dynamics coupled to a new state-following algorithm on CIS potential energy surfaces. Most clusters were found to completely dissociate and resulted in a single excited atomic state (90%), however, some trajectories formed bound, He_2^* (3%), and a few yielded excited trimers ($< 0.5\%$). Comparisons were made with available experimental information on much larger clusters.

Various applications of this state following algorithm are also presented. In addition to AIMD, these include excited-state geometry optimization and minimal energy path finding via the growing string method. When using state following we demonstrate that more physical results can be obtained with AIMD calculations. Also, the optimized geometries of three excited states of cytosine, two of which were not found without state following, and the minimal energy path between the lowest two singlet excited states of protonated formalimine are offered as example applications.

Finally, to address large clusters, a local variation of CIS was developed. This method exploits the properties of absolutely localized molecular orbitals (ALMOs) to limit the total number of excitations to scaling only linearly with cluster size, which results in formal scaling with the third power of the system size. The derivation of the equations and design of the algorithm are discussed in detail, and computational timings as well as a pilot application to the size dependence of the helium cluster spectrum are presented.

Dedicated to Bethany Leanne Closser (1989-2012)

You have been a part of my life ever since your birth and have shaped who I am today in such profound ways that you will never know. I realize you would not understand most of this thesis, but you would understand that I will miss you and love you always.

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I would never have reached or even considered graduate school without my undergraduate advisor Kevin Shea. As the first in my family to attend a four-year college I was completely clueless about anything beyond a bachelor's degree. It was also very important to know that others from Smith College believed in me, I would have been sorely tempted to quit without continued encouragement from Shizuka Hsieh, Ruth Haas and many others.

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Part I

Introduction

Chapter 1

Introduction

Electronically excited states are vital to understanding many apparently disparate phenomena: from biological reactions such as photosynthesis,^{1,2} DNA damage,^{3,4} and vision,^{5,6} to modern electronic devices⁷ and artificial light harvesting.^{8,9} When contrasted with the ground state of an atom or molecule, excited states generally exhibit much more diversity in their character, are less stable, and less well understood. All of these features result in significant demands for theoretically modeling the electronically excited states of atoms and molecules.

In this thesis, some recent developments in theoretical methods for computing the excited states of large atomic and molecular clusters, and in understanding the ultimate fate of such excitations will be addressed.

1.1 Electronic States

One of the fundamental results of quantum mechanics is that atoms and molecules exist in discrete energy states.^{10,11} This condition arises from the confinement of electrons to specific regions in space. The lowest-energy state is defined as the ground state, and higher energy states correspond to excited states.

Transitions between these states are inherently quantum mechanical processes, which more often than not result in non-equilibrium states that can then induce changes in the molecular structure.^{12,13} This can result in the formation of new chemical species, or significant changes in the molecular geometries. Often excited states are formed upon absorption of a photon, and some of the photochemical processes that can result from such an event are illustrated by the cartoon in ???. Excited states are by definition, higher in energy than the ground state and will ultimately decay back to the original ground state by emitting a photon or through radiation-less transitions, or they may undergo a reaction to form new products, giving rise to their finite lifetimes.

One challenge of excited-state electronic structure theory becomes readily apparent even in a simple two-state system such as in ??. This is determining the state of the system

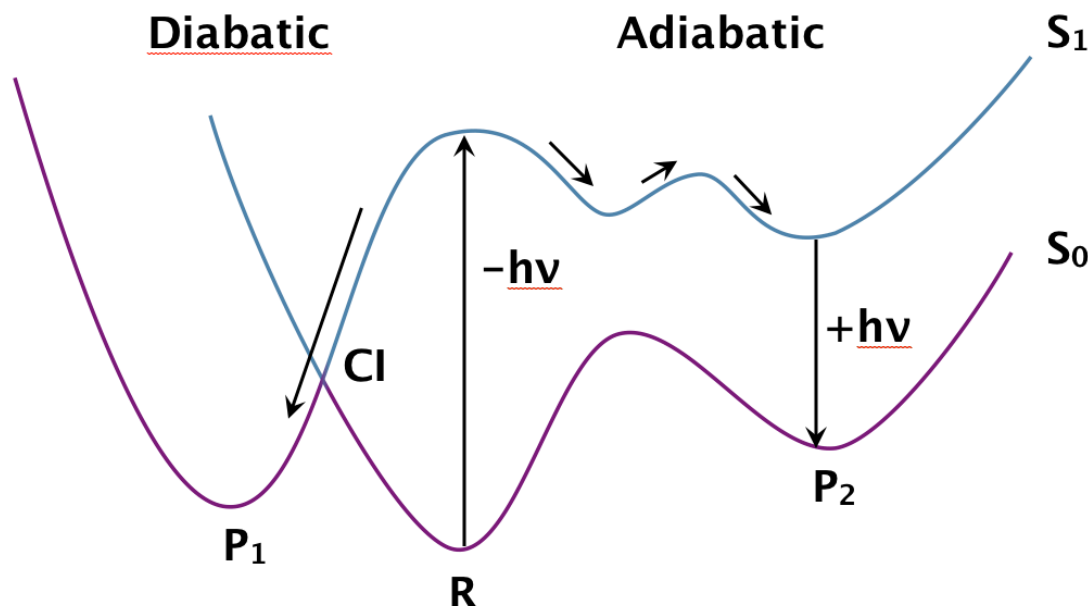


Figure 1.1: Schematic illustration of adiabatic and diabatic reaction paths after excitation from S_0 to S_1 . After vertical excitation of reactant R , if the excited electron does not immediately return to the lower state via fluorescence, it can cross back to the lower state diabatically to form product P_1 or travel along the adiabatic surface before dropping back to the ground state to form product P_2

at any given point in time. Consider that, phenomenologically, after the absorption of a photon there are two primary ways for the dynamics of the system to proceed: along the adiabatic surface where the energy ordering is preserved or along the diabatic surface where the character of the state is preserved.[?] Adiabatic surfaces are formed when the nuclei move slowly enough that the electrons can adapt instantaneously, and, in contrast, diabatic states result when the nuclei move rapidly and the electron density can not adapt in this way. Thus, diabatic states tend to preserve the character of the state (i.e. a system in a π^* -type orbital will remain in a π^* -type orbital even after rearrangement of the nuclei). This concept will be discussed further in the context of the adiabatic and Born-Oppenheimer approximations (??).

While the dynamics of the system are critical to understanding their behavior, the first challenge is to compute the relative energies of the states with sufficient accuracy to obtain the correct results. For the rest of the introduction we shift our focus to considering how these electronic states are computed using quantum mechanics and return to the concept of motion along a potential surface in ????

1.2 Quantum Chemistry

The ultimate goal of quantum chemistry is to solve the Schrödinger equation, which determines the energy and behavior of an atomic or molecular system. In the most general form this equation can be written as

$$\hat{\mathcal{H}} \left| \Phi(r_i, R_A; t) \right\rangle = i \frac{\partial}{\partial t} \left| \Phi(r_i, R_A; t) \right\rangle, \quad (1.1)$$

where $\left| \Phi(r_i, R_A; t) \right\rangle$ is a wavefunction which fully describes the system and depends on the electronic r_i and nuclear coordinates R_A (which are a function of time), and the Hamiltonian $\hat{\mathcal{H}}$ is the operator that determines the energetics and behavior of the system. In this time-dependent formulation of ?? there is no requirement that the behavior of the system remain constant as a function of time. If, however, the system does exist in a stationary state it is possible to eliminate time from the equation and use only the time-independent equation which defines the energy, E , of a stationary system.

$$\hat{\mathcal{H}} \left| \Phi(r_i, R_A) \right\rangle = E \left| \Phi(r_i, R_A) \right\rangle, \quad (1.2)$$

The Hamiltonian consists of terms relating to the potential and kinetic energies of the particles and acts on the wavefunction. It has the form:

$$\hat{\mathcal{H}} = - \sum_i^n \frac{\nabla_i^2}{2} - \sum_A^N \frac{\nabla_A^2}{2M_A} - \sum_i^n \sum_A^N \frac{Z_A}{|r_i - R_A|} + \sum_i^n \sum_{j < i}^n \frac{1}{|r_i - r_j|} + \sum_A^N \sum_{B < A}^N \frac{Z_A Z_B}{|R_A - R_B|} \quad (1.3)$$

which can be abbreviated

$$\hat{\mathcal{H}} = \hat{T}_{ee} + \hat{T}_{NN} + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN}. \quad (1.4)$$

The first two terms correspond to the kinetic energy of the electrons and nuclei respectively, the third is the nuclei-electron attraction, the fourth the electron-electron repulsion, and fifth corresponds to the nuclear repulsion. Note that this, and other equations throughout this thesis are expressed in terms of atomic units. Unfortunately, or perhaps fortunately for quantum chemists, it is only possible to exactly solve ?? or ?? for the very smallest systems. Closed form solutions of the hydrogen atom, or hydrogen-like atoms which contain a single electron are fairly straightforward to determine,[?] and the helium or helium-like atoms with two electrons can be solved numerically to extreme precision on modern computers,[?] but larger systems are still beyond reach. Thus we resort to various approximations and some of the most fundamental will be discussed in the following sections.

1.2.1 Adiabatic and Born-Oppenheimer Approximations

The Born-Oppenheimer approximation is a fundamental simplification, which allows the separation of nuclear and electron motion.[?] Since atomic nuclei are significantly more massive than electrons, $M_{proton} \approx 1800 \cdot m_e$, the nuclear and electronic motions can be treated

independently. Thus, the wave-function describing the system can be split into an electronic part, Ψ , and a nuclear part, Θ ,

$$|\Phi(r_i, R_A)\rangle = |\Psi(r_i; R_A)\rangle |\Theta(R_A)\rangle. \quad (1.5)$$

Θ depends solely on the nuclear coordinates R_A and Ψ depends explicitly on the electronic coordinates r_i and only implicitly on the nuclear coordinates. Thus, the electronic and nuclear parts of the wavefunction can be treated independently. Likewise, the Hamiltonian can also be separated into electronic and nuclear terms.

$$\hat{\mathcal{H}} = \hat{T}_{NN} + \hat{V}_{NN} + (\hat{T}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee}) = \hat{T}_{NN} + \hat{V}_{NN} + \hat{H} \quad (1.6)$$

where $\hat{H}$ is the electronic Hamiltonian and V_{NN} is a constant.

The adiabatic approximation is very closely related and asserts that the electron must exist in a single eigenstate of the Hamiltonian, thus the adiabatic states discussed in ?? are defined to be eigenstates of the Hamiltonian.⁷ So after projection on the left with the electronic wave function, and integration over the electronic coordinates, r_i , the Schrödinger equation (??) for electronic state j with energy E_j and wavefunction $|\Psi_j(r_i; R_A)\rangle$ can be written as

$$\langle \Psi_j | (\hat{T}_{NN} + \hat{H}) | \Psi_j \rangle | \Theta_j \rangle = \langle \Psi_j | E | \Psi_j \rangle | \Theta_j \rangle \quad (1.7)$$

Defining

$$D_{jj} = \langle \Psi_j | \hat{T}_{NN} | \Psi_j \rangle$$

?? can be rewritten as

$$(\hat{T}_{NN} + E_j + D_{jj}) |\Theta\rangle = E |\Theta\rangle$$

Typically for stable systems this nuclear derivative term D_{jj} is about the size of a rotational energy level, although in the adiabatic approximation it is assumed to vanish. For well separated states, the adiabatic approximation is quite reasonable, and does not introduce significant errors. However, as will later be important for this thesis, it does break down when two or more potential energy surfaces interact.

In general, the total wave function can be written as a sum over all adiabatic states.

$$\sum_j |\Psi_j\rangle |\Theta_j\rangle = E_{tot} |\Theta_j\rangle. \quad (1.8)$$

Considering the case where only two states j and k are near each other it can be shown that

$$\langle \phi_k | \nabla \phi_j \rangle = -\frac{\langle \phi_k | \nabla \hat{H} | \phi_j \rangle}{(E_k - E_j)} \quad (1.9)$$

and

$$-\sum_{\alpha} \frac{1}{M_{\alpha}} \langle \phi_k | \nabla_{\alpha} \phi_j \rangle = \sum_{\alpha} \frac{1}{M_{\alpha}} \frac{\langle \phi_k | \nabla \hat{H} | \phi_j \rangle}{(E_k - E_j)}. \quad (1.10)$$

These two nuclear-electronic coupling terms diverge as $E_k \rightarrow E_j$ and the Born-Oppenheimer approximation fails dramatically when the two surfaces approach each other.

It has been noted that adiabatic states are defined by the eigenstates of the Hamiltonian. Here note that diabatic surfaces are defined such that the coupling term in ?? vanishes although it is not generally possible to determine exact diabatic states useful approximations have been developed.?

1.2.2 Non-adiabatic transition probability

In polyatomic molecules, regions where diabatic states cross are known as conical intersections and in diatomics they are avoided crossings.??? There is no barrier for a system to pass through a conical intersection and these points very often determine the fate of excited systems. Originally thought to be a mathematical curiosity as they were first interpreted for highly symmetric systems, they are now known to be ubiquitous among excited states.

At avoided crossings, where two adiabatic surfaces approach but do not intersect, the probability of an electronic transition occurring is related to the topology between the electronic states and the energy difference between them.? For a two state system the adiabatic energies can be written as

$$E_{\pm} = \frac{1}{2} \left(H_{11} + H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right), H_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle \quad (1.11)$$

The Landau-Zener expression then gives the probability of a transition as? ?

$$\exp \left[\frac{-H_{12}^2}{h |\dot{R}| \left| \frac{\partial}{\partial R} (H_{11} - H_{22}) \right|} \right] \quad (1.12)$$

Non-adiabatic transitions will thus increase in probability for slow moving electrons relative to the nuclear motion ($|\dot{R}| \rightarrow 0$), as the surfaces approach each other ($|\frac{\partial}{\partial R} (H_{11} - H_{22})| \rightarrow 0$) and for large coupling between the surfaces $|H_{12}| \rightarrow \infty$

1.3 Ground-state electronic structure theory

Much of modern electronic structure theory is based on expanding the wave-function (or an approximation to it) in terms of a set of atomic-centered basis functions χ .?

$$\phi_i = c_i^1 \chi_1 + c_i^2 \chi_2 + \dots + c_i^n \chi_n = \sum_{\mu}^n c_i^{\mu} \chi_{\mu} \quad (1.13)$$

For efficiency in evaluating the integrals these basis functions are often chosen to be gaussians which have the form:

$$g_{nmk}(\vec{r}) = (x^n + y^m + z^k) e^{-ar^2}. \quad (1.14)$$

This basis set approximation forms the foundation for quantum chemistry.

1.3.1 Variational Principle

As it is not possible to solve the Schrödinger equation exactly, we resort to approximations. One method of doing this is based on the variational principle.[?]

Beginning from a normalized trial wavefunction $|\Psi\rangle$, the variational principle states that any energy computed from this wavefunction, $\varepsilon = \langle \Psi | \hat{H} | \Psi \rangle$, will be greater than or equal to the true ground state energy, E_0 given by the exact wavefunction $|\Phi_0\rangle$. Expanding $|\Psi\rangle$ into a set of orthonormal basis functions yields $|\Psi\rangle = \sum_{\mu} c_{\mu} |\chi_{\mu}\rangle$ and computing the expectation value with this approximate function leads to

$$\varepsilon = \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \sum_{\mu} c_{\mu} \chi_{\mu} \left| \hat{H} \right| \sum_{\nu} c_{\nu} \chi_{\nu} \right\rangle = \sum_{\mu\nu} c_{\mu} c_{\nu} E_{\mu\nu} \delta_{\mu\nu} \quad (1.15)$$

subtracting off the true ground state energy and multiplying by $1 = \sum c_{\mu}^2$ yields

$$\varepsilon - E_0 = \sum_{\mu\nu} c_{\mu} c_{\nu} E_{\mu\nu} \delta_{\mu\nu} - E_0 = \sum_{\mu} c_{\mu}^2 E_{\mu} - \sum_{\mu} c_{\mu}^2 E_0 \implies E_{\mu} \geq E_0 \quad (1.16)$$

with $E_{\mu} = E_0$ only if the corresponding wave functions are equivalent. This principle implies as long as the physical requirements are fulfilled the estimated energy can always be improved through adding degrees of freedom to a wavefunction.

1.3.2 Hartree-Fock

The simplest ground-state wave function for a multi-electron system, expressed in that possesses the minimal requirements of antisymmetry is a determinant of the form[?]

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(1) & \phi_j(1) & \dots & \phi_n(1) \\ \phi_i(2) & \phi_j(2) & \dots & \phi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(N) & \phi_j(N) & \dots & \phi_n(N) \end{vmatrix} \quad (1.17)$$

where ϕ_i are single particle wavefunctions which are expanded into basis functions χ_{μ} . Invoking the variational principle using this wavefunction, we ultimately obtain the Hartree-Fock equations:

$$\mathbf{HC} = \mathbf{SCE} \quad (1.18)$$

where $\mathbf{C}$ is a matrix of the basis set expansion coefficients and $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$

The single particle wavefunctions are then eigenvalues of the Fock operator.

$$\hat{f} |\phi_i\rangle = \varepsilon_i |\phi_i\rangle \quad (1.19)$$

$$\hat{f} = \hat{h} + \hat{J} - \hat{K}, \text{ and } \varepsilon_i = \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i (J_{ii} - K_{ii}) \quad (1.20)$$

where i and j correspond to occupied spin-orbitals (spatial-wavefunction times the spin-function) and h_i corresponds to the one-electron integral terms of the Hamiltonian (electron kinetic energy and electron-nuclear attraction ??) and the two-electron integrals are coulomb, J_{ij} , and exchange, K_{ij} integrals where

$$\langle \mu\nu | \lambda\sigma \rangle = \int \int \chi_\mu(1) \chi_\nu(2) \frac{1}{r_{12}} \chi_\lambda(1) \chi_\sigma(2) d\tau_1 d\tau_2 \quad (1.21)$$

$$J_{ij} = \sum_{\mu\nu\lambda\sigma} c_i^\mu c_j^\nu \langle \mu\nu | \lambda\sigma \rangle c_i^\lambda c_j^\sigma \text{ and } K_{ij} = \sum_{\mu\nu\lambda\sigma} c_i^\mu c_j^\nu \langle \mu\lambda | \sigma\nu \rangle c_i^\lambda c_j^\sigma \quad (1.22)$$

Note that the spin of electron 1 must be the same as the spin of electron 2 for K_{ij} to be non-zero.

1.3.3 Configuration Interaction

One appealing aspect of wave function theories is that they can generally be improved straight-forwardly through incorporating additional degrees of freedom as implied by the variational principle. The full configuration interaction (CI) wave-function is formally exact and is formed by promoting the occupied orbitals of a reference wavefunction (often chosen to be the Hartree-Fock determinant) to unoccupied (virtual) orbitals and form new determinants with these. The reference wavefunction is given by Φ_0 , and single excitations ($i \rightarrow a$) from this are denoted s , doubles d , triples t , etc.

$$|\Psi\rangle = |\Phi_0\rangle + \sum_s c_s |\Phi_s\rangle + \sum_d c_d |\Phi_d\rangle + \sum_t c_t |\Phi_t\rangle + \sum_q c_q |\Phi_q\rangle \dots \quad (1.23)$$

Full CI scales factorially as the size of the system increases and is not feasible for any but the smallest systems. Practical variants are formed by truncating the CI expansion at a given excitation level (e.g. triples) with less severe truncations generally yielding more accurate results. ??

1.4 Excited-state electronic structure theory

Solving for the ground-state energy of a system involves finding the lowest energy eigenvalue. However, higher energy roots are available and these can be considered to be estimates of the excited state energies.

1.4.1 CI Singles and Brillouin's theorem

According to Koopman's theorem, in Hartree-Fock theory the energy of the unoccupied orbitals can be considered to be estimates of the energy of electron affinity and the occupied

orbitals can be considered to be estimates of the ionization energy.[?] Thus, a singly excited electron would have energy $\varepsilon_a - \varepsilon_i$. While this single determinant excitation is notoriously a poor approximation for excited states, a more reasonable approximation is a linear combination of all such excited determinants, which determines the CI singles wavefunction (CIS).

$$|\Psi\rangle = \sum_s c_s |\Phi_s\rangle = \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a |\Phi_a^i\rangle \quad (1.24)$$

Due to Brillouin's Theorem, the Hartree-Fock wavefunction does not couple directly the singly excited states. Thus, CIS wavefunction (??) does not couple to the ground state and can be substituted directly into the time-independent Schrödinger equation.

$$\hat{H}\Psi = E\Psi \implies A\Psi = \omega\Psi \quad (1.25)$$

with $\omega = E_{CIS} - E_0$ and $A_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia||jb)$

1.4.2 Excited state variational principles

Unlike for the ground state, the variational principle for excited states is not as straightforward.[?] There have been at least three proposed versions and although there was a bitter dispute in the literature over a period of 2 to 3 decades[?] they were ultimately shown to be equivalent—provided that imaginary variations are allowed as well as real variations.[?]

The first of these is the Dirac-Frenkel variational principle, which notes that it is sufficient to consider only variations in the wave-function bra.[?]

$$\left\langle \delta\Psi \left| \hat{H} - i\frac{\partial}{\partial t} \right| \Psi \right\rangle = 0 \quad (1.26)$$

McLachlan noted that this was not a true minimum principle for certain cases and proposed the form which came to be known as the McLachlan-Ball variational principle.[?]

$$||i\theta - H\Psi||^2 = \min \quad (1.27)$$

And the third is based on the Lagrangian $\mathcal{L} = \langle\Psi| H - i\partial_t |\Psi\rangle$ and has the form[?]

$$\delta \int_{t_1}^{t_2} \mathcal{L} dt = 0 \quad (1.28)$$

Generally, the Dirac-Frenkel principle is valid for real orbitals and is still the most commonly used. It will form the starting point for deriving time-dependent Hartree-Fock theory in ??.

1.4.3 Linear-response time-dependent Hartree-Fock and density functional theory

The next excited state method we will discuss is time-dependent Hartree-Fock in the linear response formulation which is the excited state analog of HF.^{??} Here we determine the excitation energies of a restricted Hartree-Fock wave-function by evaluating the linear response to an external oscillating perturbation. Since the density oscillates with the external field, resonances are obtained (the linear response terms become dominant) when the frequency of external field matches the excitation energy of the molecule.

Expansion into one particle wave functions

Using the Slater-Condon rules for restricted orbitals we can expand the many-electron Hartree-Fock wave-function into it's single particle components as

$$\left\langle \Psi \left| \hat{H} - i \frac{\partial}{\partial t} \right| \Psi \right\rangle - E_0 \langle \Psi | \Psi \rangle = \sum_i^{occ} \left\langle \phi_i \left| 2\hat{h} + 2\hat{J} - \hat{K} - 2i \frac{\partial}{\partial t} \right| \phi_i \right\rangle - E_0 \quad (1.29)$$

where the sum runs over occupied spatial orbitals, and $\hat{J}$ and $\hat{K}$ are given by

$$\langle \phi_p | \hat{J} | \phi_q \rangle = \sum_j^{occ} \langle \phi_p \phi_j | \phi_q \phi_j \rangle \quad (1.30)$$

$$\langle \phi_p | \hat{K} | \phi_q \rangle = \sum_j^{occ} \langle \phi_p \phi_j | \phi_j \phi_q \rangle \quad (1.31)$$

Allowed variations

The variations of $\langle \delta \Psi |$ are the variations of each of the single particle functions $\langle \delta \phi_i |$. Thus, from the variational principle we obtain

$$0 = \sum_i^{occ} \left(\left\langle \delta \phi_i \left| 2\hat{h} + 2\hat{J} - \hat{K} - 2i \frac{\partial}{\partial t} \right| \phi_i \right\rangle + \left\langle \phi_i \left| 2\delta \hat{J} - \delta \hat{K} \right| \phi_i \right\rangle \right) \quad (1.32)$$

Note

$$\sum_i^{occ} \langle \phi_i | \delta \hat{J} | \phi_i \rangle = \sum_{ij}^{occ} \langle \phi_i \delta \phi_j | \phi_i \phi_j \rangle = \sum_{ij}^{occ} \langle \delta \phi_j \phi_i | \phi_j \phi_i \rangle = \sum_i^{occ} \langle \delta \phi_i | \hat{J} | \phi_i \rangle \quad (1.33)$$

and likewise for $\delta \hat{K}$.

Thus

$$0 = \sum_i^{occ} \left\langle \delta \phi_i \left| \hat{h} + 2\hat{J} - \hat{K} - i \frac{\partial}{\partial t} \right| \phi_i \right\rangle = \sum_i^{occ} \left\langle \delta \phi_i \left| \hat{F} - i \frac{\partial}{\partial t} \right| \phi_i \right\rangle \quad (1.34)$$

Time-Dependent Fock Equations

Provided the variations are independent and arbitrary, we can consider each term individually and obtain the time-dependent Fock equations

$$\hat{F}(t) |\phi_i(t)\rangle = i \frac{\partial}{\partial t} |\phi_i(t)\rangle \quad (1.35)$$

1.4.4 Linear Response

To obtain the linear response of the system, we apply a time-dependent perturbation and solve for the poles where the linear-response terms become dominant. The frequencies at which the linear-response terms dominate, then correspond to the excitation energies of the system. The perturbation we use is of the form of an oscillating electric field:

$$\frac{\varepsilon_\omega}{2} (e^{-i\omega t} + e^{i\omega t}) = \varepsilon_\omega \cos \omega t \quad (1.36)$$

Thus, the first order response of the Hamiltonian is from the coupling of the dipole to the electric field and takes the form:

$$\hat{H}^{(1)} = \frac{\varepsilon_\omega}{2} \hat{\mu} (e^{-i\omega t} + e^{i\omega t}) \quad (1.37)$$

To determine the first order response of the single particle wave-functions, we note that the time dependent orbitals can be expressed as a linear combination of the time independent orbitals, where all the time dependence is carried in the coefficients,

$$|\phi_p(t)\rangle = \sum_q^{all} c_{pq}(t) |\phi_q(0)\rangle \quad (1.38)$$

The time-dependence of the orbital coefficients can be expressed as a unitary transformation of the ground state coefficients as the single-particle wave-functions remain orthonormal at all times.

$$\mathbf{C}(t) = \mathbf{U}(t)\mathbf{C}(0) \quad (1.39)$$

This unitary transformation is of the form $\mathbf{e}^\Delta$ and can be expanded in terms of the electric field as

$$\mathbf{U}(t) = \mathbf{U}^{(0)} + \varepsilon_\omega \mathbf{U}^{(1)} + \varepsilon_\omega^2 \mathbf{U}^{(2)} + \dots \quad (1.40)$$

Where $\mathbf{U}^{(0)} = \mathbb{1}$. We also note that to first order $\mathbf{U}^{\dagger(0)}\mathbf{U}^{(1)} + \mathbf{U}^{\dagger(1)}\mathbf{U}^{(0)} = \mathbb{0}$ since $\mathbf{U}$ is unitary. Thus, since $\mathbf{U}^{(1)}$ must have a component that oscillates as $e^{-i\omega t}$ and a component that oscillates as $e^{i\omega t}$, and must have the form

$$\mathbf{U}^{(1)} = \frac{1}{2} (\mathbf{V}e^{-i\omega t} + \mathbf{W}e^{i\omega t}) = \frac{1}{2} (\mathbf{V}e^{-i\omega t} - \mathbf{V}^\dagger e^{i\omega t}) \quad (1.41)$$

Where the components of $\mathbf{V}$ must be determined. To first order, occupied-occupied mixings and virtual-virtual mixings will not affect the energy, thus we can simplify $\mathbf{V}$ as

$$\mathbf{V} = \begin{bmatrix} \mathbb{0} & \mathbf{X} \\ -\mathbf{Y} & \mathbb{0} \end{bmatrix} \quad (1.42)$$

where X_{ia} and Y_{ia} are now the values that must be determined. Thus, the first order response of the coefficients is given by

$$\mathbf{C}^{(1)} = \varepsilon_\omega \mathbf{U}^{(1)} \mathbf{C}^{(0)} \quad (1.43)$$

or explicitly we have

$$\left| \phi_i^{(1)} \right\rangle = \sum_a^{virt} \frac{\varepsilon_\omega}{2} (X_{ia} e^{-i\omega t} + Y_{ia}^* e^{i\omega t}) \left| \phi_a^{(0)} \right\rangle \quad (1.44)$$

$$\left| \phi_a^{(1)} \right\rangle = - \sum_i^{occ} \frac{\varepsilon_\omega}{2} (X_{ai}^* e^{i\omega t} + Y_{ai} e^{-i\omega t}) \left| \phi_i^{(0)} \right\rangle \quad (1.45)$$

Now we expand the time-dependent Fock equations to first order after projecting with $\langle \phi_a(t) |$ since first order changes in the wave-function will be with respect to the virtual orbitals.

$$\langle \phi_a(t) | \hat{F}(t) | \phi_i(t) \rangle = i \left\langle \phi_a(t) \left| \frac{\partial}{\partial t} \right| \phi_i(t) \right\rangle \quad (1.46)$$

$$\Rightarrow \langle \phi_a^{(1)} | \hat{F}^{(0)} | \phi_i^{(0)} \rangle + \langle \phi_a^{(0)} | \hat{F}^{(0)} | \phi_i^{(1)} \rangle + \langle \phi_a^{(0)} | \hat{F}^{(1)} | \phi_i^{(0)} \rangle = i \left\langle \phi_a^{(0)} \left| \frac{\partial}{\partial t} \right| \phi_i^{(1)} \right\rangle \quad (1.47)$$

$$\begin{aligned} \Rightarrow & (\epsilon_a - \epsilon_i) (X_{ia} e^{-i\omega t} + Y_{ia}^* e^{i\omega t}) + \langle \phi_a | \hat{\mu} | \phi_i \rangle (e^{-i\omega t} + e^{i\omega t}) + \\ & \sum_j^{occ} \sum_b^{virt} \left[(2 \langle \phi_a \phi_j | \phi_i \phi_b \rangle - \langle \phi_a \phi_j | \phi_b \phi_i \rangle) (X_{jb} e^{-i\omega t} + Y_{jb}^* e^{i\omega t}) + \right. \\ & \left. (2 \langle \phi_a \phi_b | \phi_i \phi_j \rangle - \langle \phi_a \phi_b | \phi_j \phi_i \rangle) (X_{bj}^* e^{i\omega t} + Y_{bj} e^{-i\omega t}) \right] = \omega (X_{ia} e^{-i\omega t} - Y_{ia}^* e^{i\omega t}) \end{aligned} \quad (1.48)$$

Solving independently for the $e^{-i\omega t}$ and $e^{i\omega t}$ terms we form the following non-Hermitian eigenvalue equation (note the dipole terms have been dropped as they are not necessary to obtain the excitation energies, however they are necessary for computing the frequency dependent polarizabilities).

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \quad (1.49)$$

where

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (2 \langle \phi_a \phi_j | \phi_i \phi_b \rangle - \langle \phi_a \phi_j | \phi_b \phi_i \rangle) \quad (1.50)$$

$$B_{ia,jb} = (2 \langle \phi_a \phi_b | \phi_i \phi_j \rangle - \langle \phi_a \phi_b | \phi_j \phi_i \rangle). \quad (1.51)$$

The CIS equations are equivalent to the diagonal terms of TDHF, and thus CIS can be imagined as an approximation to TDHF. In practice, however, TDHF is rarely used as it often performs worse than CIS and does not offer much of a practical advantage.

Closely related to TDHF is time-dependent Kohn-Sham density functional theory (TDDFT), which is exact if the exchange correlation functional is exact. As the exact functional is unknown it is also in practice an approximate method. It is well known that exchange-correlation functionals are generally not systematically improvable which can make it necessary to use caution when applying TDDFT to novel systems. Furthermore, nearly all functionals have been developed for ground state systems, so the reliability of the density functional theory is not always clear. Despite these limitations it is by far the most widely used method for computing electronically excited states,^{???} and can be derived in an analogous fashion using the Kohn-Sham orbitals in place of the Hartree-Fock orbitals.[?] The final equations are very similar (here for unrestricted orbitals) with the primary difference being the addition of the exchange-correlation terms.

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (\phi_i \phi_a | \phi_j \phi_b) + (\phi_i \phi_a | f_{xc} | \phi_j \phi_b) \quad (1.52)$$

$$B_{ia,jb} = (\phi_i \phi_a | \phi_b \phi_j) + (\phi_i \phi_a | f_{xc} | \phi_b \phi_j) \quad (1.53)$$

The Tamm-Dancoff approximation (TDA) is then equivalent to CIS in that the off-diagonal blocks are neglected.

Although not used much throughout this thesis, TDDFT is a ready expansion of the methods developed and due to its popularity and significant success it deserves consideration.

1.5 Overview

Overall this thesis presents several new developments in excited state electronic structure theory. There is also significant application of the methods to a very unusual system for excited state studies: helium clusters. Part of why helium clusters are so unique and thus have motivated much of the trajectory of this work is due to their dense manifold of nearly degenerate states and large sizes. The next two chapters focus primarily on the results for helium clusters, and the final two explore methodological developments.

1.5.1 Chapter 2: Helium cluster excited states

The chapter explores the vertical excitation energies of small helium clusters, He₇ and He₂₅, which were calculated using configuration interaction singles. The character of the excited states was determined using attachment/detachment density analysis and it was found that in the $n = 2$ manifold the excitations could generally be interpreted as superpositions of atomic states. Excitations on the surface of the clusters appeared at lower energies than those in the bulk. For the $n = 2$ states that had significant density on the interior of the cluster, mixing with the atomic $n = 3$ states resulted in lower excitation energies. The $n = 3$

states were also computed for the 7-atom clusters and here the spatial extent of the excited-state density can be much larger than the size of the cluster, making analysis of the states more difficult and highly dependent on the internuclear distances. Introducing disorder into the clusters results in some localization of the excited states, although at least some highly delocalized states are always observed in these small clusters. In addition, experimental results for small clusters are interpreted in terms of these findings. This chapter has been published as a paper in the Journal of Physical Chemistry A.[?]

1.5.2 Chapter 3: State-following dynamics in He₇ clusters

The dynamics resulting from electronic excitations of helium clusters were explored using ab initio molecular dynamics. The simulations were performed with configuration interaction singles and adiabatic classical dynamics coupled to a state-following algorithm. 100 different configurations of He₇ were excited into the 2s and 2p manifolds to form a total of 2800 trajectories. The most frequent outcome (90%) was complete fragmentation of the clusters to form 6 ground state atoms and 1 excited state atom. However, 3% of trajectories formed bound, He₂^{*}, and < 0.5% yielded an excited helium trimer. The nature of the dynamics, kinetic energy release, and connections to experiments are discussed. This chapter has been published in the Journal of Chemical Physics.[?]

1.5.3 Chapter 4: Additional applications of state-following

This chapter expands upon the state-following method developed in ?? detailing the algorithm and exploring applications to excited-state geometry optimization, ab initio molecular dynamics and locating a minimal energy path between two excited states. The geometry optimization of cytosine with and without state following is presented, with the result that the optimization of higher excited states became possible. The effects of state-following in the context of ab initio molecular dynamics with helium clusters are discussed and it is found that more physically accurate results could be obtained using this method. Finally, coupling the growing string method to the state following algorithm provides a way to determine the minimal energy path between two excited states and estimate the location of conical intersections. The utility of method was demonstrated by application to the first two singlet excited states of protonated formalimine, CH₂NH₂⁺.

1.5.4 Chapter 5: Development of a local electronic structure method

A variant of configuration interaction singles (CIS) which uses absolutely localized molecular orbitals (ALMOs) has been developed. This fragment based method excludes charge transfer between well defined fragments, thus limiting the available number of excitations and allowing for much larger systems to be treated. It formally scales with the third power of the system size, and clusters with up to 250 atoms have been computed. The derivation of

the equations and design of the algorithm are discussed in detail. Then the accuracy of the model is explored by comparison to the He₂₅ results and the empirical timings are computed. A pilot application to the size dependence of the helium cluster spectrum is also presented.

Part II

Results

Chapter 2

Ab initio calculations on the electronically excited states of small helium clusters

2.1 Introduction

Helium clusters have attracted significant interest due to their unique properties and potential applications.[?] They remain liquid at all temperatures due to helium's small mass and weak interactions. Clusters larger than about 60 atoms also exhibit superfluidity, as does bulk helium.^{???} These properties have inspired many possible applications such as using helium clusters as a spectroscopic medium,^{??} or as ultra-cold reaction chambers.[?] Despite this interest in helium clusters, very little is known about their electronically excited states due to experimental, as well as theoretical difficulties.

Experiments are difficult since the clusters possess only weak binding energies and are unstable. Also, they produce small signals and have electronic excitations which occur at very high energies. From luminescence, and fluorescence spectroscopy it has been determined that the cluster absorption is dominated by broad bands ranging from 21-25 eV.^{?????} The lowest energy band centered at 21.5 eV is likely due to states that are closely related to the $1s \rightarrow 2p$ atomic excitations, with a small shoulder on the lower energy side due to transitions into the $2s$ atomic-like states. These states are blue-shifted from those of the free atoms, due to repulsive interactions of an atom centered excited state with neighboring atoms. The character of the higher energy states has not yet been definitively determined, and will likely depend upon the cluster size. In smaller clusters, $\lesssim 500$ atoms, it has been proposed that they correspond to $3p$ and $4p$ excitations, but in larger clusters this is unlikely as the intensity of the ' $4p$ ' increases more rapidly than that of the ' $3p$ ' band, and the strength generally decreases at higher quantum numbers for molecular or Frenkel exciton models.[?] Excitonic models have also been proposed, but are problematic due to the very low densities of the clusters, and furthermore there is the possibility that there are Rydberg states involving the

entire cluster.[?]

In addition, there have been experimental efforts focused on determining the dynamics of helium clusters.^{???} For example, Toennies and coworkers have used photoionization spectroscopy to study the dynamics of helium droplets ranging from 10^2 to 10^7 atoms. They determined ionization occurs by direct excitation, as well as by auto-ionization from electronically excited states below the ionization threshold.[?] The location of the initial excitation, and exactly how it decays are still debated. One possibility is that the initial excitation is localized and is then ejected from the cluster such ‘bubble states’ indicate that the initial electronic excitation first localizes on He atoms or molecules and then bubbles form around them.[?] Kornilov et al. have also recently published intriguing time resolved data for relaxation dynamics, but have been unable to conclusively determine the mechanism.[?] They found two characteristic time scales one of 2.8 ± 0.4 ps, and a second of $280 + 100/-50$ fs. However there is uncertainty as to whether they are due to independent or correlated processes within the droplet, and whether they take place on the surface or interior of the droplet.

To our knowledge, there was only one previous computational study on the excited states of helium clusters when this work began,[?] which was limited to excitations of the central atom in a 7-atom octahedral cluster. Despite the small size of their cluster and high symmetry, they computed the potential energy curves of the excited states as a function of the density, and conclude that the $2s$ and $2p$ orbitals are essentially unchanged from the atomic orbitals, as their spatial extent is smaller than the internuclear distance, and that higher excitations are only slightly affected by changing the inter-atomic spacing.

Here we theoretically study the electronically excited states in the $n = 2$ manifold of small helium clusters consisting of 7 and 25-atoms and the $n = 3$ manifold of the 7-atom clusters. The effects of size, order and density on the excited states will all be addressed.

2.2 Methods

All calculations were performed using Q-Chem.[?] Excitation energies were calculated using configuration interaction singles (CIS)[?] with the 6-311G basis set containing additional diffuse basis functions.

The CIS wavefunction is a linear combination of all singly excited Slater determinants formed from the Hartree-Fock molecular orbitals.

$$|\Psi_{CIS}\rangle = \sum_i^{occ} \sum_a^{virt} c_{ia} |\Phi_i^a\rangle$$

where $|\Phi_i^a\rangle$ is a determinant with the one-electron occupied molecular orbital, ϕ_i , replaced by the unoccupied orbital, ϕ_a . Since the singly excited states do not mix with the Hartree-Fock ground state by Brillouin’s Theorem, this method provides the excited state analogue of Hartree-Fock theory, i.e. electron correlation between electrons of the same spin is neglected. CIS has been shown to be an adequate starting point for excited states which are not

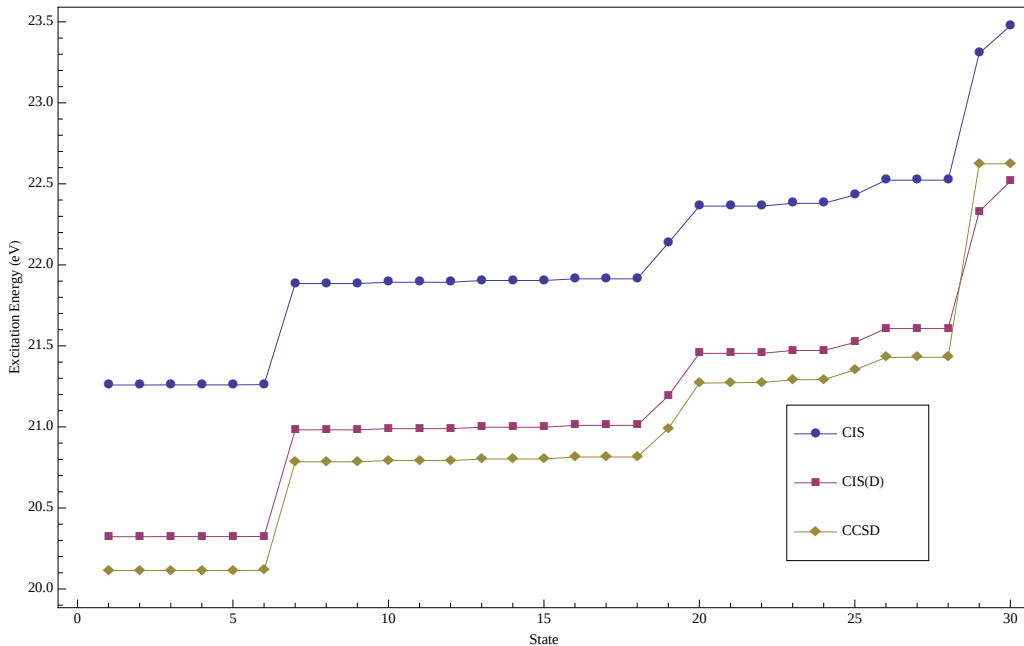


Figure 2.1: Comparison of methods for an octahedral He_7 cluster. Note that the basis set here is only valid for excitations through state 28.

predominantly multi-reference in character, although it often yields excitation energies which differ by 1 eV or more.^{??}

Using higher levels of theory which incorporate electron correlation in the excited states, either perturbatively including double excitation as in CIS(D),[?] or by incorporating the double excitations fully as in EOM-CCSD,[?] provided qualitatively similar results. A significant but mostly constant offset results, as illustrated by ???. Note that the excitation energies of the central atom are lowered slightly more than the surface atom excitations with the introduction of electron correlation, however this is a small effect and should not qualitatively affect the final results. Also, TDDFT was not used due to the known difficulties with self-interaction error for Rydberg excitations.^{??}

Thus, while we do not expect the CIS method to yield quantitatively correct results, this chapter will primarily focus on interpreting the character and relative energetics of the excited states, so using CIS should not create additional difficulties. Furthermore, we ultimately hope to study large clusters with hundreds or even thousands of atoms and thus using the cheapest adequate computational method is highly desirable.

Attachment and detachment densities were analyzed to determine the character of the excited states. Plots of these densities illustrate the change in electron density before and after the excitation[?]. Generally the difference in density between the ground and excited states, is given by

$$\Delta = \mathbf{P}_{\text{e}_i} - \mathbf{P}_{\text{g}}$$

where $\mathbf{P}_g$ and $\mathbf{P}_{e_i}$ are the one-particle density matrices in the molecular orbital basis for the ground and i^{th} excited state respectively. This difference matrix is then diagonalized to form δ ,

$$\Delta = \mathbf{U}\delta\mathbf{U}^\dagger$$

where δ can then be split into a sum of two matrices δ_+ and δ_- which contain the positive and negative eigenvalues of δ respectively. Finally we transform these back to the original basis to obtain

$$\mathbf{A} = \mathbf{U}\delta_+\mathbf{U}^\dagger, \text{ and } \mathbf{D} = \mathbf{U}\delta_-\mathbf{U}^\dagger.$$

Now

$$\Delta = \mathbf{A} - \mathbf{D}$$

where $\mathbf{A}$ and $\mathbf{D}$ are defined as the attachment and detachment densities. Thus, the attachment density corresponds to the density that is added to the excited state after the transition, and the detachment density corresponds to the density that is removed from the ground state. The attachment and detachment density can also be loosely thought of as the electron and hole densities respectively in the excited state. Their difference is equivalent to the difference density, and contains the same information, but in a form that is more readily interpreted.

The densities in the $n = 2$ and $n = 3$ manifold were visualized using Avogadro[?] with isodensity surfaces at 0.0002, and 0.00005 respectively. Note that using the same isodensity surfaces in the attachment and detachment plots means that a greater percentage of the total density is captured with the detachment surfaces where the electron density is less diffuse. For helium, as there is only a single occupied orbital in the ground state the number of significant eigenvalues in the detachment and attachment densities correspond to the number of atoms that are involved in the excitation.

The diffuse basis sets used were not standard. For He_7 , three additional sp functions were added, as well as two sets of d functions; this basis is labeled 6-311(3+/2d)G. The first set of sp and d functions used the exponents determined by Yin and MacKerell,[?] and additional functions were determined by scaling the exponents by 1/3.32, which is automatically done in Q-Chem. It was found that a third set of d functions did not affect the energies and thus was not included. Also, for the $n = 2$ energy levels, using only two sets of sp functions yielded essentially the same results, this significantly smaller basis will be labeled as 6-311(2+)G. Thus, for the energies of the He_{25} clusters where only the excitations up to $n = 2$ were calculated, the smaller basis set was used.

Two corresponding minimal bases that exactly reproduce the $n = 1, 2$ atomic states at the CIS/6-311(2+)G level of theory, labeled N2, and the $n = 1-3$ atomic states at the CIS/6-311(3+/2d) level of theory (N3) were also formed. The atomic detachment and attachment densities in the large bases each have a single significant eigenvalue and the corresponding eigenvector yields the molecular orbital coefficients for the atomic orbitals. The eigenvector corresponding to the detachment density for all states, yields the 1s orbital, and the eigenvector corresponding to the first attachment density of the first excited state yields the 2s

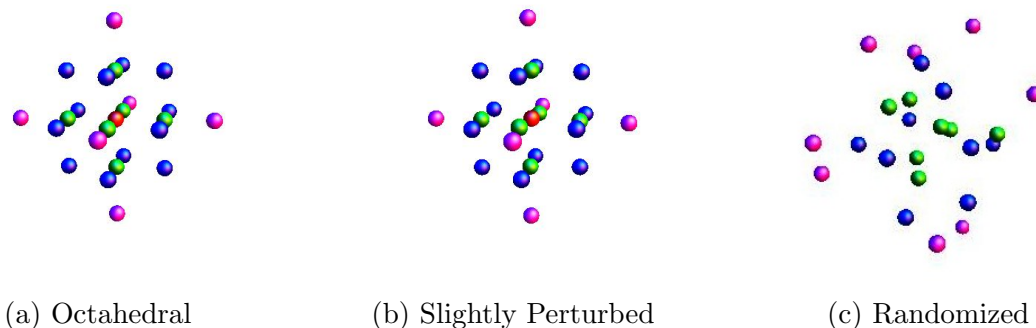


Figure 2.2: Sample geometries of He_{25} . Colors indicate position of atoms, center = red, middle = green, surface (face) = blue, surface (corner) = pink. In the randomized structure it is not clear to define a central atom, or corner atoms so the outermost atoms are shown in pink, and the innermost are green

orbital. Likewise, the higher excited states correspond to higher energy orbitals. Unlike the orbitals obtained from Koopman’s theorem, the orbitals from the attachment/detachment analysis are exact for the atom within the basis used to compute the attachment and detachment densities. Bases exact for atoms are not generally used in *ab initio* calculations as molecular orbitals are not generally well described by the atomic orbitals, however, it should be useful for understanding weakly interacting noble gas systems.

An octahedral geometry was chosen for the initial structure, because it is well defined and also because bulk liquid helium has 6 nearest neighbors near absolute 0.^{??} The 7-atom cluster is the smallest cluster containing a central atom surrounded by 6 others. Using a cluster of this size we studied the excited states up to and including the $n = 3$ manifold, resulting in thirteen atomic-like excited states per atom. The 25-atom cluster results from adding a second layer of atoms to the central helium. Only the $n = 2$ excited state manifold, consisting of four excited states per atom, was computed for these larger clusters due to data processing and computer memory limitations.

An inter-atomic distance of 3.00 Å was used as the primary spacing as this is very close to the MP2 optimized radius in the ground state of 2.96 Å, and thus represents a minimal inter-atomic distance for the cluster. In actuality, at finite temperatures or with the addition of zero-point energy, the average distances between atoms will be significantly larger, and are predicted to be around 3.6 Å in bulk liquid helium[?] and actually closer to 5 Å in very small helium clusters.^{??} Thus, the 3 Å octahedral cluster will be a very poor reflection of the actual 7 or 25-atom clusters, but it is a useful starting point for further calculations. To understand the effect of larger inter-atomic spacing, and thus of lowering the cluster density, the octahedral 7-atom cluster was dilated up to an atomic separation of 9 Å.

For investigating the effect of disorder on the system, these octahedral clusters were then perturbed to obtain asymmetric geometries in two different ways. In the first method, a “slightly perturbed” octahedral cluster was formed by adding a random number between 0 and 0.3 (up to 10% of the bond length) to the x , y , and z coordinates of each atom. Then

in the second method, “random” clusters were created by adding a random number between 0 and 3.0 (up to 100% of the bond length) to each of the coordinates and optimizing the resulting geometries with MP2/6-311G. It was necessary to perform the geometry optimization as the strong geometric perturbation often produced clusters with the atoms extremely close together, which are highly unstable and would not reflect the fact that at experimental temperatures the clusters are extremely cold at 0.4 K. In order to illustrate the effects of each of the randomization method, sample geometries used for He_{25} are shown in ???. It is readily seen that while the perturbed geometries still retain overall structure of the octahedron, the “random” clusters are virtually unrelated to the initial octahedral geometries. This supports our intuition that real clusters are unlikely to exhibit such high symmetry. For each size cluster, 100 of these randomized geometries were generated and no identical structures were found. Considering only one nearest neighbor for each atom in each of the clusters, the average nearest neighbor distance produced by this method for He_7 is 3.66 Å and for He_{25} is 3.38 Å. These values seem reasonable for the ground states of the clusters considering the Neumark group’s data for 100 atom simulations with periodic boundary conditions, and the expectation that the atom density decrease with decreasing cluster size.[?]

In order to compute the excitation spectra, the excitation energy was plotted as a function of the CIS oscillator strengths. The theoretical spectra were found by averaging the oscillator strengths for the 100 random geometries. Note that these were initially grouped into two batches of 50 to verify that we had a sufficient number of geometries to provide a representative sample and these were the same within the method error. Thus they were all combined in the final reported spectrum in order to give the cleanest (least noisy) spectrum. We expect that adding more geometries should not significantly change the spectrum but will likely make it smoother.

2.3 Results

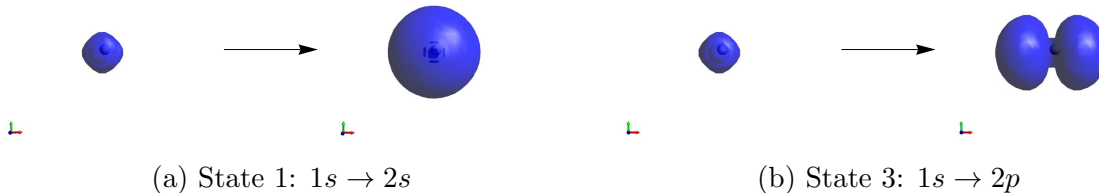
2.3.1 Atom

In order to calibrate and demonstrate the utility of our methods, we first looked at the excited states of the helium atom.

The excitation energies and oscillator strengths for the lowest energy atomic excitations, along with experimental values are shown in ??. In this case the transitions can be easily assigned by their oscillator strengths and degeneracies. However, the character of the excited states can be confirmed from the attachment and detachment densities shown in ??, which clearly show the $1s \rightarrow 2s$ and $1s \rightarrow 2p$ transitions. In both cases, the detachment density corresponds to the removal of density from the $1s$ orbital. Then the attachment densities shown in ??(a) and ??(b) correspond to excitations into the $2s$ and $2p$ orbitals respectively. Thus the physical interpretation is that an electron is being excited from a helium $1s$ orbital to an excited $n = 2$ orbital. The second $1s$ electron is in the same orbital throughout and does not appear in this analysis.

Transition	6-311(2+)G		6-311(3+/2d)G		Experimental [?]
	Energy (eV)	Osc. Strength	Energy (eV)	Osc. Strength	
$1s \rightarrow 2s$	21.1385	0.0000	21.1339	0.0000	20.60177
$1s \rightarrow 2p$	21.8331	0.0487	21.8331	0.0487	21.20361
$1s \rightarrow 3s$	23.9492	0.0000	23.3663	0.0000	22.90475
$1s \rightarrow 3p$	23.8360	0.0326	23.5630	0.0136	23.07134
$1s \rightarrow 3d$			23.4891	0.0000	23.05841

Table 2.1: Energies and oscillator strengths for He atom

Figure 2.3: Detachment $\rightarrow$ attachment densities for the helium atom

Even in the atom, the need for a third set of diffuse functions is readily apparent for qualitatively obtaining the correct ordering of the $n = 3$ states. However, the smaller basis with only two sets of diffuse sp functions yields almost exactly the same results ($< 0.1\%$ difference) for excitations to the $n = 2$ states and is sufficient for studying the lowest energy states, although when looking at $n = 3$ type excitations, it is absolutely necessary to include the additional diffuse functions as well as two sets of diffuse d functions. Note that the $n = 2, 3$ states can be identically reproduced by using a minimal basis formed from the eigenvectors of the detachment and attachment densities for a total 13 atomic basis functions, as opposed to 25 in the 6-311(3+/2d)G basis. Or the $n = 2$ states can be reproduced using a minimal basis with 5 basis functions instead of the 13 in 6-311(2+)G. The fact that these minimal bases are exactly the same for the atom as the larger bases is exploited to gain insight into the excited states of the clusters.

The computational values are consistently about 0.5 eV higher than the published experimental values[?], with the most significant contribution to this error introduced by using CIS, which does not account for electron correlation in the excited states but as mentioned in ?? this should not create any issues for interpreting our results qualitatively.

Thus, the data from the atom confirms the utility of the attachment/detachment density analysis, and shows that the methods are at least valid at the atomic level.

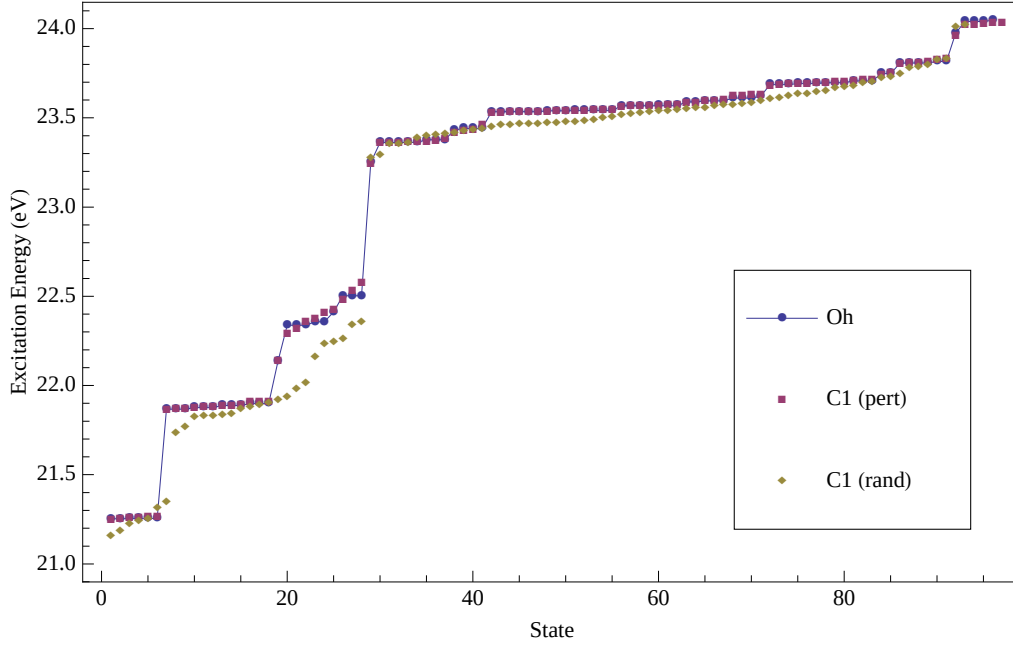


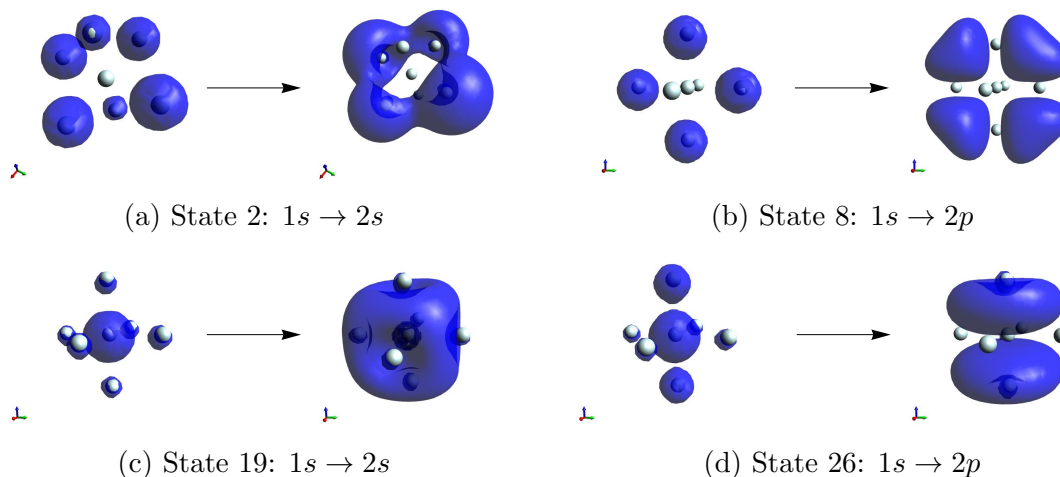
Figure 2.4: Vertical excitation energies of 3 Å He_7 clusters for octahedral, perturbed, and randomized geometries

2.3.2 He_7

After evaluating the methods, our attention turned to the 7-atom helium clusters where it is possible to see different types of excited states.

In ?? the energy as a function of increasing state number is plotted for the octahedral cluster at 3.00 Å, for a corresponding perturbed cluster and a randomized cluster. While real clusters would have atoms that are much more separated, this is a reasonable starting model for considering the 7-atom cluster to be a small sample of the atoms in a larger cluster. By viewing the attachment/detachment density plots, ????, we can gain insight into the nature of the excited states, and determine that for the $1s \rightarrow 2s$ and $2p$ excitations they can be interpreted in terms of superpositions of atomic states. Note that although it may appear that there are more atoms involved by looking only at the detachment densities as in ????, this is an artifact of the isodensity surfaces. By choosing a lower value for the attachment densities, it is seen that there is no discrepancy, and we can indeed interpret them as superpositions of atomic excited states. Furthermore, the number of atoms involved in the excitations has been confirmed from the non-zero eigenvalues of the detachment or attachment densities.

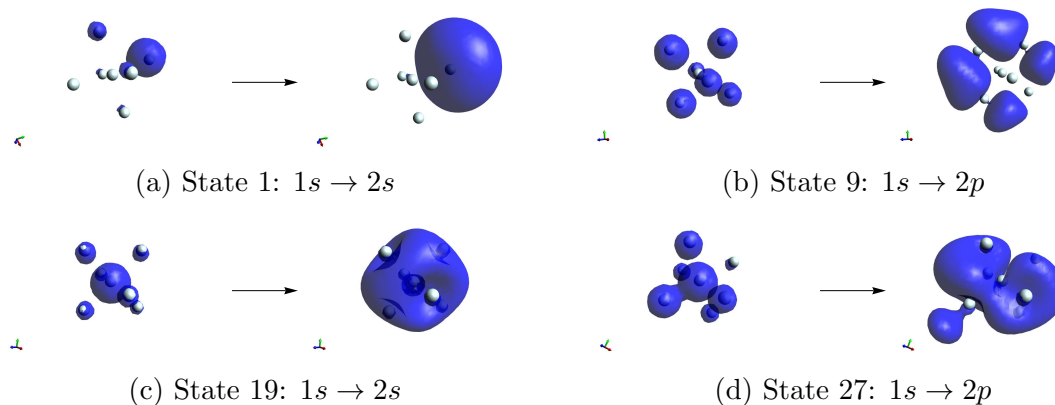
In the octahedral and slightly perturbed clusters the first 6 states are separated by about 0.6 eV from the higher excited states, and can readily be seen as superpositions of the $1s \rightarrow 2s$ transitions of the outer atoms, ????. The $1s \rightarrow 2s$ transition of the central atom is blue shifted by nearly 1 eV relative to the transitions on the outer atoms and is

Figure 2.5: Representative attachment detachment densities for He_7 (O_h)

state 19, ????. As will be discussed later, this shift is due to the interaction of the excited state density with the other atoms in the cluster, and decreases rapidly as the atoms are moved to larger separations. In the randomized cluster, the central atom is no longer fully surrounded, and thus there is less of a distinction between the surface and central atoms. The central atom then appears at a very similar energy to that of the outer atoms, and there are seven low energy states grouped closely together. Also interesting to note is that while in the octahedral cluster, the excited $2s$ states are delocalized over the full cluster, but when perturbed, the $2s$ states mostly localize onto a single atom.

States 7-18 in the octahedral and slightly perturbed clusters then correspond to $1s \rightarrow 2p$ transitions of the outer atoms for the p orbitals that are not oriented facing into the cluster, (e.g. ???). States 20-25 then result from the $1s \rightarrow 2p$ excitations of the outer atoms where the p orbitals are directed towards the center of the cluster. Finally, states 26-28 result primarily from the $1s \rightarrow 2p$ excitation on the inner atom, ????. Note that in the higher energy states, we do observe some mixing between states on both the inner and outer atoms, and this effect becomes more pronounced as the geometry is perturbed. In the randomized clusters, states 8-28 correspond primarily to superpositions of $1s \rightarrow 2p$ transitions. The states without significant density on the interior of the cluster still appear at lower energies than those only on the surface, but mixing between the inner and outer shells of helium atoms is definitely observed. For the $2p$ orbitals, some localization occurs when perturbing the geometry, but very few excited states localize on a single atom as was observed for the $1s$ states.

In ??, the $n = 2$ excitations are replotted to illustrate the effect of switching to the N2 minimal basis which is exactly the same as 6-311(2+)G for the atomic excitations. This basis would give the same results as the larger basis if the superpositions of atomic excitations in the helium clusters were completely unchanged from the $n = 2$ excitations in the atom. We see that they do match well except for states which involve significant density on the

Figure 2.6: Representative attachment detachment densities for He_7 (C_1)

interior of the cluster. If instead the N3 basis, which describes the $n = 2$ and $n = 3$ excited states of the atom identically to the 6-311(3+/2d)G basis, most of the error for the states with density inside the clusters is eliminated. This indicates that in the cluster there must be mixing of the atomic $n = 3$ states with the $n = 2$ states resulting in lowered excitation energies. The fact that a significant amount of the excitation energy can be accounted for with just the N2 basis indicates that the excited states can primarily be described in terms of slightly perturbed atomic states. Due partly to this fact that the excited states can be well described in terms of atomic excitations, we anticipate that the effect of any charge-transfer in the excited states will be negligible. This is also supported by the eigenvalues of the attachment and detachment densities discussed earlier. The exact amount of charge-transfer has not yet been numerically verified, and this issue will be addressed in future work.

States 29-91 then correspond to excitations into the $n = 3$ manifold. It rapidly becomes much more difficult to interpret the cluster excitations in terms of atomic excitations for clusters with atoms so close together due to the fact that for a 3 Å internuclear distance, the spatial extent of the orbitals are much larger than the size of the cluster and so there is a high degree of overlap between the states on different atoms. However, in the octahedral cluster, it is still fairly clear to pick out atomic-like states in some of the cases. Thus, we find that excitation into states 29-34 are $1s \rightarrow 3s$ type transitions, 35-37, 52-62 and 84-85 are $1s \rightarrow 3d$ transitions, 39-50 and 65-67, are $1s \rightarrow 3p$ transitions. The other states in this range seem to result from combinations of orbitals on different atoms with different angular momentum, and this mixing is only exacerbated when the geometry is perturbed. At larger internuclear separations, it does become possible to identify all the excitations as essentially those of the atoms.

Above state 91 are excitations into the $n = 4$ manifold which our basis is not large enough to treat accurately, and so these are not considered any further here.

Stick spectra for the 3 Å octahedral, and a slightly perturbed cluster are given from the computed oscillator strengths in ???. In ??? we can see a weak line at 21.25 eV corresponding to excitations into the $2s$ states, followed by lines at 21.9 eV and 33.32 eV which are from the

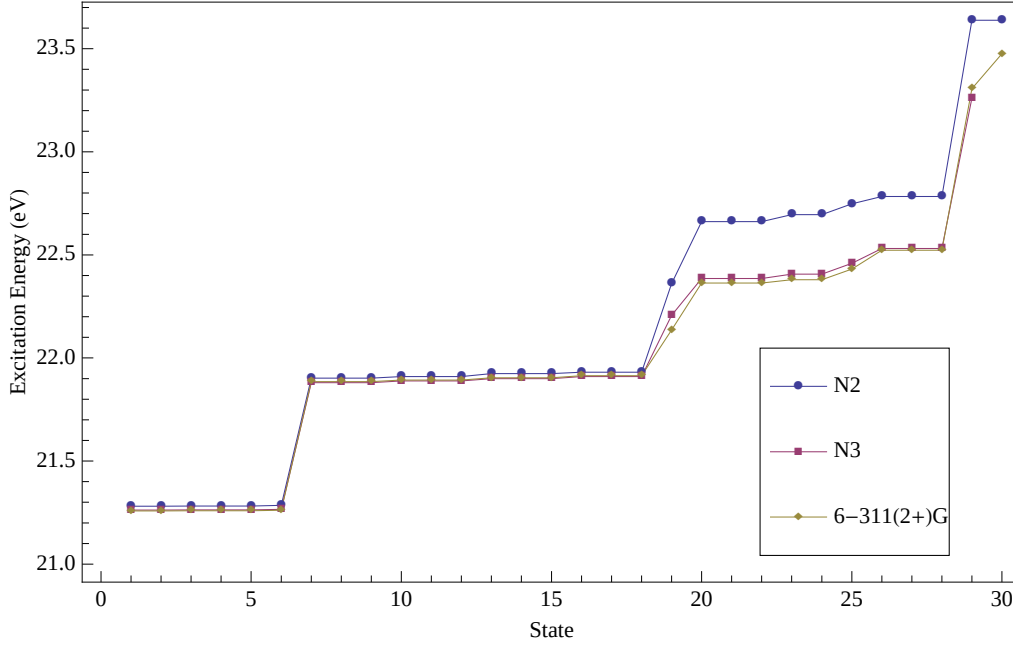


Figure 2.7: Excitation energies into the $n = 2$ manifold of the 3 Å He_7 (O_h) cluster. N2 is a minimal basis which matches 6-311(2+)G for the atom, and N3 matches 6-311(3+/2d)G for the atom

$1s \rightarrow 2p$ excitations of the outer atoms. There is also a line at 22.5 eV which is from the $1s \rightarrow 2p$ excitations of the central atom. The only line with any appreciable oscillator strength above 23 eV is at 23.6 eV and corresponds to $1s \rightarrow 3p$ transitions. The slightly perturbed cluster, ??, shows the same pattern, with the peaks beginning to broaden due to the loss of symmetry. It is also interesting to note here that while the excitations on the surface are only slightly spread out, states with significant density inside the cluster experience much greater broadening. The spectrum computed from 100 randomized clusters is shown in ??, which shows only broad features. First the very small peak from the $1s \rightarrow 2s$ symmetry forbidden states, and a large peak strongly skewed to the right from the $1s \rightarrow 2p$ states. Finally there is a peak at 23.5 eV that is also skewed right, but less strongly, corresponding to $1s \rightarrow 3p$ transitions. This skewing results from the interior states spreading more than those on the surface, and is also observed experimentally,[?] and we will return to this result in the investigations on the 25-atom clusters.

The excitations of He_7 octahedral clusters with an interatomic distance of 3.0 to 9.0 Å were calculated to illustrate the effect of lowering the cluster density, as well as to aid in the interpretation of the $n = 3$ excited states. ?? shows the states on the central atom, and a representative state on the outer atoms, as a function of the atomic spacing. For the central atom states, we see the same trends as observed by von Haeften and Fink,[?] but

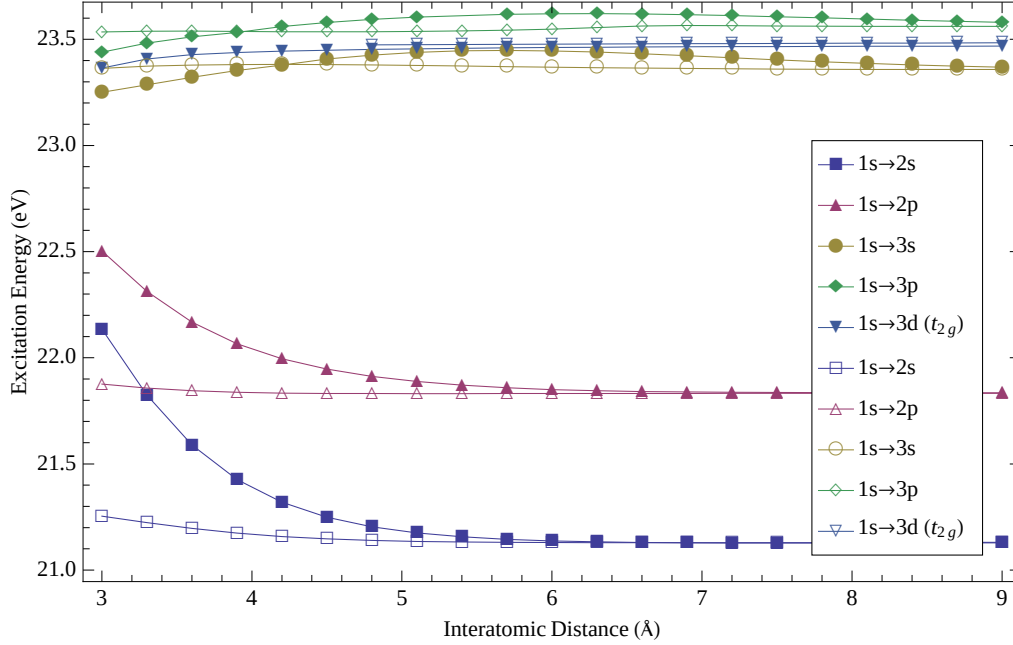
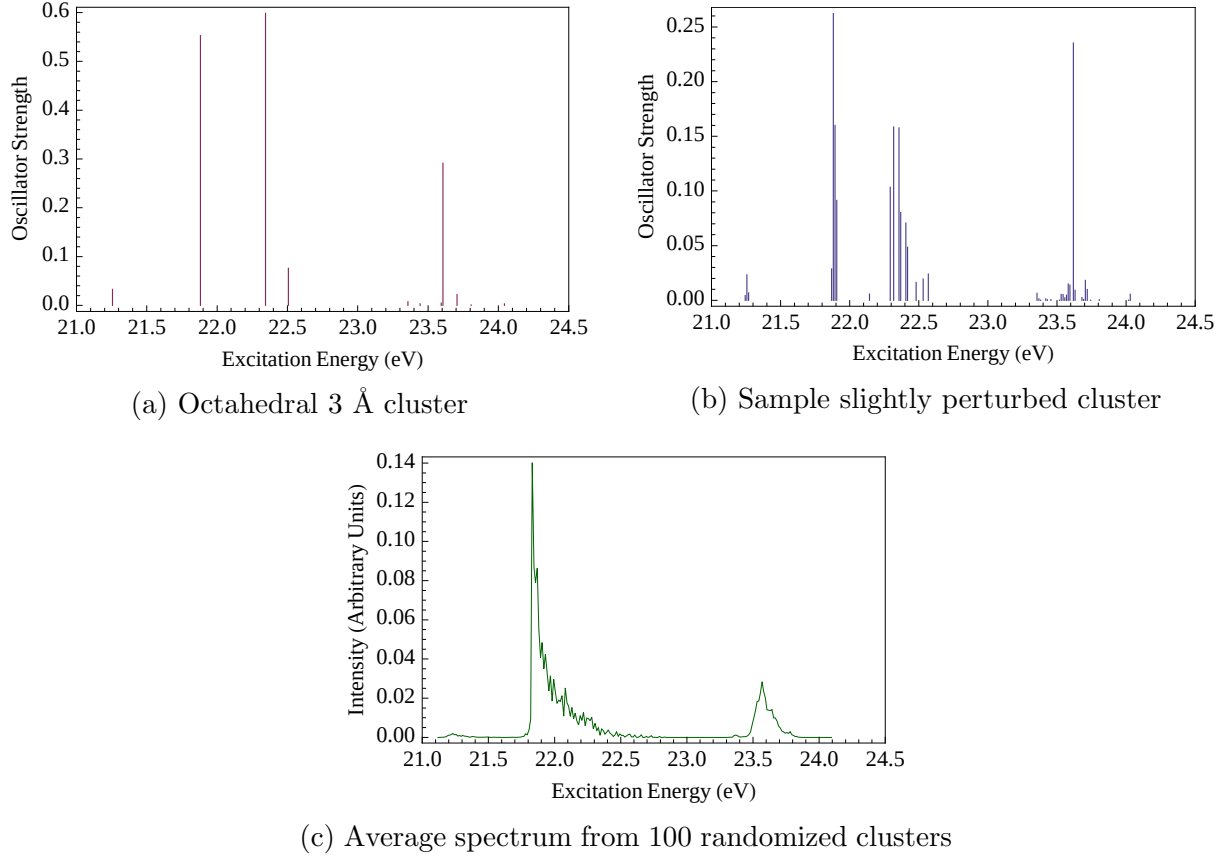


Figure 2.8: Vertical excitation energies as a function of internuclear distance for the He_7 (O_h) cluster. Filled symbols indicate excitations of the central atom, and empty symbols indicate excitations of the outer atoms

they are shifted to higher energies due to our neglect of electron correlation. In all cases, the cluster excitations approach the energies of the atomic excitations as calculated using CIS/6-311(3+/2d)G, as the atoms are separated. At small nuclear distances the $n = 2$ excitations of the central atom are raised by 0.5 eV over the excitations of the surface atoms. By 6 Å of separation all excitations on atoms both in the center and on the surface are equivalent. In these $n = 2$ levels, the excited state density of the central atom remains inside the cluster for all inter-atomic distances investigated, and thus interacts repulsively with the electrons of the surface atoms causing an increase in the energy with respect to the free atom. For the $n = 3$ levels, a different effect is observed as the central atom excitations are stabilized relative to excitations on the outer atoms. The energies of the central atom excitations then rise some, while the excitation energies of the surface atoms remain constant, ultimately reversing this ordering of the states. This is due to the fact that at the smallest inter-atomic separations the bulk of the electron density in the $n = 3$ states is outside of the cluster, resulting in the excited state energy being the same, or lower energy than the same state in the atom. Then as the atoms are further separated, the excitations of the central atom increase due to increasing interactions with the surface atom electrons in the cluster until the density is entirely inside the cluster when then decreases again to asymptotically approach the excitations of the atom. Overall, the energy change of the central and surface atoms in

Figure 2.9: Stick spectra of He_7 clusters

the $n = 3$ levels is much smaller than that of the $n = 2$ levels.

Stick spectra for the 3 Å octahedral, and a slightly perturbed cluster are given from the computed oscillator strengths in ???. In ??? we can see a weak line at 21.25 eV corresponding to excitations into the $2s$ states, followed by lines at 21.9 eV and 23.32 eV which are from the $1s \rightarrow 2p$ excitations of the outer atoms. There is also a line at 22.5 eV which is from the $1s \rightarrow 2p$ excitations of the central atom. The only line with any appreciable oscillator strength above 23 eV is at 23.6 eV and corresponds to $1s \rightarrow 3p$ transitions. The slightly perturbed cluster, ???, shows the same general pattern, with the peaks beginning to broaden due to the loss of symmetry. It is also interesting to note here that while the excitations on the surface are only slightly spread out, states with significant density inside the cluster experience much greater broadening. The octahedral cluster is not a good depiction of the true helium cluster geometry, so to really understand the excitations it is necessary to look at the spectrum produced from the clusters of randomized geometries. The spectrum computed from 100 randomized clusters is shown in ???, which shows only broad features. First the very

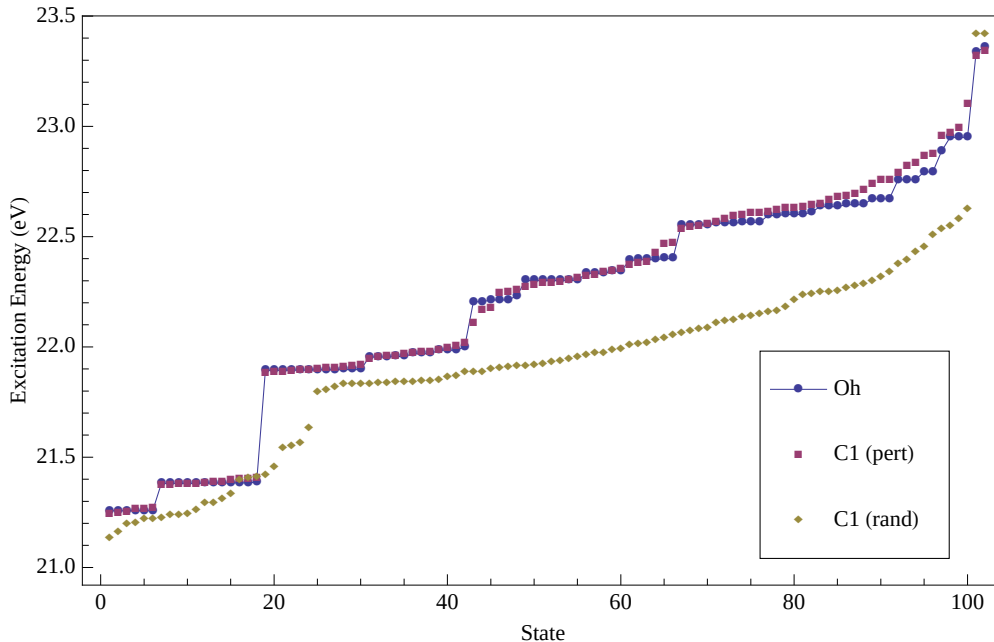


Figure 2.10: Vertical excitation energies of He_{25} clusters for octahedral, perturbed, and randomized geometries

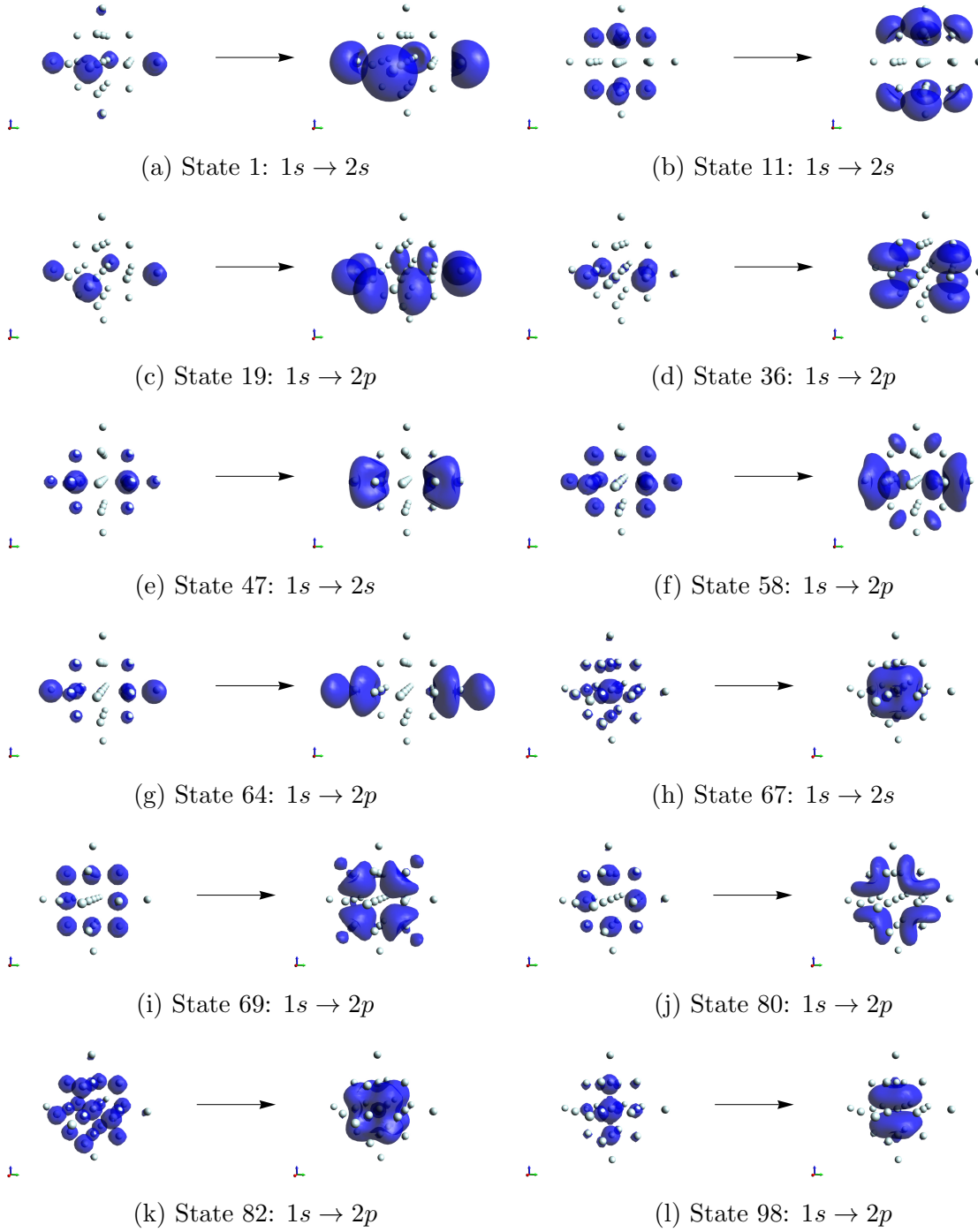
small peak from the $1s \rightarrow 2s$ symmetry forbidden states, and a large peak strongly skewed to the right from the $1s \rightarrow 2p$ states. Finally there is a peak at 23.5 eV that is also skewed right, but less strongly, corresponding to $1s \rightarrow 3p$ transitions. Note that for real clusters of this size, the atoms would be spread further apart which would cause all the excited states to be more atom-like and would result in narrower peaks. This skewing results from the interior states spreading more than those on the surface, and is also observed experimentally.⁷ We will return to this result in the discussion.

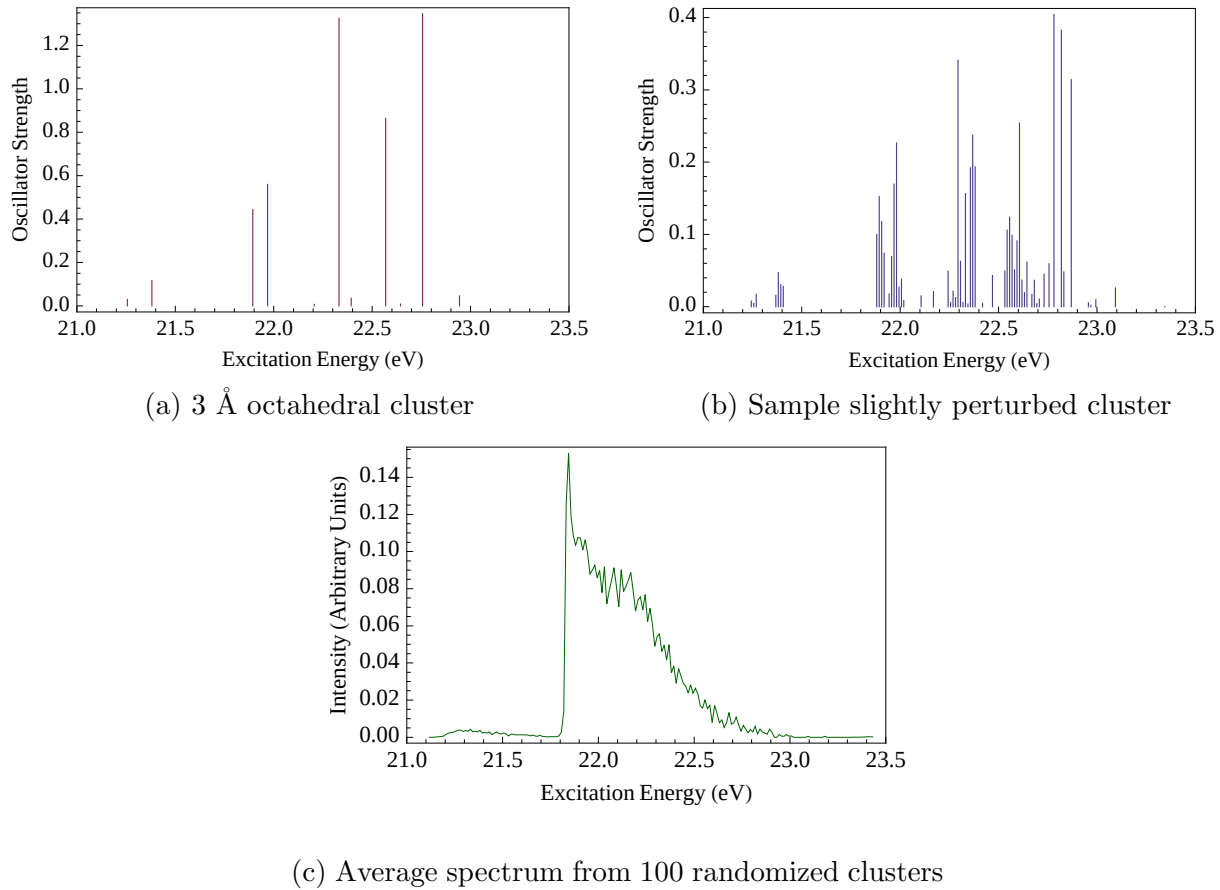
2.3.3 He_{25}

Next we turn to look at a larger cluster which contains a higher percentage of interior to surface atoms.

In the 25-atom cluster, the first 100 excited states correspond to the $n = 2$ states. Here the effects are largely the same as those in the 7-atom cluster. ?? shows the lowest energy states for the octahedral, a slightly perturbed, and a sample randomized geometry. The first few states in the $n = 3$ level are also shown to illustrate the gap between the levels, however, the basis used is not sufficiently diffuse to describe these higher energy states accurately.

Representative attachment and detachment densities of the octahedral cluster, are given in ?. In the $n = 2$ levels, we find that the excitations of the corner atoms (pink in ??) are the lowest in energy, and most similar to the atomic excitations. Then, the other surface


 Figure 2.11: Representative attachment detachment densities for 3 Å He_{25} (O_h) cluster

Figure 2.12: Stick spectra of He_{25} clusters

atom excitations (blue) are next lowest in energy, followed by excitations in the middle layer (green), then the excitation energies of the central atom (red) are highest. Examples of $1s \rightarrow 2s$ transitions are: corner atoms ??, surface atoms ??, middle atoms ?? and central atom ??. There are also the corresponding $1s \rightarrow 2p$ transitions: corner atoms ????, surface atoms ??, middle atoms ??, and central atom ??. Note that in the case of the p -type excitations those not directed into the cluster center appear at lower energies than those that are directed into the center as in the 7-atom cluster. Finally, there are also states where the excitation is from a combination of atoms in different shells such as ??????. Note again that these do indeed appear to all be superpositions of atomic states. Despite the appearance from some of the attachment and detachment plots that different numbers of atoms are involved (e.g. ????) this is not the case after looking at the eigenvalues or lower density contour values.

Performing the slight geometric perturbation on the 25-atom cluster does not significantly change the order of the states. However, it does introduce some localization, and also results in breaking many of the degeneracies. When looking at the stick spectrum of the octahedral

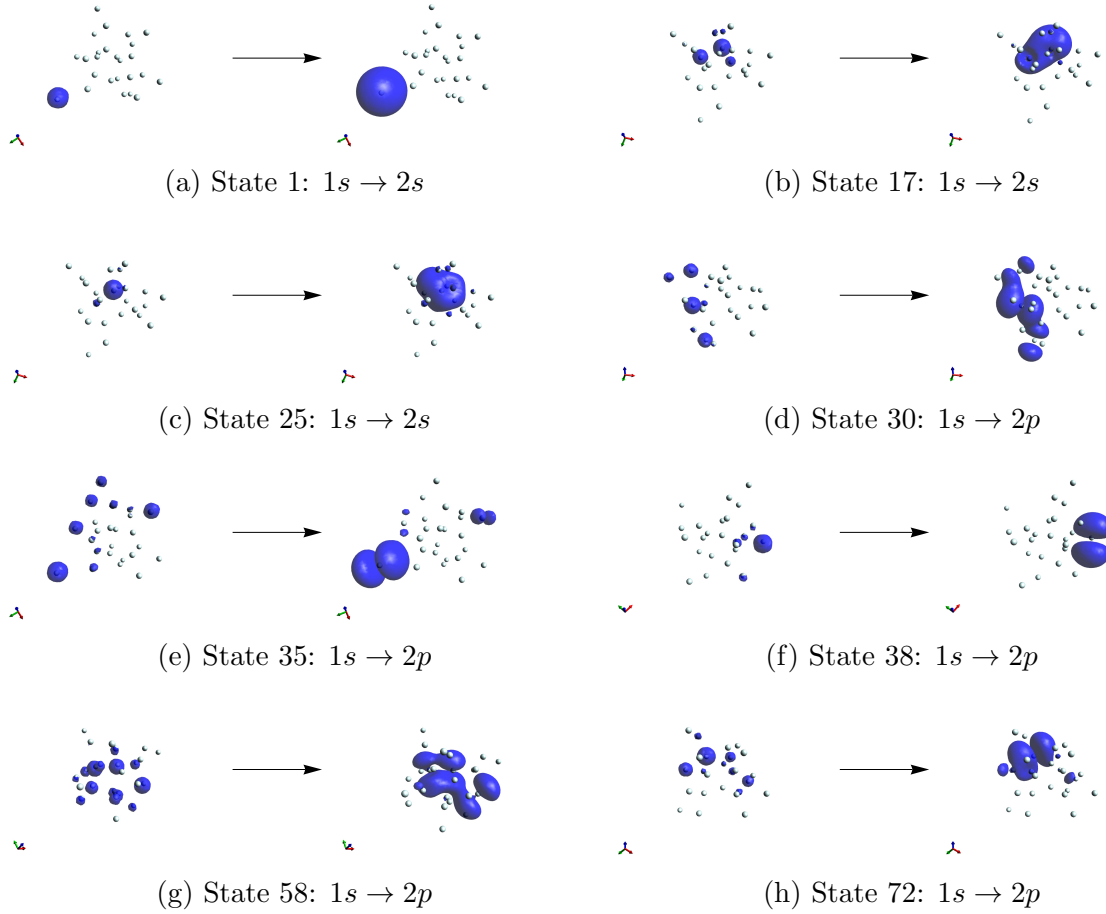


Figure 2.13: Representative attachment detachment densities for a randomized He_{25} cluster.

cluster, $??$, and the perturbed cluster, $??$, this results in the broadening of the peaks. In both cases, there are very weak contributions from the $1s \rightarrow 2s$ transitions below 21.5 eV, and then significant contributions from the $1s \rightarrow 2p$ transitions at higher energies as in the case for the 7-atom cluster.

For the randomized clusters whose states are shown in $??$, we find that the first 25 states correspond to what appear to be superpositions of $1s \rightarrow 2s$ excitations, and then the next 75 states correspond to superpositions of $1s \rightarrow 2p$ excitations. While the majority of these excitations appear to be localized on a single atom (e.g. $??????$), some are localized onto two adjacent atoms (e.g. $??$), and some are spread over more atoms. Of the more delocalized states, most excitations are on adjacent atoms such as $??????$, but there are a few that appear to be atomic superpositions on opposite ends of the clusters, $??$. However, in this state there are actually small contributions from other atoms all across the cluster which do not appear until lower isodensity values, indicating that this is just a highly delocalized

state.

In the randomized clusters, it is difficult to distinguish distinct layers as in the octahedral cluster, but we still find that the lower energy states are generally located on the exterior of the cluster (e.g. $1s \rightarrow 2p$), while the interior states generally appear at higher energies (e.g. $2s \rightarrow 2p$).

Looking at the disordered 25-atom clusters we can start to see something that looks very much like the experimental spectrum. From the averaged spectrum of 100 states, $??$ we can still see that it is mostly dominated by the dipole allowed $1s \rightarrow 2p$ type excitations, and that this peak is again skewed right, with the surface states contributing to the peak at the lower energy. There is also a small hump at 21.2 eV that corresponds to the $2s$ excited states which is a forbidden electronic transition. Again, real 25-atom clusters will be lower density, and this may cause a narrowing of the peaks, but these densities are fairly close to what would be expected in clusters of a few hundred atoms.

2.4 Discussion and Conclusions

In all of the clusters, there is a clear range of excited states that correspond to superpositions of atomic-like excitations into the $n = 2$ states. In He_N these are the $4N$ lowest energy excited states. They generally appear at excitation energies equal to or higher than the excitations of the atom due to the repulsive interaction of the excited electron with the other atoms in the cluster. Using the results calculated with the custom optimized bases, N2 which is exact for the $n = 2$ excitations of the helium atom at the 6-311(2+)G/CIS level of theory and N3 which is exact for the $n = 2$ and $n = 3$ levels at the 6-311(3+/2d)G/CIS level of theory, we can conclude that the $n = 2$ excited states with density inside the cluster are mixed with those of the $n = 3$ states. As seen from the results of separating the atoms in $??$, this state mixing decreases at larger internuclear distances, when all the excitations approach those of the atoms.

The $n = 3$ excitations were only computed for the seven-atom clusters and consist of states 29 to 91. While these are neatly described as atomic excitations at large nuclear separations, in the 3 Å cluster, the excited state density extends well beyond the cluster radius, resulting in significant overlap of the excited states. Also, it is not always the case that the surface states are lower in energy. Although for less dense clusters, it may be anticipated that the $n = 3$ states will behave more like the $n = 2$ states when the spatial distribution of the excited states is smaller than the distance between atoms.

In the octahedral and slightly perturbed clusters, the same ordering of states is observed. The primary difference being the loss of symmetry, which results in some localization of excitations and spreading of the states. In the octahedral clusters, the excitations are spread over the whole cluster, whereas in the perturbed clusters the excitations primarily originate from a single atom or from a superposition on adjacent atoms with a few exceptions where the excited state density is highly delocalized. In the fully randomized clusters there is

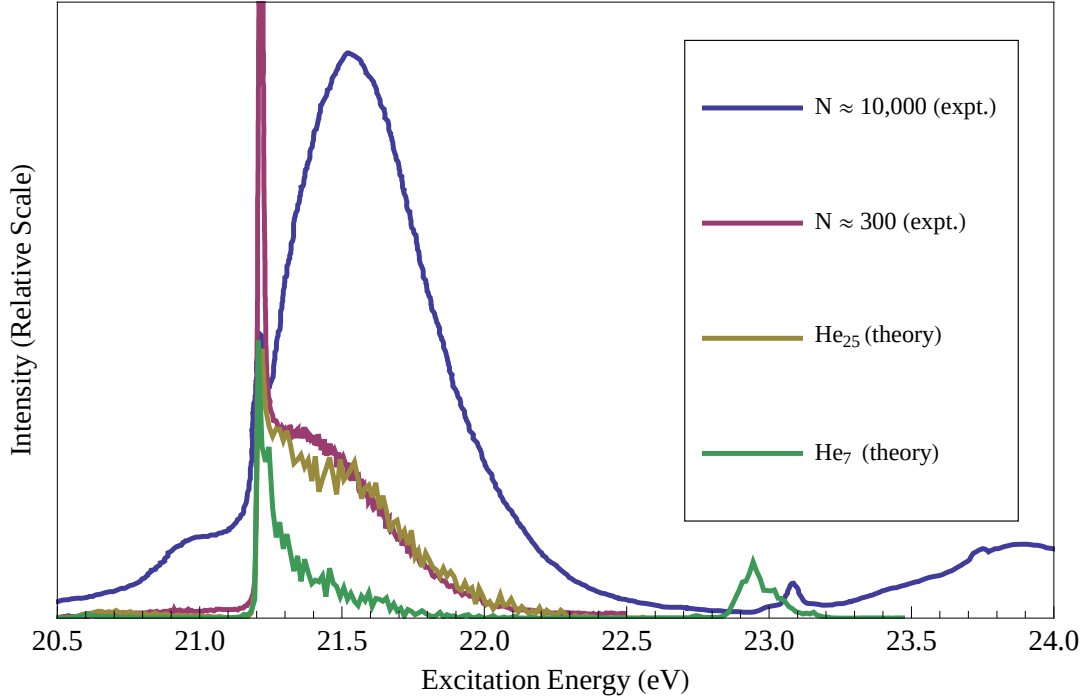


Figure 2.14: Comparison of experimental spectra ($\approx 10^4$ atoms[?] and 300 atoms[?]) and theoretical spectra for He₇ and He₂₅. The theoretical spectra have been shifted by 0.625 eV and scaled to have the same maximum, and the experimental spectra have been scaled to fit on the same plot. See text for further details.

significant rearranging of the states, with large mixings of s and p states, and interior with surface states.

Looking at the spectra obtained from the randomized clusters, we can see that in larger clusters, the contribution of the surface states decreases, while the bulk states increases due to the smaller surface to volume ratio. Thus we expect the $n = 2$ peaks to be less strongly skewed for larger clusters, which is what we observe in moving from He₇ to He₂₅.

Furthermore, the obtained theoretical results can be compared to the experimental excitation spectra (??) such as those obtained by Möller's group for He₃₀₀,[?] and for clusters of $\approx 10^4$ atoms.[?] After shifting the theoretical spectra by 0.625 eV to account for the systematic CIS error, and scaling so that they have the same maxima, we find that we reproduce the shape of the He₃₀₀ $n = 2$ bands extremely well with an He₂₅ cluster of a similar density. Note that the experimental spectrum contains a sharp peak from atoms present with the clusters though, so we can not directly see the ratio of the surface vs. the bulk contribution as we can in the computed spectrum. This result suggests that it may be possible to use small clusters at the density of larger clusters to reproduce the results for larger clusters. However, the spectra from the large clusters containing 10^4 atoms exhibit quite different shapes, and

intensities than the theoretical spectra and from the 300 atom spectra indicating that there may be other effects that become important in the larger clusters that are not present in the small clusters.

While we do not see any evidence of excitonic excitations in these clusters, it has been proposed that they do not appear in clusters smaller than 500 atoms.[?] Thus, the character of the excited states may change in significantly larger clusters. However, in order to investigate significantly larger clusters or higher excited states it will be necessary to develop a method capable of computing large numbers of excited states in a moderately sized basis. Currently the excited state methods available for computing electronic states are incapable of handling the number of states required for this problem. Another issue that must be addressed is that of the data analysis, as very large numbers of states will be generated, and the attachment/detachment visual analysis will become intractable. Efforts are being made in both of these directions.

We also do not directly see the formation of eximers, or excited dimers, in the these clusters, and it may be that they are formed after the initial excitations which would require that we look at the time evolution of the excited states. Thus, we separately intend to investigate the initial forces on the helium clusters which may also be of direct interest for interpreting the experimental results.[?]

In this chapter we have investigated the electronically excited states of several small helium clusters, including the effects of cluster size, disorder and inter-atomic distance on the character of the states. Even with these small clusters we can reproduce most of the features seen in the experimental spectrum for the $n = 2$ and $n = 3$ manifolds. We have also shown that the $n = 2$ excited states of these small clusters can be readily understood in terms of superpositions of atomic-like excitations, and that the $n = 3$ states, while somewhat more difficult to interpret, are also essentially highly overlapping superpositions of atomic-like states.

Chapter 3

Simulations of the dissociation of small helium clusters with *ab initio* molecular dynamics in electronically excited states

3.1 Introduction

The apparent, beautiful simplicity and unique properties of pure helium clusters attract ever increasing attention to their fundamental properties and potential applications.¹⁻⁶ Excited states of helium clusters are interesting from a basic science perspective, in particular, for the study of solvent-solute interactions such as energy- and charge-transfer between the superfluid helium matrix and dopant atoms and molecules.⁷⁻⁹

Despite a growing number of experimental and theoretical studies, it is only quite recently that the tools have become available for detailing the electronic structure of excited helium clusters and to follow their dynamic evolution.¹⁰⁻¹⁴ Experimentally, generating sufficient energy (> 20 eV) for electronic excitations, the non-uniformity of the cluster sizes, and the multitude of simultaneously progressing dynamic channels pose significant challenges.¹⁵ Recent work by the Berkeley Lab group has added greatly to the current understanding of electronically excited states and found, at least for large clusters, that excitations lead to different relaxation channels based on the energy and location of the initial excitation.¹⁶⁻¹⁸ However, significant uncertainties remain on the mechanism of the excitation decay, especially at the atomic scale.

Theoretical studies of helium clusters have also been rather limited due to the inherent challenges in computing excited states of extended systems with many nearly degenerate states. Large scale semi-empirical models, such as the step potential model with hard sphere scattering,¹⁹ and the liquid drop model,²⁰ do not contain any microscopic information and are not capable of capturing atomic level details. *Ab initio* dynamics of ground-state

neutral^{2,3} and ionized helium clusters⁴ have been investigated, but dynamics in the excited states remain elusive. Our earlier work⁵ on 7- and 25-atom clusters and that of von Haeften and Fink⁶ on He₇ probed the vertically excited states of small helium clusters yielding insight at the atomic level for static states. However, these did not account for any dynamics resulting from the initial excitation.

Treating both the nuclei and electrons quantum mechanically rapidly becomes intractable as the system size grows. Thus, most *ab initio* molecular dynamics (AIMD) calculations rely on mixed quantum-classical methods where the nuclei are propagated classically and the electrons quantum mechanically on a single state of the system. Adiabatic or Born-Oppenheimer AIMD of ground electronic states has an extensive history and can be a useful tool for studying non-stationary systems.^{7,8} This method does not require any foreknowledge of the behavior of the system, and the adiabatic approximation is generally valid as long as the Born-Oppenheimer approximation holds. Near conical intersections and avoided crossings, the motion of nuclei and electrons cannot be straightforwardly separated and the adiabatic picture breaks down.

Attempts to expand AIMD to excited states and non-adiabatic dynamics have met with varying degrees of success.⁹⁻¹² The most common methods for contending with interacting potential surfaces, which give rise to non-adiabatic transitions, are variations of Tully's surface hopping.⁹⁻¹¹ Surface hopping algorithms probabilistically allow switching between surfaces and necessarily involve large numbers of trajectories for each initial state. They also lack a fully rigorous derivation, and are especially problematic when multiple nearly degenerate regions exist or when passing through more than one interaction region.¹² Alternative methods for computing molecular dynamics involve following the excited state Born-Oppenheimer (adiabatic) surface, transforming to a diabatic representation, and Ehrenfest (mean-field) dynamics¹³. All of these also have their weaknesses. Purely Born-Oppenheimer dynamics often do not give physically relevant results,⁹ converting to diabatic representations is not entirely well defined,^{10,11} and Ehrenfest dynamics are not microscopically reversible.¹²

Our primary interest here is to determine the fate of helium cluster excitations. Since the excitations are into a dense manifold of states it is impractical to run statistically relevant numbers of trajectories in all possible states. Thus, we have adopted a slightly different approach and use a deterministic algorithm, which is similar to Born-Oppenheimer dynamics much of the time, but preferentially follows the diabatic state when near-degeneracies occur. A single trajectory for each excited state is launched with zero kinetic energy, which implies that all kinetic energy developed during the course of the trajectory is a direct result of the forces exerted by the excited state. After the initial excitation, a recently developed state following algorithm selects the subsequent state based on the character and energy of the previous state.¹⁴

The high cost of calculating trajectories "on the fly" dictates the underlying electronic structure method be as efficient as possible. For excited states, time-dependent density functional theory (TDDFT) is often the best option. It is efficient and can give very good results, provided the functional is chosen carefully.^{15,16} Wavefunction based methods may

also be attractive in some cases as they generally have more predictable errors. However, with the notable exceptions of configuration interaction singles (CIS) and time-dependent Hartree-Fock (TDHF), they are computationally more demanding.^{???} For most systems CIS and TDHF yield poorer results than TDDFT due to the lack of electron-correlation, but in certain circumstances they may be preferable. One such instance is with Rydberg states that suffer from self-interaction error for standard density functionals.^{??}

Previously, we reported[?] theoretical studies on the static excited states of small clusters (He_n , $n = 7, 25$) for $2s$ and $2p$ excited states. It was found that a good description of the excited states could be obtained using comparatively cheap CIS calculations and that the excitation depth, at least for the $2s$ and $2p$ states, correlated strongly with the blue shift of the excitation. Here, we investigate the fate of He_7 excitations by AIMD coupled with state following, and present the results of atomically resolved dynamics for relaxation of He_7^* clusters excited initially into the $n = 2$ manifold (< 23 eV).

3.2 Methods

We compute helium cluster excited states using configuration interaction singles (CIS) and use standard Born-Oppenheimer dynamics coupled with a state-following algorithm to determine their fates. The overlap of the attachment and detachment densities from nearby excited states assesses their character and determines their population from the current state when near degeneracies occur. All calculations run on a single processor using a developmental version of Q-CHEM 4.0[?].

3.2.1 Geometries

We generate the initial cluster geometries as in our previous work[?]. A random distance between 0 and 3 Å is added to the x , y , and z coordinates of each atom in a 3 Å octahedral cluster[?]. The randomized cluster is then optimized using MP2 with a standard Pople 6-311G basis set. Due to the extremely shallow potential well, a myriad of local minima with similar energies exist, and no duplicate geometries occurred for 100 such clusters. The spread of the ground state MP2 energies for the optimized clusters is 6 meV, which is extremely small relative to the excitation energies $\gtrsim 21$ eV, and the errors in CIS are generally far larger than this difference. The average inter-atomic distance for He_7 clusters generated using this randomization procedure is 3.7 Å, which is very close to the previously determined pair-distribution function result of 3.60 Å for much larger clusters.^{??} Selecting only the absolute nearest-neighbor distance for each initial geometry yields an average of 3.0 Å, which also correlates very closely to the large cluster nearest-neighbor distance of ≈ 3.05 Å.^{??}

In such small clusters the definition of surface and bulk states is ill-defined. The surface region for large, finite clusters may be defined by the variation of the bulk value, which, for large helium droplets (He_N , $N \geq 1000$), is ≈ 6 Å thick.^{??} The absolute largest interatomic distance in the model systems presented here was 7.6 Å, and thus these calculations do not

include bulk effects. However, microscopic dynamics in large helium clusters are frequently discussed considering local atom-atom interactions in which the droplet environment surrounding an excited atom is represented either by an average potential or by a single nearest neighbor atom.^{???} The dynamics simulations presented here offer an opportunity to extend this picture to a quantitative description of excitations and interactions including virtually all nearest neighbor atoms of an excited cluster moiety. This approach may provide valuable benchmarks, in particular, to guide the interpretation of experiments that provide increasing evidence for marked differences between dynamics proceeding in the bulk and surface regions of large helium clusters.^{???}

3.2.2 Vertical excitations

The excited state energies and forces are calculated with CIS^{??} in the 6-311(2+)G Pople basis. This is the standard 6-311G basis supplemented with two sets of diffuse functions and is the smallest basis yielding qualitatively good results for the $n = 2$ excitation manifold. The first set of diffuse functions uses the coefficients from Yin and MacKerell[?], and the second set results from scaling the exponents of the first by $1/3$.³² CIS is among the lowest scaling *ab initio* methods for excited states and, for small helium clusters, gives results qualitatively similar to higher level wavefunction methods such as equation of motion coupled-cluster singles and doubles (EOM-CCSD).^{??} Contrasted with single-point calculations, the impact of computational cost increases dramatically for trajectory calculations, therefore a low-scaling method is crucial for AIMD calculations. The density functional equivalent of CIS is the Tamm-Dancoff approximation to TDDFT.^{???} However, self-interaction error is an issue with standard density functionals when computing diffuse Rydberg states so a wavefunction based method is preferred in this instance.^{??}

In addition to the energy, when performing dynamics simulations the electronic gradient of the excited state will also be crucial. To assess whether the CIS forces were reasonable we also computed the initial forces using EOM-CCSD. The average magnitude of the CIS forces is $0.036 \text{ eV/\AA}$ and for EOM-CCSD is $0.041 \text{ eV/\AA}$. Subtracting the EOM-CCSD gradient from the CIS gradient component-wise and then evaluating the magnitude of the difference gave a root mean square deviation of $0.002 \text{ eV/\AA}$. Thus, the CIS forces are slightly smaller in magnitude (99% confidence).

3.2.3 Dynamics

Classical nuclear dynamics with a standard velocity-Verlet algorithm[?] propagate the nuclei. Each atom is initialized with zero velocity so that all kinetic energy (KE) developed during the course of the trajectory is due to excited state forces. The selection of the electronic state at each time-step is based on a newly developed algorithm that will be briefly described here and detailed in a forthcoming publication.[?]

We compute the AIMD trajectories using a step size of 5 a.u. $\approx 0.1 \text{ fs}$ ($1 \text{ a.u.} = 0.0242 \text{ fs}$) for a minimum of 242 fs (2000 steps) and a maximum of 968 fs (8000 steps). In order to

optimize computational resources, any time a trajectory clearly results in full fragmentation or reaches a stationary point, the calculation terminates. Cluster trajectories associated with partial fragmentation that do not stagnate are computed until the maximal time. The criteria we use for halting the trajectories are the magnitude of the electronic gradient at the current time step ($< 1 \times 10^{-4} E_h/a_o$), and either the difference in energy ($< 1 \times 10^{-8} E_h$) or the difference in magnitude of all atomic displacements ($< 1.2 \times 10^{-4} \text{ \AA}$) between successive time steps. This produces essentially the same product distribution as if all trajectories were run to 968 fs.

All 28 singlet $n = 2$ vertically excited states are populated at t_0 and subsequent electronic states are selected based on energy and character. Most often this corresponds to simply following the adiabatic surface, but if multiple states exist very near each other the character of the nearby states is evaluated and the one with the most similar character is chosen provided there is an obvious choice. Curve crossings in helium clusters with this method are quite rare events. The majority of the trajectories ($\approx 60\%$) experience 0 crossings and 90% have ≤ 10 crossings. Also, despite the high density of states there is rarely uncertainty about which state should be chosen. About 0.05% of the time steps had nearly degenerate states that could not be described well in terms of the character of the state from the previous time step. Of these uncertain steps, 40% result from basis set discontinuities, which can occur when atoms collide.

The definition of nearness to a given state k (energy E_k) is controlled by the user-set parameter γ_E such that all states n within the window $E_n < (E_k \pm \gamma_E)$ are accessible and $\gamma_E = 0$ corresponds to pure adiabatic dynamics. The estimated E_n for the current time step includes the energy of the previous state and the propagated kinetic energy. For helium clusters a value corresponding to $\gamma_E = 0.0005 E_h$ (≈ 0.01 eV and roughly 0.5% of the $n = 2$ excited state band) is chosen. This window is sufficient to contain all nearly degenerate states while preventing erroneous switching into a state of a similar character but significantly different energy. The trajectory fates are relatively insensitive to this parameter. However, if chosen to be too large for the system (e.g. 0.5 eV), unphysical, non-energy conserving products can result. For example multiple dimers can form that have a total energy much higher than the initial excitation.

If no more than one state is predicted to be near state k at time t_i the state closest in energy is chosen for t_{i+1} . When multiple states may be accessed their attachment (**A**) and detachment (**D**) densities are compared to those of the previous state. This provides an overlap metric for the particle and hole densities which is not sensitive to phase instabilities.[?] A scale from 0-1 is used where a value of 0 indicates that both densities have no points in common and 1 correlates to states with identical densities at t_i and t_{i+1} . The magnitude of the difference density, $\mathcal{S} = 1 - \frac{1}{2} |\mathbf{A}_{t_{i+1}} - \mathbf{A}_{t_i} - (\mathbf{D}_{t_{i+1}} - \mathbf{D}_{t_i})|$, defines the similarity scale. To determine similar character a threshold of 50% ($\mathcal{S} \geq 0.5$) was used and the state with the largest overlap greater than this value was selected. The dynamics are also not highly sensitive to this threshold for a wide range of values and it primarily exists for other applications of this state-following algorithm, such as in excited-state geometry optimizations.[?] In the

occasional instance where a time step did have an overlap below the γ_S the state following code defaulted to selecting the adiabatic state (nearest in energy). This uncertainty in state selection occurred in $\approx 0.05\%$ of the time steps and was often due to basis set discontinuities (primarily when atoms collide) or when passing through a conical intersection where all states dramatically change character between time t_i and t_{i+1} .

State-switching was found to be quite a rare event. The majority (56%) of the trajectories had no changes, 87% had ≤ 5 and 90% had ≤ 10 state-switches. Furthermore, when considering all computed time steps (7.7×10^6) only 1.4×10^4 ($\leq 0.02\%$) steps had a state that changed from the previous step. Thus, this dynamics algorithm produces largely adiabatic trajectories, with state switches based on the excited-state character allowed only when more than one state occurs in a small energy window.

Trajectories were initialized on all helium $n = 2$ states accessible by single photon absorption. CIS does not allow changes in electron spin and helium has low spin-orbit coupling so triplet states are neglected and only singlet states are computed. In He_7 clusters, the seven lowest-energy states correspond to superpositions of $2s \leftarrow 1s$ atomic-like excitations and 8 through 28 correspond to superpositions of $2p \leftarrow 1s$. Conservatively, for $2s \leftarrow 1s$ and $2p \leftarrow 1s$ transitions, 14 states and 28 states respectively are calculated at each step along the trajectory. Energy conservation dictates the potential energy must decrease for any increase in KE so only states with potential energies lower than the initial excitation are ever accessible. A significant energy gap between the highest energy $n = 2$ state and the lowest $n = 3$ state prohibits crossing into a state with $n \geq 3$ for any initial excitations to the $n = 2$ manifold. Finally, even though by single photon excitation the p states are primarily populated, we consider all singlet $2s$ and $2p$ states for each of the 100 He_7 clusters as it is possible for a $2p$ state to undergo a non-radiative transition into a $2s$ state. Thus, a total of 2800 trajectories were computed.

3.3 Results and discussion

The density of states in the $n = 2$ singlet manifold is shown in ?? for all 100 of the He_7 clusters. There are two distinct bands peaked at the atomic $2s$ and $2p$ states. While some mixing of states was observed in the vertical excitation, it was always fairly straightforward to classify the state as dominantly $2s$ - or $2p$ -like (σ - or π -like). This is due to the energy separation between the s - and p -type states of helium. The bands are strongly skewed with blue shifted tails and the $n = 2$ manifold spans over 2 eV. Note that these are calculated with CIS/6-311(2+)G and are shifted by ≈ 0.6 eV from the generally accepted values.[?] This constant shift is due to the error inherent to CIS and this finite basis,[?] and as we focus on qualitative effects the results are presented in their uncorrected form.

The single photon excitation spectrum is also given in the inset of ?. It is estimated by weighting the density of states with the oscillator strengths. As expected from dipole selection rules, the p states strongly dominate in intensity, though there is a small contribution

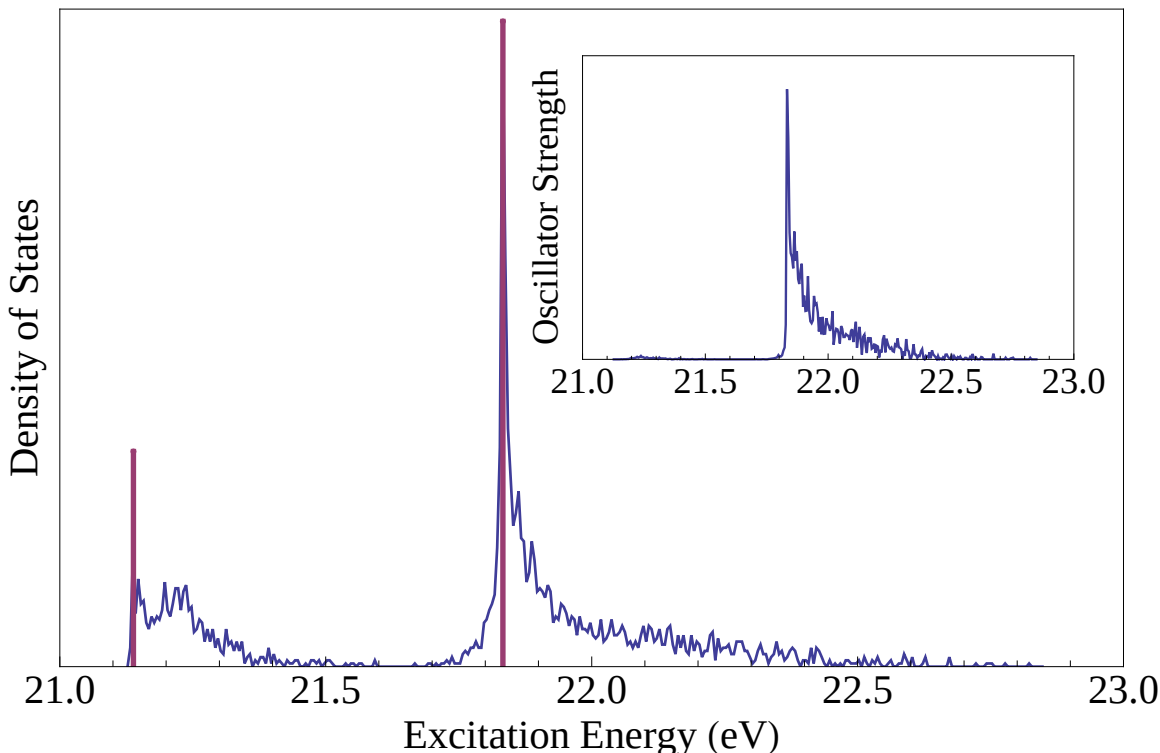


Figure 3.1: Density of states in He_7 singlet excited state manifold (100 optimized ground state geometries) with atomic excitation energies marked by vertical lines. The inset shows weighting by oscillator strength.

from s -type states due to s and p mixing. Trajectories are initiated in all states, although in single photon experiments the population of $2p$ states clearly dwarfs the $2s$ states.

Much information and some calibration of the expectations can be obtained by analyzing He_2 and so we begin there before detailing the results of the He_7 cluster dynamics.

3.3.1 Helium Dimer

In order to develop a qualitative intuition for the excited-state forces that drive nuclear motion during cluster relaxation, we first analyze the potential energy curves of helium dimers in the $n = 2$ Rydberg manifold. The potential curves were calculated using the same model chemistry that was used for the trajectory calculations, CIS/6-311(2+)G, so that we can directly apply the dimer results to what is expected using this method. ?? shows the ground and first 8 excited states of the neutral dimer as well as the ground state of the cation, He_2^+ .

The essentially unbound ground molecular state ($^1\Sigma_g$), dissociates into two $1s$ ground state atoms. Since He atoms contain two paired electrons in the filled $1s$ shell, the separated

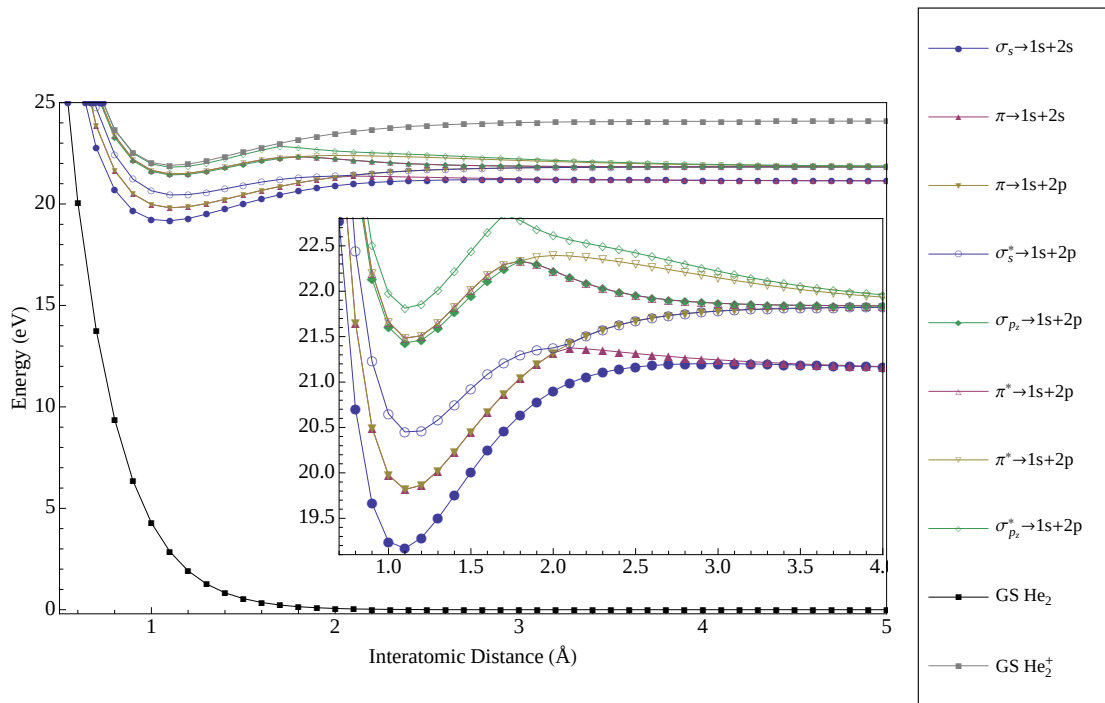


Figure 3.2: Potential energy curves of He_2 , with CIS/6-311(2+)G. All bound excited states shown have a minimum at $\approx 1.1 \text{ \AA}$ and four dissociation limits are shown: $\text{He}(1s) + \text{He}(1s)$, $\text{He}(1s) + \text{He}(2s)$, $\text{He}(1s) + \text{He}(2p)$ and $\text{He}^+(1s) + \text{He}(1s)$. The $\text{He}_2^+ \sigma_s$ state nearly parallels the He_2^+ curve except for the slight repulsion in the neutral dimer.

atoms are extremely stable and do not readily bond with each other. He_2 is completely unbound in the mean-field limit and must rely on dispersive forces to obtain its extremely shallow potential well.[?] This is also what one would predict from the textbook molecular orbital (MO) picture because the ground-state dimer has four electrons with equal numbers in bonding (1σ) and anti-bonding ($1\sigma^*$) orbitals.

The excited states of helium all necessarily involve higher principle quantum numbers, $n \geq 2$, and, contrasting with the ground state, some of the excited states exhibit regions of significant binding. Again, this can be predicted by basic MO theory; in the lowest excited states of He_2 an electron from a $1\sigma^*$ orbital is promoted to a bonding orbital (2σ or 2π). In atomic He^* the excited electron enters a diffuse Rydberg orbital and although it is neutral it may be interpreted as a positively charged He^+ core with a distant electron. Similarly, excited states of the dimer behave as a He_2^+ core surrounded by a remote electron, though this trend does not obviously hold for larger excited clusters.^{??} In He_2^+ the atoms are actually held together by electrostatic forces and thus He_2^+ has a very stable bound core.

The lowest excited state dissociation limit is the doubly degenerate $\text{He}(1s) + \text{He}(2s)$ which is followed by the sextuply degenerate $\text{He}(1s) + \text{He}(2p)$. The fourth dissociation limit in ??

results in ionized $\text{He}^+(1s)+\text{He}(1s)$. In order to properly describe states with $n \geq 3$ a significantly larger basis is required and these states will not be discussed further.

At equilibrium, the first excited state is bound by just over 2 eV and has σ_s character. The second and third states are of π character resulting from the p_x and p_y atomic orbitals with one dissociating to atomic $1s+2s$ and the other to $1s+2p$. The σ_{p_z} state resulting from the p_z atomic orbitals is actually the fifth state when ordered energetically. It is significantly higher in energy than the other bonding states and also has a lower binding energy of 0.5 eV. The corresponding σ_s^* , $\sigma_{p_z}^*$ and doubly degenerate π^* are also shown in the figure. All of the asymptotically anti-bonding states have bonding character at short internuclear distances. The potential well minima lie at least ≈ 0.5 eV below the correlated dissociation limits, with the exception of $\sigma_{p_z}^*$, which is barely bound. A close inspection of ?? reveals that the potential minimum of all He_2^* states occurs at 1.1 Å as does the He_2^+ ground state. This is consistent with interpreting He_2^* as a cationic core with a distant and diffuse excited electron.

At larger inter-atomic distances $\gtrsim 3$ Å, the excited states of the dimer are all very weakly attractive or repulsive. Of these 3/8 are attractive and tend towards the bound region, and 5/8 are repulsive resulting in fully-separated atoms. Thus we expect the majority of trajectories to dissociate, and those that do remain bound will likely contain significant vibrational energy.

Using a harmonic approximation the vibrational state spacing in both the ground state of He_2^+ and first excited state of He_2 is roughly 1600 cm^{-1} . This corresponds to a zero-point energy of $\approx 800 \text{ cm}^{-1}$ and an oscillation period of approximately 21 fs. Fitting to a Morse potential reveals that vibrational states near the top of the well have periods over an order of magnitude longer. The π and σ_s excited states are the broadest and, thus, they are expected to support longer periods than other He_2^* states which have narrower and shallower wells.

3.3.2 Illustrative trajectories

Sample trajectories for He_7^* clusters are shown in ??. Snapshots of the atoms every 1 fs are shown, with the final geometry given by the large (red) atoms. The most commonly observed outcome is full fragmentation into seven separate atoms one of which carries the electronic excitation, $\text{He}^* + 6 \text{ He}$. In principle excited clusters from He_2^* to He_7^* can also be formed although only He_2^* and He_3^* are observed. In the dimer the majority of the excited states are weakly repulsive at interatomic distances that are characteristic of those found in the interior of large clusters (?). Thus, it may be expected that a He_7 cluster most commonly undergoes full dissociation after excitation, but we may also anticipate effects of attractive forces at short internuclear distances which give rise to complex relaxation dynamics.

Atomization

Two possible ways full fragmentation may occur include direct dissociation as illustrated by the trajectory in ?? or involving collisions between atoms as shown in ??. This fragmentation is to six ground state atoms and one atom that is excited to a $2s$ or $2p$ state. The excitation

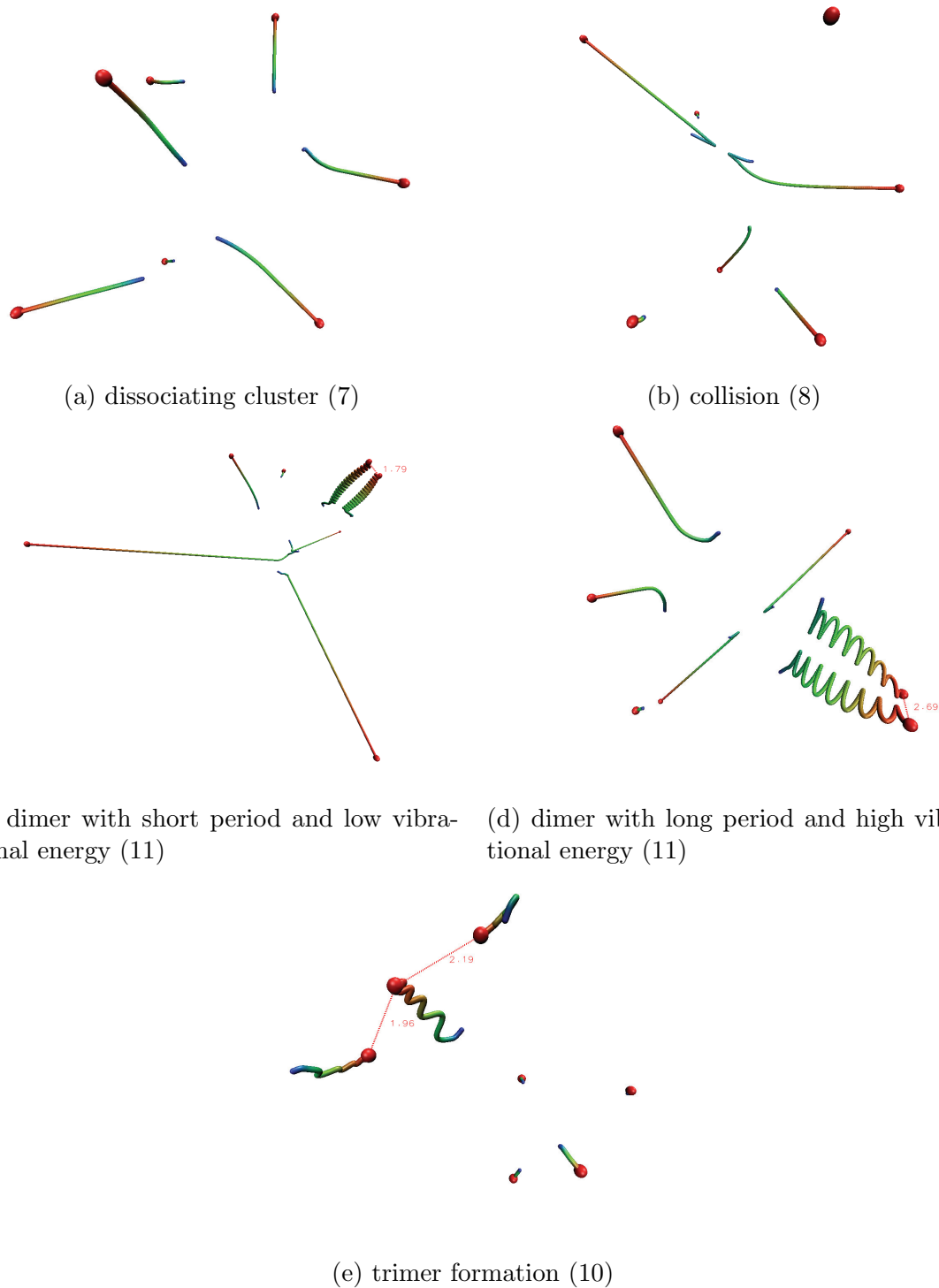


Figure 3.3: Sample Trajectories: blue initial point, red (large) final point. The number in parentheses indicates the state populated in the initial excitation and corresponds to the n^{th} excited state in the singlet manifold of He_7 .

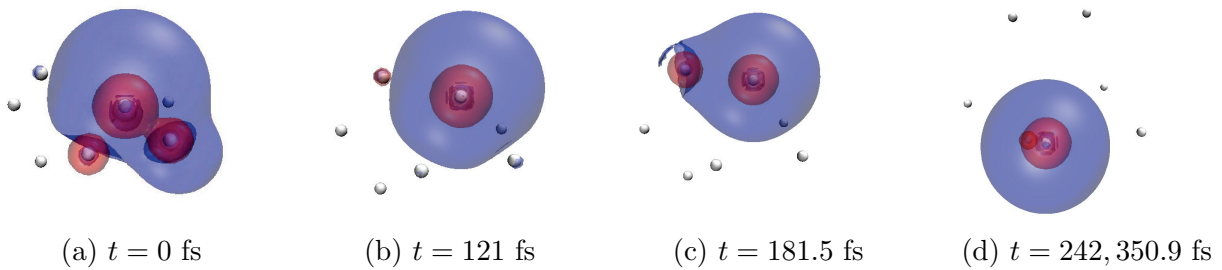


Figure 3.4: Attachment/detachment densities for the dissociating trajectory shown in ???. The detachment (hole) densities are in red and the attachment (particle) densities are in blue. The initial excitation is into a superposition of $2s$ states and the excitation ultimately ends on a $2s$ -atomic like state. The excitation moves about until about ≈ 200 fs. Note the atoms are slightly moved between $t = 242$ and $t = 350.9$ fs, but the excitation appears the same.

localizes onto a single atom at large internuclear separations as the vertical excitation energy is not large enough to support multiple excited atoms.

Careful attachment and detachment analysis was performed for many individual trajectories. ??? illustrates detachment (red) and attachment (blue) densities at various steps along the trajectory shown in ???. The initial excitation into a semi-delocalized $2s$ -type orbital moves about the cluster before settling onto a single atom after ≈ 200 fs, where it remains for the duration of the trajectory. The two time steps in ??? have slightly different atomic positions, but the excitation is qualitatively the same in both. ??? shows the densities associated with the colliding trajectory of ???. Here, an initially delocalized $2p$ -state localizes onto two atoms beginning around $t = 12$ fs (???). This excited dimer then undergoes an elastic collision between 90 and 120 fs. The atoms do not remain together because the kinetic energy of their approach, which is not dissipated by interactions with additional atoms, is too high to allow bonding in this case. Ultimately, this cluster fully dissociates and results in a single $2s$ excited atom by ≈ 300 fs (???).

Dimerization

Approximately 3% of all trajectories lead to the formation of stable, excited dimers. The dimers form with varying amounts of vibrational energy as illustrated by the trajectories in ?? and ??. Longer periods of vibration usually, and for purposes of this study, always correspond to states with higher vibrational energy. As seen in ??, for bound states the potential well broadens as the vibrational excitation increases and the corresponding decrease in the potential gradient leads to longer vibrational periods.

?? shows the detachment/attachment density evolution associated with the dimer forming trajectory of ???. Here, the initial excited state is a highly delocalized superposition of atomic $2p \leftarrow 1s$ states. At ≈ 120 fs some localization is observed, and by 240 fs the excitation has fully localized onto a single pair of atoms. Note that the apparent partial charge-transfer

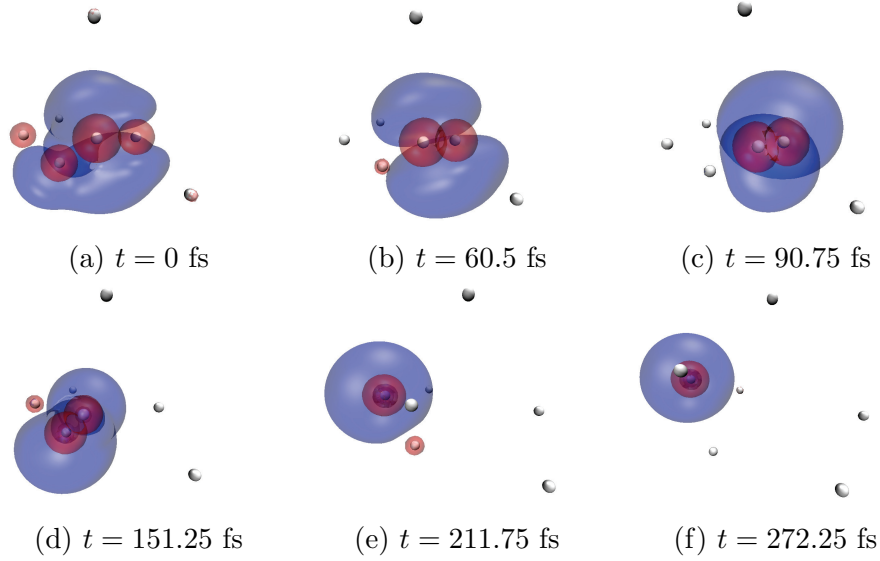


Figure 3.5: Attachment/detachment densities for the collision trajectory shown in ???. The collision occurs between $90 < t < 120$ fs and these plots show the initially delocalized $2p$ superposition state localize onto 2 atoms and end on a single atom after the collision.

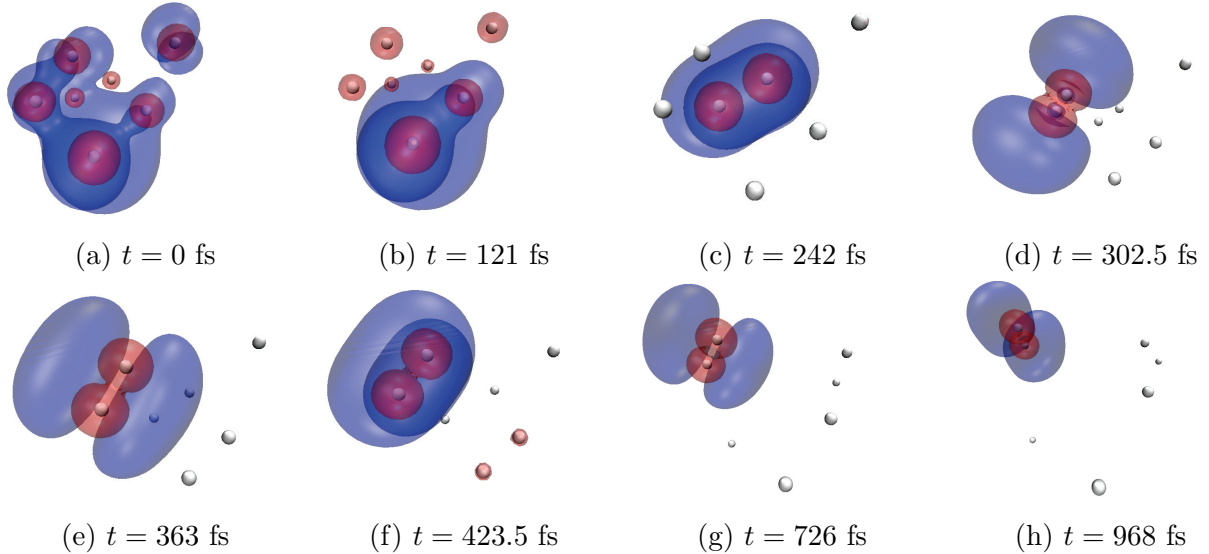


Figure 3.6: Attachment/detachment densities for the dimer forming trajectory shown in ???. The trajectory shows the initially very delocalized $2p$ -type state localize onto a dimer at $t \approx 240$ fs and remain there.

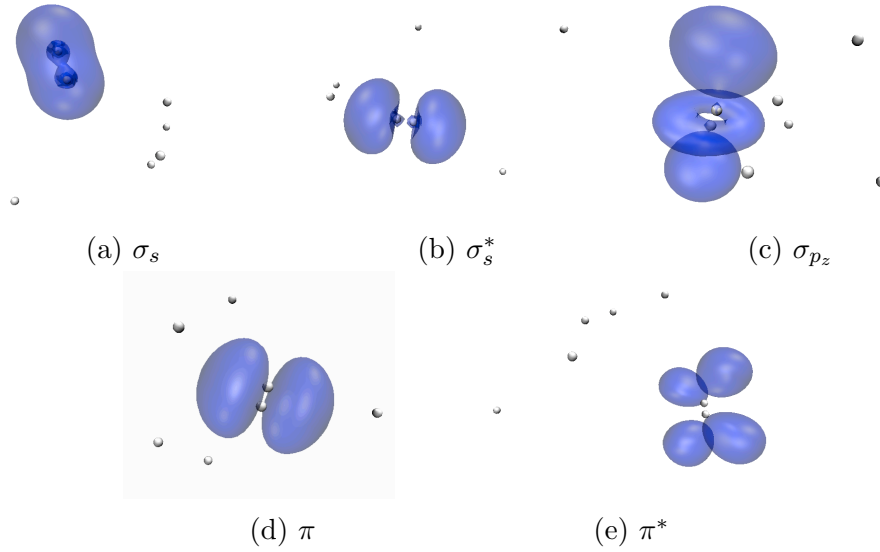


Figure 3.7: Attachment densities for each type of stable dimer found in the cluster trajectories. All possible states are observed except the anti-bonding $\sigma_{p_z}^*$ which is barely bound relative to $\text{He } (1s) + \text{He } (2p_z)$.

character (spatial separation of red and blue zones) of the state in of ?? is an artifact due to the graphic representation of the isosurface; decreasing the contour value reveals the attachment density also surrounds the atom that appears to carry isolated detachment densities. In ?? the dimer is in a π state that morphs into a σ^* state (??) and back to a π state (??). In this case it occurs through a series of non-adiabatic transitions. The vibronic oscillation of the excited dimer continues to the end of the 968 fs trajectory with an average period of 88.5 fs. The vibrational period of this dimer is long compared with that of the trajectory shown in ?? indicating that different states of He_2^* are formed. The trajectory of ?? also happens to form a π -state dimer, but with much lower vibrational energy. In addition to varying vibrational periods we also observed dimers in nearly all possible electronic states: σ_s , σ_s^* , π , π^* , and σ_{p_z} . ?? shows sample attachment densities for each type of He_2^* electronic state at the final point of their respective trajectories.

Trimerization

Even more rarely, He_3^* fragments are detected. ?? shows the formation of an excited trimer and ?? shows the corresponding attachment and detachment densities. Here the state is initially more or less a localized $2p \leftarrow 1s$ atomic state with very small excitation amplitudes on neighboring atoms. The excitation then spreads until it is located on two non-adjacent atoms separated by over 5 Å. Between 280 and 660 fs (?????????) the excitation remains on the same two atoms and undergoes oscillations of the excited state density on a time scale of ≈ 100 fs. After 660 fs, the excitation spreads to the middle atom of the trimer and then

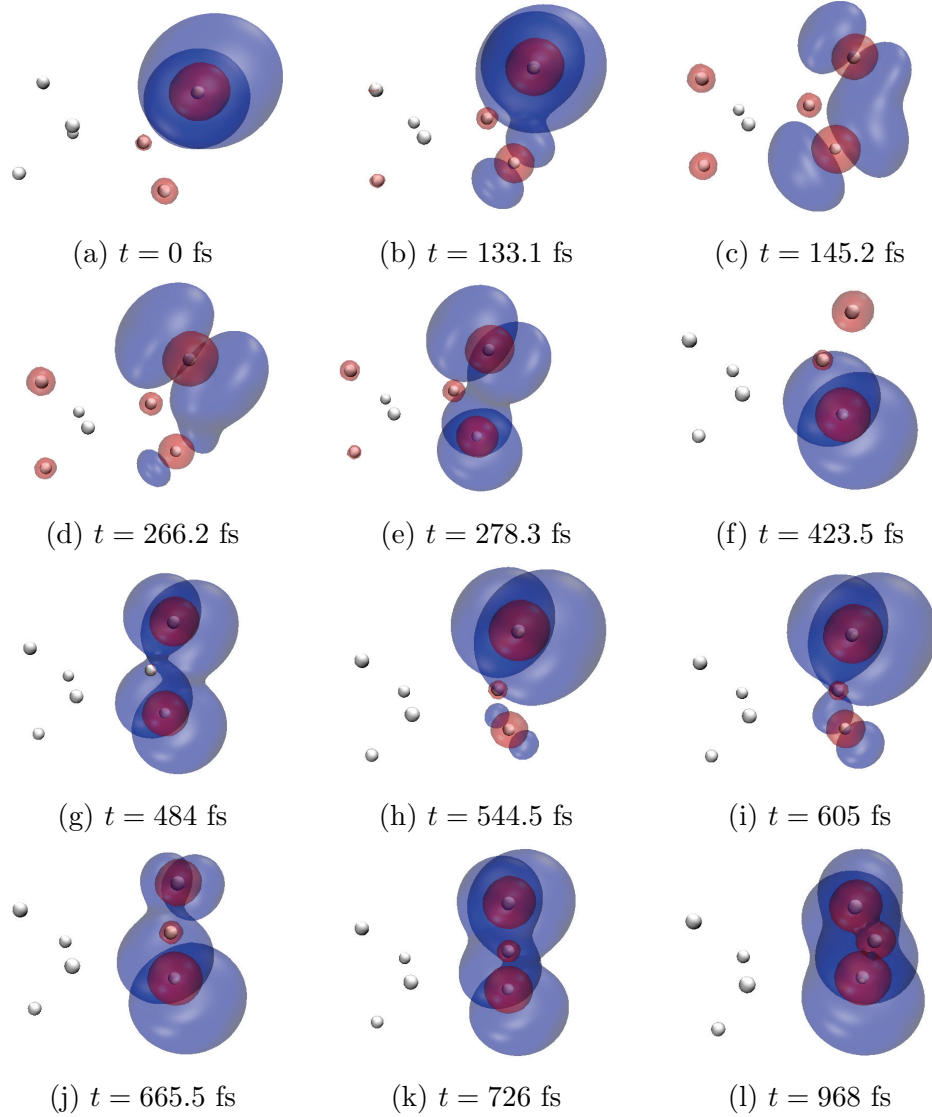


Figure 3.8: Attachment/detachment densities for the trimer forming trajectory shown in ???. The initial excitation is into a $2p$ state localized on a single atom and ends in a π -state spread over 3 atoms. At 130 fs the excitation begins spreading to nearby atoms, and then exists for an extended period of time on the two non-adjacent atoms that eventually become the end atoms of the excited trimer.

remains on all three atoms for the duration of the trajectory (??????). The excitation does not appreciably spread over all three atoms until the distance between the central atom and each of the side atoms is less than $\approx 3 \text{ \AA}$.

The excited trimer, He_3^* , is very weakly bound according to high-level theoretical calculations ($2.27 \text{ mK} \approx 2 \times 10^{-4} \text{ meV}$) and has not been observed experimentally.?? The

corresponding linear cation He_3^+ , is strongly bound relative to 3 fully separated atoms but only weakly relative to $\text{He}_2^+ + \text{He}$. Careful calculations (CCSD(T)/aug-cc-pVQZ) have determined He_3^+ to be bound by 2.65 eV relative to the three-body dissociation limit and only by 0.29 eV relative to $\text{He}_2^+ + \text{He}$.⁷ The CIS/6-311(2+)G values relevant for this work are 1.6 eV relative to $2\text{He} + \text{He}^+$ and 0.01 eV relative to $\text{He}_2^+ + \text{He}$. While it is clear that our low-level calculations of He_3^+ yield much smaller energies than the CCSD(T) results they qualitatively agree. Due to the very weak binding energy of He_3^* and the instability of He_3^+ relative to He_2^+ , we did not anticipate observing any trimers from small He_7 clusters. The conditions required to form the trimer are quite precise and it is very rarely ($< 0.5\%$) that the atoms approach slowly enough to form the excited trimer. To form a trimer, the atoms never approach as closely as in the vibrating dimer and all three atoms must contain very low kinetic energies.

Stagnation

Stagnation occurs when the initially excited electron does not interact strongly with other atoms, or when the initial excitation is too delocalized to exert any significant force. The first scenario is most likely to occur in trajectories arising from excitation into states very near to the atomic $2s$ and $2p$ excitation energies, which are states at the outer edges of the clusters that have little density inside the cluster.⁷ The second possibility most often occurs in very delocalized states which tend to occur at the highest initial excitation energies.

In such trajectories it is not possible to unambiguously determine the end products and so they were simply classified as indeterminate. They are not necessarily completely free of interactions and on a much longer time scale ($\gg 1$ ps) the majority of the stagnated trajectories should fully dissociate.

Larger excited helium clusters, He_n^* with $n = 4 - 6$, might be said to exist in a few of the stagnated trajectories, however they are not stable with any finite amount of kinetic energy. These result from very delocalized initial excitations and essentially no motion of the atoms is observed over the length of the computed trajectories. In contrast, the trajectories classified as forming He_2^* and He_3^* all had significant atomic motion and vibrational energy throughout the trajectory.

3.3.3 Product distribution

?? gives the number of trajectories resulting in each of the possible end products. By the end of the calculated trajectories, 90% have dissociated to atoms, 3% to dimers, $< 0.5\%$ to trimers and 7% are stagnant and indeterminate. At 242 fs, stagnated and obviously dissociating trajectories were first allowed to terminate. At $t = 242$ fs just over 91% were classified as fully dissociating and the remaining trajectories were undetermined. Thus only $\approx 1\%$ of the dissociating trajectories from $t = 242$ fs ultimately experienced other interactions and a different fate.

	Atoms	Dimers	Trimers	Other
242 fs	2536	–	–	264
968 fs	2509	87	11	193

Table 3.1: Number of trajectories forming the observed products. Most dissociate into individual atoms, with some forming He_2^* and He_3^* . “Other” refers to trajectories which were not classifiable and primarily result from stagnated trajectories.

Focusing first on the 87 dimer-forming trajectories, 85% originate from the 8 – 11th energy-ordered states. A further 10% arise from states 12 and 13 and the remaining 5% from states 3-7. States 8-14 correspond to the lower energy range of the $2p$ -type states, and originate from atoms on the outer edges of the cluster.[?] Only states at the low end of the $2p$ manifold are observed to produce dimers because those at the high energy end of the spectrum either collide with too much energy to remain bound, or have very delocalized states with small forces. Most of the dimers, 82, originate from p -type excitations while only 5 occur after excitation into a $2s$ -type state.

The character of the dimers at the end of the trajectory is determined by the attachment densities. 43 (49%) of the dimers end in π states, 21 (24%) in σ_s^* , 11 (13%) in π^* , 11 (13%) in σ_s , and 1 (1%) in σ_{p_z} . Vertically excited π states are prohibited from directly forming σ_s dimers as seen from the dimer potential curve (??). Imagining that all excited states rapidly decay to the lowest energy in the $n = 2$ band, the σ_s state would be highly favored. However, due to symmetry restrictions, 75% of the $n = 2$ dimer states may not directly access the σ_s state, with the result that the slightly higher energy π and σ_s^* states have much larger populations.

It is not possible to generalize much about the trimers because so few of them are formed. In all trimers the minimal interatomic distance is significantly greater than that observed for the dimers. If the atoms come too close together or with any significant amount of KE the dimer is preferentially formed. Trimers only appear when the atoms approach slowly and the atoms are always more separated than in the dimers. They also do not appear to be fully equilibrated at the end of a 968 fs trajectory.

The end products for most trajectories are rapidly identified considering only the absolute nearest-neighbor (NN) distances. ?? shows the nearest neighbor distance as a function of time for each excited state in the $n = 2$ manifold from one of the initial geometries. It is clear that the majority of the trajectories result in fully dissociated clusters as indicated by the steadily increasing NN distance.

When two atoms collide, their NN distance rapidly decreases and reaches a minimum well below the equilibrium distance of 1.1 Å. All, save one, of the initial geometries had ≥ 1 of its 28 excited states undergo a collision. Dimers as seen in ?? have a periodic NN function and can be identified by multiple minima below 1.1 Å which are separated by similar time intervals. Once formed, most dimers persist until the end of the trajectory. However, there are cases where something occurs, such as a collision of the dimer with another atom, and

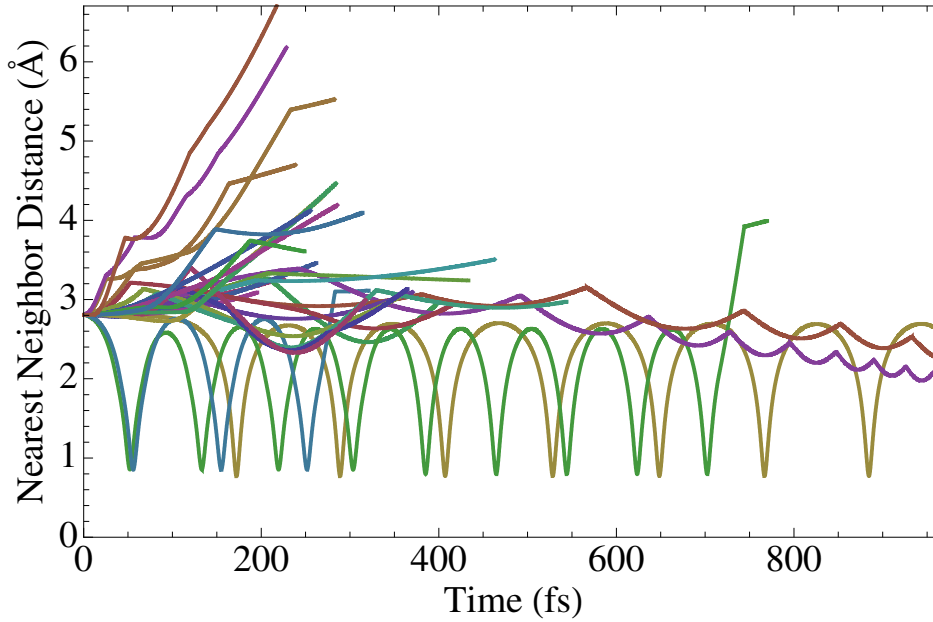
the dimer ultimately dissociates to $\text{He} + \text{He}^*$.

To identify trimers unambiguously, it is also necessary to consider the second nearest neighbor (2NN) distances. Periodic behavior of both the NN and 2NN distances could result from two separate oscillating dimers, a single trimer, or more generally from larger clusters. The trajectory forms a trimer or larger excited cluster if the NN and 2NN distances are periodic and share a common atom. This occurred in 11 of the 2800 trajectories, and these were inspected individually to be certain that He_3^* was the largest excited cluster. It is unsurprising we did not observe larger clusters because unexcited helium atoms are only bound by weak dispersive forces, which are completely neglected in our calculations, and He_3^* is already barely bound. The trimer is extremely fragile with respect to decomposition into a dimer and an atom and this is also true for larger excited clusters. The case of double dimers requires more energy than is available from the initial excitation and these were observed only when γ_E was chosen to be too large to enforce energy conservation. In principle energy is always conserved, however, because of the finite step sizes used in AIMD in practice this may not always be true. Furthermore, the possibility of having states with similar character but differing energies, amplifies issues associated with energy conservation.

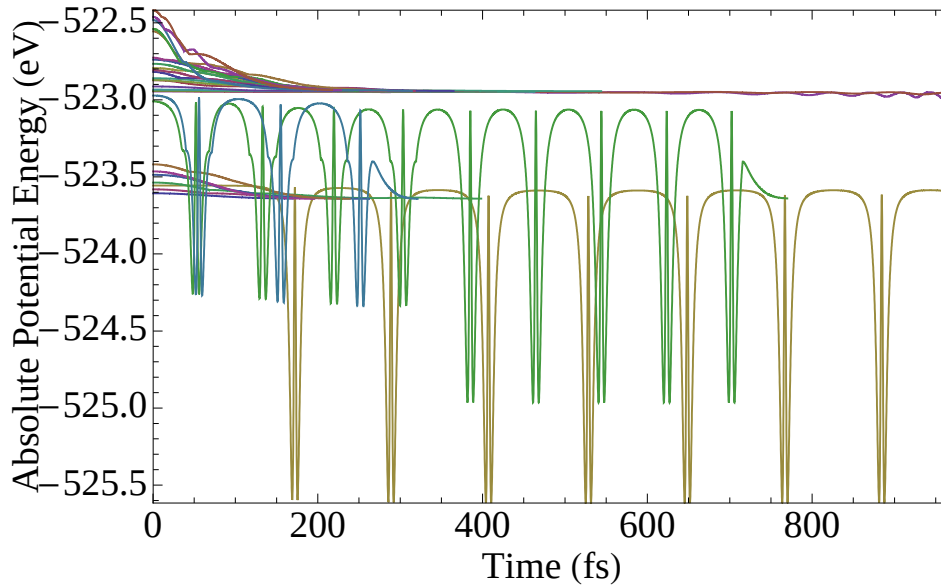
In the stagnated trajectories with indeterminable final products, the excitation may be very diffuse, or on a non-interacting atom that is separated from the main cluster. As there is no initial kinetic energy the pseudo-stability of the delocalized excitations from states near the upper energy range of the $n = 2$ manifold is due to a lack of any motion. If propagated for much longer times these states may ultimately result in clusters with interesting dynamics but the majority will fully dissociate into atoms. Most commonly, stagnant trajectories arise when the initial excitation that does not significantly interact with other atoms in the cluster. These states contain only weak repulsive forces and eventually all separate into atoms. Stagnation results in nearly unchanging NN distances, however, this is not a sufficient condition to determine that a cluster is stagnate as the other five atoms may still be dissociating.

?? shows the energies of all states from a single initial geometry. While much of the same information from ?? is contained in this plot, it is also possible to see different final states of the dimer and the very small variations in the energy change for the trimers. Furthermore, it also shows that many of the fully dissociating states are largely parallel, which is consistent with the small number of state changes that arise from these state-following trajectories (90% had ≤ 10 switches).

Overall, no statistically significant correlation was found between the initial geometry and the final products. It was also not possible to reliably predict the end products based on the atomic spread of the vertical excitations or from initial forces. The initial forces are often quite small and slight changes can significantly affect the final outcome. As the CIS forces are likely a bit weaker than the true forces, the ratio of product formation may actually somewhat favor dimers and trimers as more trajectories will experience strong collisions where full dissociation results. The energy and character of the initial states are the crucial factors for predicting the products. Also interesting is the fact that most of the product distribution, and thus the interesting dynamics, occur during the first quarter of the trajectory ≈ 250 fs.



(a) Nearest neighbor distances. Note the periodic oscillation of the dimers and discontinuities due to the formation of trimers. Most trajectories ultimately dissociate but one forms a dimer (periodic, yellow) and two form trimers (discontinuous, brown and purple). Dimers may also be formed transiently as seen by the green trajectory.



(b) Absolute potential energies. Two primary dissociation limits correspond to $\text{He}^*(2s)+6\text{ He}$ and $\text{He}^*(2p)+6\text{ He}$, the others are a state from He_2^* and He_3^* . The dimers experience much larger changes in energy and bond length than the trimers.

Figure 3.9: Trajectories for each of the 28 states associated with a single initial geometry.

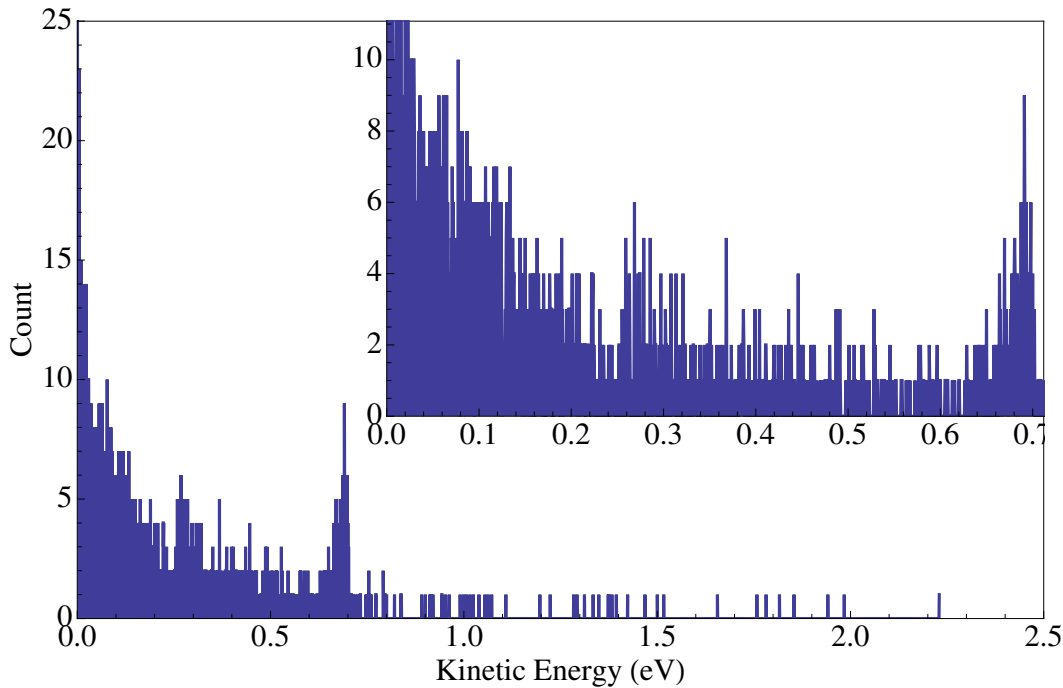


Figure 3.10: Kinetic energy of the trajectories at their end point. The total KE is the sum of kinetic energies of all atoms in each cluster. The peak at 0.7 eV is due to relaxation from the $2p$ manifold to the $2s$ manifold.

3.3.4 Kinetic energy distribution

The maximum total kinetic energy distribution for all clusters is shown in ???. This is the difference in potential energy from the beginning and the end of the trajectories, for all trajectory types. The clusters are launched with zero initial KE, thus, KE can only increase. Most trajectories accumulate very small KEs, although the highest KE values extend to 2 eV. The peak at about 0.7 eV correlates with the energy gap between the atomic $2s$ and $2p$ states. It arises because trajectories initialized and propagated solely on the $2p$ (or $2s$) manifold do not develop significant KE, whereas trajectories which are initialized into a $2p$ -type state and transition to a state in the $2s$ manifold will on average gain about 0.7 eV of KE. Note that for excited dimers, this distribution is a poor description because the end of the trajectory is arbitrary in terms of the vibrational period and most of the KE is internal. However, the small number of dimer forming trajectories means they do not significantly affect the overall shape of ??, and they are separately treated in more depth.

The KE distribution, from individual atoms in the fully dissociating clusters at the end of their trajectories, is shown in ??. The maximum amount of KE gained by a single atom is about 0.7 eV which is again the difference between $2s$ and $2p$ states of He. ?? also includes the kinetic energy distribution considering only the atoms which carry all or part of the

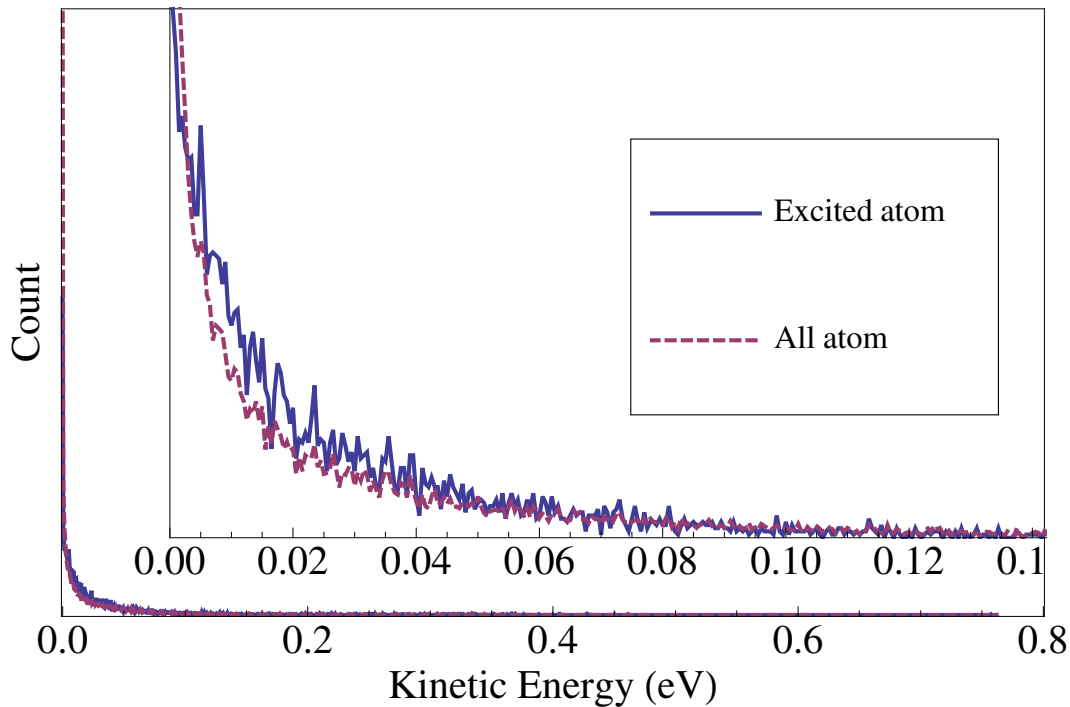


Figure 3.11: Kinetic energy distribution of all individual atoms and only the individual excited atoms at the end points of the trajectories. The curves were scaled to equal area.

excitation. These are the atoms preferentially detected in pump-probe experiments. The distributions in ?? are scaled to contain equal area and their mean values are statistically indistinguishable. The excited atom KE distribution contains more atoms in the mid-range, but has fewer atoms with very high or very low kinetic energies than the KE distribution of all the atoms.

The kinetic energies of the final dimers are shown sorted by increasing total KE in ?. Here the KE for each dimer is computed at the potential minimum (1.1 Å), which is the point of maximum internal KE. The internal KE is then taken as the difference in the total and center of mass (COM) KE. The COM KE values are quite low, and it is readily apparent that the primary portion of the dimer KE is from internal energy due to vibrational excitation. The highest energies are around 2 eV, which also corresponds to the potential well depth of the bound σ_s and π dimers (?). ? indicates the character of each dimer and shows the internal energy of He_2^* as a function of the vibrational period. The longest periods align with the largest internal energies and arise from π and σ_s states as may be expected from their broad potential wells (?). The other types of states are all associated with much shorter periods, and therefore, less vibrational excitation. There are two clear branches in this figure resulting from the difference in the minimum potential energy of the π and σ_s states and the σ_s^* states.

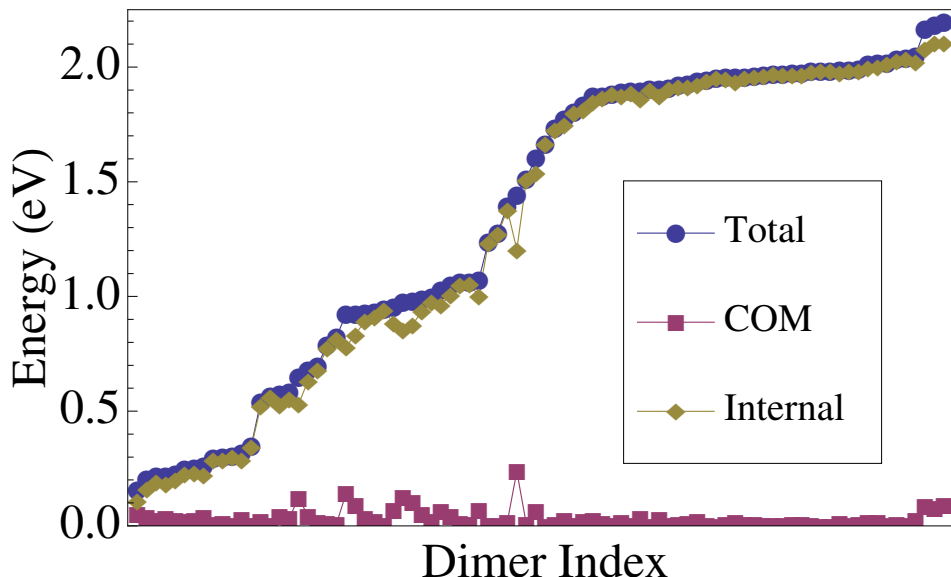


Figure 3.12: Kinetic energies of excited helium dimers including center of mass (COM) and internal components. The KE was determined at the potential minimum, which has the maximal KE. The internal KE is the difference of the total KE and the COM KE.

3.3.5 Comparison To Experiments

Experimental data on the formation of excited neutral fragments after electronic excitation of helium clusters are scarce. The ejection of Rydberg atoms and molecules from electronically excited He droplets was first detected by the Möller group.[?] The most detailed studies to date employ ultrashort extreme ultraviolet (EUV) pulses to excited large (He_n , $n \geq 10^6$) droplets into electronic bands associated with $n = 3, 4$ manifolds. Neutral intermediates and products are probed by ionization with a second pulse in the infrared (IR) regime that is delayed with respect to the excitation on a femto- to picosecond time scale.^{??} While the cluster sizes and excitation energy regimes in these measurements differ quite starkly from those discussed here, it is interesting to compare general trends and product formation channels that are evident in both experiment and theory.^{???}

The He_7 clusters studied in this chapter primarily undergo full dissociation forming 6 ground state atoms and a single excited atom with a significantly smaller number of trajectories resulting in He_2^* and He_3^* . Experimentally, upon excitation into the $n = 3, 4$ manifolds, atomic ions are also clearly the dominant detected species, accounting for more than 70% of the signal from neutral product ionization.[?] Dimers and trimers comprise most of the

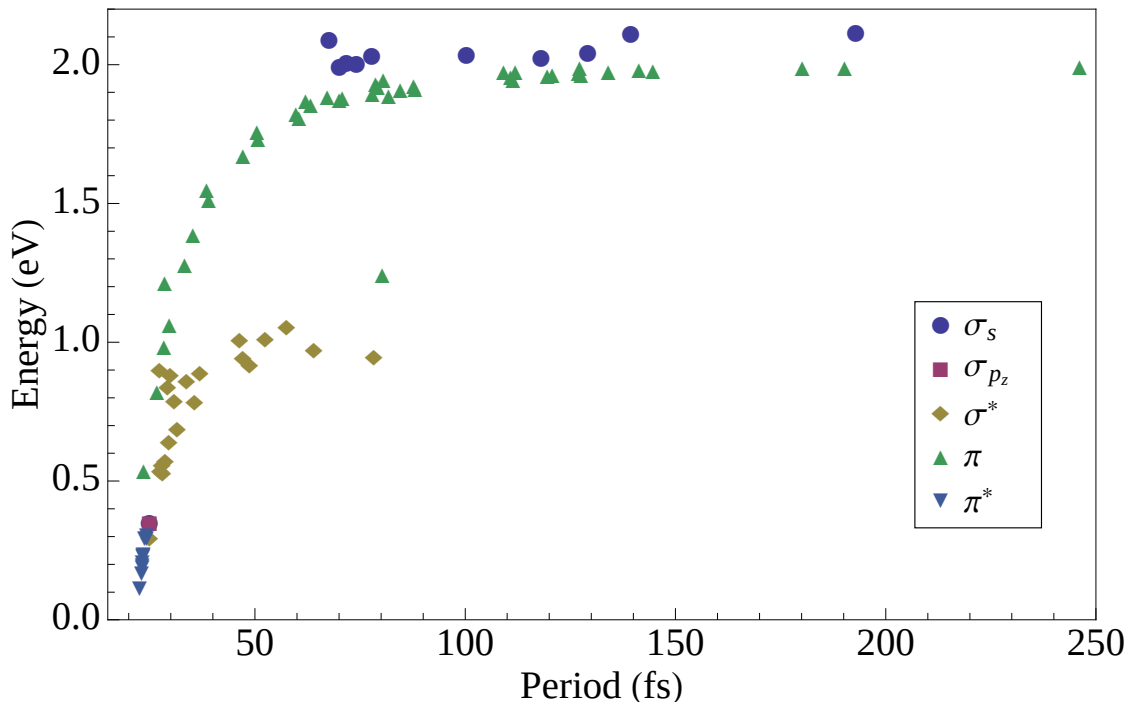


Figure 3.13: Period of dimer in femtoseconds vs. the internal energy of the dimer. The variation in period arises from different electronic states and amounts of vibrational excitation.

remaining contribution to the signal with $< 5\%$ of the total ion signal due to trimers.[?]

We note that the atomic KE distributions calculated here (??) exhibit a qualitative resemblance with low-energy contributions in experimentally determined Rydberg atom KE distributions. It was previously speculated that these contributions may be due to multi-body interactions that were not captured in a simplified cluster excitation model based on an average, repulsive interaction of localized atomic excitations with the surrounding He bath.[?] The results presented here indicate that *ab initio* cluster calculations may be able to unravel some of the physics that is responsible for product channels with low KE release.

The formation of dimers in our calculations proceeds on time scales comparable to the dimer vibrational periods. This is also the time scale that seems to determine the product distribution. Interestingly, the estimated dimer vibrational periods are all ≤ 250 fs, which is similar to the experimentally observed formation time of excited dimer fragments of 220 fs.[?] While significantly more experimental and theoretical work is needed to understand the intricate coupled electronic and nuclear dynamics in the cluster environment, it is encouraging that several common trends and benchmark values can be recognized in both types of studies.

3.4 Conclusions

The delicate and weak van der Waals attractions that bind helium clusters together are strongly perturbed by electronic excitation of the cluster. In the $n = 2$ manifold, cluster excited states blue-shift relative to the free atom by anywhere from near zero to over 0.5 eV,[?] which is a driving force for at least partial dissociation of the cluster. While there have already been intriguing experimental results probing the fate of excited clusters, there have been no detailed atomistic simulations.^{?????} This work begins to fill that gap.

Using small He₇ clusters for computational tractability, we have investigated their fate by *ab initio* molecular dynamics calculations after excitation into the $n = 2$ manifold. On the 1 ps timescale of the simulation, a large majority (90%) of the 2800 trajectories exhibit full dissociation to 6 He + He*, with kinetic energy releases commensurate with the blue shift discussed above. A small fraction (3%) of the trajectories yield bound excited dimers, as anticipated from the isolated dimer calculations where He₂* is bound and acts as a He₂⁺ core and an outer Rydberg electron. An even smaller fraction (< 0.5%) of trajectories results in trimers. The methods used are not quantitatively accurate, but even if the absolute percentages vary, we anticipate that qualitative conclusions will be mostly unaltered. Higher level theoretical methods incorporating electron correlation or non-adiabatic couplings should not change the facts that a large majority of the clusters will still dissociate and most of the dimer and trimer products will arise from the lowest energy $2p$ -type states. For these 7-atom clusters, we did not observe any statistically meaningful correlation between the localization/delocalization of the vertical excitations, and the final products. Nor does the initial localization seem to be strongly correlated with the energy. The most important factors determining the fate of the clusters appear to be the energy and the character (s/p) of the vertical excitation.

In addition to overall statistics, we have reported on the dynamics leading to the different products, through illustrative trajectories. These results suggest the most important dynamics occur during the first 250 fs, indicating that future work with larger clusters may not require as long trajectories as used herein. The dissociation timescale, the kinetic energy release, and the range of products all bear interesting and suggestive similarities to the experimental results for $n = 3, 4$ excitations in clusters four orders of magnitude larger. Caution is needed in such comparisons, of course, not just due to the previously discussed physical differences, but also because of limitations in the trajectory simulations. These include the relatively simple single-excitation treatment of the excited states and use of classical, largely adiabatic state-following trajectories that do not properly treat the quantum nuclei or fully describe non-adiabatic effects. Lacking experimental or more accurate theoretical data, we assessed our method using a higher level of theory for the initial excitations. Another interesting aspect that is not covered by our current results is an explicit time-scale for excitation hopping. Accordingly, the present results leave plenty of opportunity for further work on these fascinating systems.

Chapter 4

Excited state geometry optimization, *ab initio* molecular dynamics and minimal energy path determination using a state-following algorithm

4.1 Introduction

Calculating single point energies on the ground state potential surface at the mean-field level is fairly straightforward for most systems consisting of $\leq 10^2$ to 10^3 main group elements, and even determining optimal geometries or reaction paths is often feasible. However, the routine nature of such calculations vanishes when electronically excited states must also be considered. Contrasted with the ground state, excited states are more likely to interact with other states resulting in dramatic failures of the Born-Oppenheimer approximation.^{??} Consequently, they often can not be considered in isolation, especially when one is interested in multiple points on the potential energy surface (PES) as small changes in geometry can significantly alter the local environment. Additionally, excited states are generally much more varied than ground states (e.g. valence, Rydberg, multi-configuration, etc.) often making a balanced treatment of multiple states very challenging. Understanding excited state potential energy surfaces is an active area of research and has been highlighted in many recent reviews.^{?????}

As single point calculations do not begin to address issues such as the ultimate fate of an excited electron or how an excited molecule may react it is often important to understand additional points of the potential surfaces.[?] Yet the exploration of potential energy surfaces with reasonable accuracy rapidly becomes intractable as expensive electronic structure calculations must be performed at each point.^{??} In this paper we present an algorithm for deterministically exploring excited state potential energy surfaces based upon their energy and character, and demonstrate its applicability to geometry optimization, *ab initio*

molecular dynamics (AIMD) and finding the minimal energy path (MEP) between two excited states. This method adiabatically steps along a potential energy surface, so long as there are no other nearby states. When encountering multiple states, which are energetically reachable, the algorithm selects either the diabatic (most similar character) surface or the adiabatic (most energetically similar) surface based upon the overlap of the excited state particle and hole densities. In this way we develop a deterministic method for traversing an excited state potential.

The adiabatic or Born-Oppenheimer approximation assumes that nuclei move slowly enough that the electrons can adapt instantaneously. This allows full separation of the electronic and nuclear degrees of freedom. While moving along a surface adiabatically the electron density changes continuously in response to nuclear motion and correspondingly can change character during the course of a trajectory. Adiabatic states are eigenstates of the Hamiltonian at a given nuclear geometry and are defined by their eigenvalues. Thus, they can be described by their energetic ordering such that if a system begins in the second excited state after some period of time it will remain in the second excited state. In contrast, diabatic motion is defined by the electron density remaining constant. Diabatic states are classified by their character, and may change order relative to other states.[?] For example a system may be excited into a state with $\pi \rightarrow \pi^*$ character, which is energetically the second state at the ground state geometry, but after some time it may cross the first state with e.g. $n \rightarrow \pi^*$ character such that at the final geometry the first excited state now has $\pi \rightarrow \pi^*$ character. Although it is generally not possible to construct exact diabatic bases,[?] approximate versions have still been useful to increase our understanding of many excited state systems.^{???} Due to the nature of the uncertainty principle a system may also evolve non-adiabatically on two or more surfaces simultaneously, but for the purposes of this paper it is assumed that the system must exist in a single state.

The points or seams where two or more states cross are generally known as conical intersections.^{??} When first discovered, they were regarded as a mathematical curiosity, but it has been shown that they are pivotal to understanding photochemical reactions and excited-state lifetimes.^{???}

Excited state geometry optimization can often be described as an art. If one can intuit a starting structure, which is close enough to the optimized structure such that there are no state crossings, it is apparent that using the gradient of the desired state is correct. However, if the potential surfaces cross, or even worse, if it is unknown whether or not they cross, it can be nearly impossible to form a reasonable guess.[?] As an illustration consider a system where the first two states cross between the ground state geometry and the optimized geometry of the second state. Initially selecting the gradient of second state will lead to an optimized structure with the incorrect structure and character. Selecting the first state will also generally lead to a state of the incorrect geometry and character. Thus, if specific states are desired and curve crossings are present at some point it becomes necessary to switch the target state.^{??} Additional difficulties arise when optimizing specific excited states in that many standard algorithms for geometry optimization do not smoothly traverse the potential surface and it becomes difficult to remain on a particular state.[?] Our algorithm for state

following allows for the selection of a state based on its character and automatically selects the most similar state so that the user is not required to determine where crossings occur or even know about their existence.

Determining the motions of nuclei as a function of time is another active area of research. Molecular dynamics are often applied to gain an understanding of the chemical reactivity of a system and can be computed from a broad range of quantum, classical and semi-classical methods.[?] While full quantum mechanical treatment of nuclei can be done by quantum Monte-Carlo, it is not practical for systems containing more than a few atoms.^{??} At the other extreme are purely classical methods which apply Newtonian dynamics to all particles. However, electrons are inherently non-classical, and these methods rapidly break down when there is a significant rearrangement of chemical bonds. Semi-classical methods combine aspects of both quantum and classical calculations and have often been the method of choice since Car and Parrinello introduced the concept of *ab initio* molecular dynamics (AIMD) in 1985.[?] Under this formulation, the electrons are fully quantum particles and nuclei are treated classically in the field generated by the electrons.^{???}

As for geometry optimizations, trajectories can be straightforwardly propagated on a single adiabatic surface, but the situation becomes much more interesting when multiple surfaces interact and can undergo non-adiabatic dynamics.^{???} One popular method for incorporating non-adiabatic transitions is through Tully's fewest switches surface hopping (FSSH) dynamics.^{????} In FSSH, the electrons are treated quantum mechanically, the nuclei classically and transitions between states occur with a probability related to the non-adiabatic coupling of the states. There are also many variations on this method, which can improve the results for certain classes of systems,[?] although drawbacks regarding a lack of nuclear quantum effects, over-coherence, and the lack of a rigorous derivation remain.[?] Alternatives to the surface hopping methods include using mean field (Ehrenfest) dynamics,[?] *ab initio* molecular spawning (AIMS),^{??} and applying the quantum-classical Liouville equation.[?] All probabilistic surface hopping methods require large numbers of trajectories to yield statistically relevant results and often this requires $10^3 - 10^6$ trajectories.^{??} Thus, there are occasions where a deterministic method is desirable, and our algorithm can be applied to AIMD calculations to selectively follow a surface diabatically or adiabatically.

Both geometry optimizations and AIMD calculations begin from a single starting points, however, many times both the reactants and the products of a photochemical reaction are known and it is desirable to determine the path between them and any related conical intersections. Locating conical intersections is an important, but non-trivial challenge for quantum chemistry. Interpolating between states to find minimal energy pathways and locate saddle points such as occur at conical intersections can be done with a variety of methods. The nudged elastic band method was developed for determining reaction paths and transition states and has also been employed to locate conical intersections.^{??} The growing string method (GSM)^{???} and its approximate cousin the freezing string method,^{??} provide an alternative method to connect two points on a potential surface. With the GSM nodes are added to the string from both the reactant and product sides and optimized at each step to determine the MEP. The combination of our state-following algorithm with GSM provides

a method of approximating the location of conical intersections.

For any exploration of potential surfaces, the underlying electronic structure method is important in determining the reliability of the results. Currently, the most accurate vertical excitation energies may be obtained using quantum chemical methods such as equation of motion coupled cluster theory (e.g. EOM-CCSD, EOM-CCSD(T))[?], multi-configuration time-dependent Hartree-Fock (MCTDHF)[?] and full configuration interaction (CI), however these are impractical for most problems involving nuclear dynamics which require computing the electronic structure at hundreds or thousands of points.

Time-dependent density functional theory (TD-DFT) is by far the most widely used method for computing the electronic structure of excited states and was also shown to be capable of describing qualitatively correct non-adiabatic paths[?]. This method often yields good results as it incorporates some correlation effects, although results are highly dependent on the chosen functional and not generally systematically improvable.^{?????} Among the computationally least expensive wave-function based methods are configuration interaction singles (CIS) and time-dependent Hartree-Fock (TDHF).^{??} Although their computational cost is similar to TD-DFT they are used much less frequently.

In principle the algorithm presented in this paper is not restricted to CIS, TDHF and TD-DFT, however, due to the high cost of other methods we have currently restricted our explorations to these methods, which are sufficient for many systems. After a thorough discussion of the algorithm, results for the optimization of the first two singlet excited states of cytosine, AIMD in the excited states of helium clusters and the determination of the MEP between the first two excited states of protonated formalimine will be presented.

4.2 Algorithm

The algorithm developed for following electronically excited states is based upon two properties: the energy difference between states, and the overlap of the particle/hole densities. The latter quantity is determined using the attachment and detachment densities.[?] These are formed for each state by diagonalizing the difference density and separating the components corresponding to the positive and negative eigenvalues. The detachment density can be interpreted as the hole density and the attachment density as the particle density of the excited state.

To briefly describe the algorithm, the relevant information is stored at $t = 0$, and then at later time steps, $t + 1$, the currently accessible states are compared to the the stored state at time t . A decision is then made as to which state to select, and this state supplies the forces to reach the subsequent step, $??$. The algorithm is slightly more complex for the minimal surface finding option because both the first (t_0) and last (t_n) points are used for reference. The rest of this section will detail each of the steps and the differences which arise for the various applications.

The stored information for the state s_t includes the attachment and detachment densities, the SCF and excitation energies, and the number of basis functions. Additionally, the kinetic

Algorithm 4.1: Main for state-following

 $s_t ==$ selected excited state at step t **if** $t=0$ **then**└ Store(s_0)**else**└ Compare(s_{t+1}, s_t)└ Store(s_{t+1})

energy for AIMD and information for both end points of MEP calculations is also kept. The attachment and detachment densities, which effectively correspond to the particle and hole densities, were selected for determining the character similarity between excited states because they do not suffer from phase instabilities and clearly characterize singly excited states.[?]

The critical part of the algorithm is the method of selecting states. Two physically-defined thresholds control this selection of states. The first is the energy window over which states are said to interact, and the second is a threshold for the minimal overlap between states.

The energy window is defined by γ_E such that the possible states s_k are considered to be near to the current state s_t if they are within the energy range $E(s_t) - \gamma_E \leq E(s_k) \leq E(s_t) + \gamma_E$. In the limit of a small window (less than energy level gap) this results in the nearest energetic (adiabatic) state being selected while a larger window including two or more states will generally lead to the selection of the state most similar in character (diabatic).

The similarity metric is defined as

$$\mathcal{S} = 1 - \frac{1}{2} \left| \mathbf{A}_{t+1} - \mathbf{A}_t - (\mathbf{D}_{t+1} - \mathbf{D}_t) \right|. \quad (4.1)$$

A value of 1 indicates perfect overlap of the attachment (detachment) densities at the two time steps and 0 indicates they have no common density elements. These densities are evaluated in the atomic orbital basis, and the assumption is made that the basis functions do not change between time steps. This approximation appears not to make a difference in the final results the systems explored thus far, but if there are large geometric changes between steps it may be necessary to account for the changing basis functions. The threshold γ_S controls the relative importance of the energy and the character. If no states with similarity higher than γ_S exist, as can happen near conical intersections or due to numerical issues such as basis set discontinuities, the algorithm defaults to selecting adiabatic state. Most calculations are not highly sensitive to this value between ≈ 0.25 to 0.75 , but if set much higher the adiabatic state will almost always be favored, and if lower the algorithm can lead to results that are not energetically reasonable.

Algorithm 4.2: Compare initial and final states

```

Compute  $E_{t+1}^{Est}$  from  $E_t$ 
for  $\forall$  states  $\kappa$  do
  Read  $E_{t+1}^{(\kappa)}$ 
  if  $(E_{t+1}^{Est} - \gamma_E) \leq E_{t+1}^{(\kappa)} \leq (E_{t+1}^{Est} + \gamma_E)$  then
    Count near states:  $n_\kappa = n_\kappa + 1$ 
  Determine state  $s_{t+1} = \kappa$  with  $E_{t+1}^{(\kappa)}$  nearest  $E_{t+1}^{Est}$ 

if  $n_\kappa == 1$  then
  Select  $s_{t+1}$  as the new state

else if  $n_\kappa > 1$  then
  for  $\kappa = 1, n_\kappa$  do
    Make att/det densities:  $\text{MakeAD}(D_{t+1}^{(\kappa)}, A_{t+1}^{(\kappa)})$ 
    Read  $D_t, A_t$  from disk
    Evaluate  $\mathcal{S} = 1 - \frac{1}{2} |\mathbf{A}_{t+1} - \mathbf{A}_t - (\mathbf{D}_{t+1} - \mathbf{D}_t)|$ 
    if  $\mathcal{S} \geq \gamma_S$  then
      Count states below threshold:  $n_\lambda = n_\lambda + 1$ 
      Determine state  $s_{t+1}^{(m)} = \kappa$  with largest overlap  $\mathcal{S}_{max}$ 
    if  $n_\lambda \geq 1$  then
       $s_{t+1} = s_{t+1}^{(m)}$ 
    else
      Print warning that no near states have similar character
      Select state  $s_{t+1}$  as the new state
  else
    Check for basis set discontinuity
    if Discontinuous then
      Repeat search with  $\gamma_{E'} = 10\gamma_E$ 

return  $s_{t+1}$ 

```

?? illustrates the selection of the new state s_{t+1} from the stored state s_t . First, the ground state potential and all computed excitation energies are imported. For MEP this includes the ground and excited states for both reactant and product sides, and for AIMD the kinetic energies of the current and previous steps are also read. Then, depending on the type of calculation, an estimated energy is determined E^{Est} . For geometry optimizations the estimated energy is simply taken as the energy of the previous step.

$$E_{t+1}^{Est} = E_t \quad (4.2a)$$

In this case it is necessary to choose a relatively large value for γ_E to ensure that the important states are captured by the energy window.

For AIMD calculations the estimated energy is the average of the total energy of the original and prior steps.

$$E_{t+1}^{Est} = \frac{1}{2}(E_0^K + E_0^V + E_t^K + E_t^V) \quad (4.2b)$$

with E^K and E^V as the kinetic and potential energies respectively. It was found that using the total energy from the initial step as well as the previous step resulted in much better energy conservation by providing some degree of stabilization.

Finally for minimum energy path calculations, computed using the growing string method the estimated energy of a given point is a weighted averaged of the initial reactant and product nodes.

$$E_{t+1}^{Est} = d_t E_0^R + (1 - d_t) E_0^P \quad (4.2c)$$

The weighting factor d is the normalized distance from the reactant node to the current node. Here, using the end points of the string was necessary to ensure the character of the desired states was enforced.

If a single state κ has an energy $E^{(\kappa)}$ falls within the energy window $E^{Est} \pm \gamma_E$ it is selected as the current state. In this case with only one energetically available state there is no possibility of switching to a different state.

If there are two or more states n_κ in the selected energy range, the character of all nearby states is evaluated. Attachment and detachment densities are calculated for each state κ near the estimated state. These are then compared against the attachment and detachment densities stored from the the previous step through $\mathcal{S}$. Note that for a MEP, the overlaps of both the reactant and product densities are actually considered and weighted by the distance from the reactant node (d_t) so

$$\mathcal{S} = d_t \mathcal{S}_0^R + (1 - d_t) \mathcal{S}_0^P. \quad (4.3)$$

It is necessary to include this information from both endpoints to obtain convergence of the string. The state with the largest value of $\mathcal{S}$ is selected, provided at least one state has $\mathcal{S} \geq \gamma_S$.

If a state at $t + 1$ possessing sufficient overlap with the state at step t does not exist the selection of the final state defaults to the adiabatic state. The only exception is that if there

is a basis set discontinuity between the steps. In this case the search is repeated with an energy window ten times larger, $\gamma_E' = 10\gamma_E$, before selecting the adiabatic state.

This state-following algorithm is currently implemented for single reference excited state methods including configuration interaction singles (CIS), time-dependent Hartree-Fock (TDHF) and time-dependent density functional theory (TD-DFT) in a developmental version of Q-CHEM 4.2.[?]

4.3 Results

This method of state following can be applied in situations where it is desirable to use a deterministic method for exploring excited state potential energy surfaces. The following three examples illustrate the applicability of this method: the geometry optimization of cytosine, ab initio molecular dynamics of helium clusters, and the growing string method for determining a minimal energy pathway between the first two excited states of protonated formaldehyde.

4.3.1 Geometry Optimization: Cytosine, $C_4H_5N_3O$

The excited states of nucleic acid bases are critical in understanding the mechanisms of DNA damage.^{???} In solution, they are characterized by very broad spectral peaks and it is challenging to extract detailed information from experiment.[?] As they are not trivial systems to study and also very important biologically, nucleic acids have been very popular targets of both experimental and theoretical studies.^{??????}

Here the keto tautomer of cytosine is selected, in part because there has historically been significant debate about the ordering of the excited states. It is known that the S_1 and S_2 states lie very near each other energetically, there is a conical intersection connecting them, and the planar ground state undergoes strong geometric distortion upon electron excitation into the S_2 state.^{????} In fact, using a 6-31G** basis set with CASSCF the lowest two vertical excitations are at 5.41 eV ($n_O \rightarrow \pi^*$) and 5.43 eV ($\pi \rightarrow \pi^*$), but with CASPT2 the order reverses (4.50 eV $\pi \rightarrow \pi^*$ and 4.88 eV $n_O \rightarrow \pi^*$).[?] It is now fairly well accepted that the $\pi \rightarrow \pi^*$ state is the lowest in energy, but it still provides an interesting system for investigating using our state following algorithm.

The ground state geometry of cytosine was determined by using density functional theory (DFT) with the B3LYP functional and the 6-31+G* basis set. Excited states were then calculated using TDDFT also using the B3LYP functional and this basis set. For singly excited states in DNA bases B3LYP was shown to yield results as good or better than more modern functionals.[?]

The geometry optimizations of the lowest three states were computed with and without state following from the same initial geometries. A relatively large energy window ($\gamma_E = 0.1$ eV) and low overlap threshold ($\gamma_S = 0.5$) were used and this combination results in the excited states being optimized primarily based on their character. It is also necessary to

set the maximum optimization step to be fairly small to ensure that the character does not change too dramatically between steps.

Results and Discussion

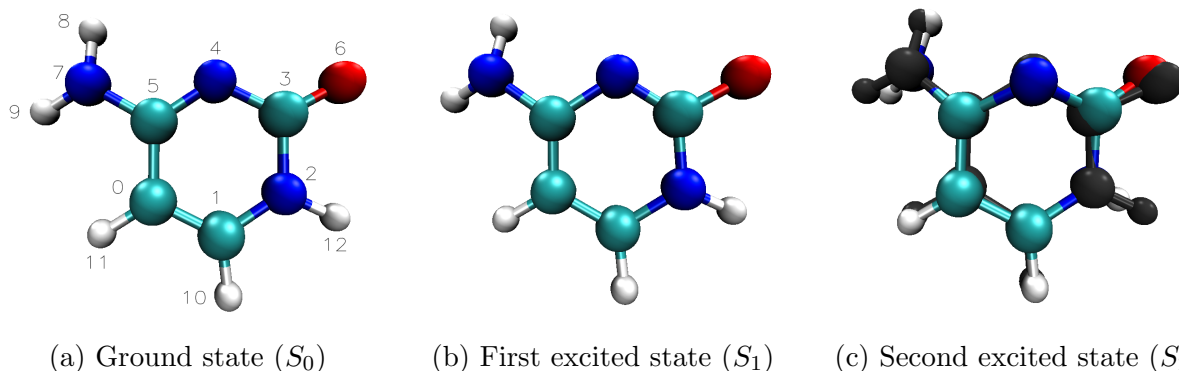


Figure 4.1: Optimized geometries of cytosine. The gray S_2 structure is from optimization without state following

The optimized geometries of the ground state (S_0) and first two singlet excited states (S_1 and S_2) of cytosine are shown in ???. The bond lengths and selected dihedral angles for the ground and first three excited states are given in ?? and ?? respectively.

Bond	S_0	S_1	S_1^{sf}	S_2	S_2^{sf}	$S_3^{\dagger}$	S_3^{sf}
C_0C_1	1.36	1.41	1.41	1.41	1.40	—	1.41
C_1N_2	1.36	1.42	1.42	1.41	1.41	—	1.41
N_2C_3	1.43	1.35	1.35	1.36	1.41	—	1.36
C_3N_4	1.37	1.29	1.29	1.29	1.36	—	1.29
N_4C_5	1.32	1.41	1.41	1.43	1.39	—	1.43
C_0C_5	1.44	1.37	1.37	1.37	1.39	—	1.37
C_3O_6	1.22	1.34	1.34	1.35	1.22	—	1.35
C_5N_7	1.36	1.39	1.38	1.37	1.38	—	1.37

Table 4.1: Bond lengths of optimized states of cytosine in Å. The ground and first 3 excited states without and with state following ($^{\text{sf}}$) are shown. † State 3 remained unconverged after 1000 GDIIIS optimization steps without state following.

The ground state is essentially planar and, while the NH_2 functional group changes position, the ring of the S_1 and S_3 states also remains mostly planar (??). For the S_1 state, identical results were obtained through optimization both with and without applying the

Dihedral	S_0	S_1	S_1^{sf}	S_2	S_2^{sf}	$S_3^\dagger$	S_3^{sf}
$\text{C}_1\text{N}_2\text{C}_3\text{O}_6$	179.9	-173.1	-173.1	179.1	-177.5	—	178.8
$\text{O}_6\text{C}_3\text{N}_4\text{C}_5$	-179.8	178.8	178.7	179.5	145.1	—	179.7
$\text{C}_3\text{N}_4\text{C}_5\text{N}_7$	178.2	176.4	176.5	177.7	-131.3	—	177.5
$\text{N}_4\text{C}_5\text{N}_7\text{H}_8$	9.4	20.9	20.8	19.6	13.3	—	19.8

Table 4.2: Selected dihedral angles of optimized states of cytosine in degrees. The ground and first 3 excited states without and with state following (^{sf}) are shown. [†] State 3 remained unconverged after 1000 GDIIS optimization steps without state following.

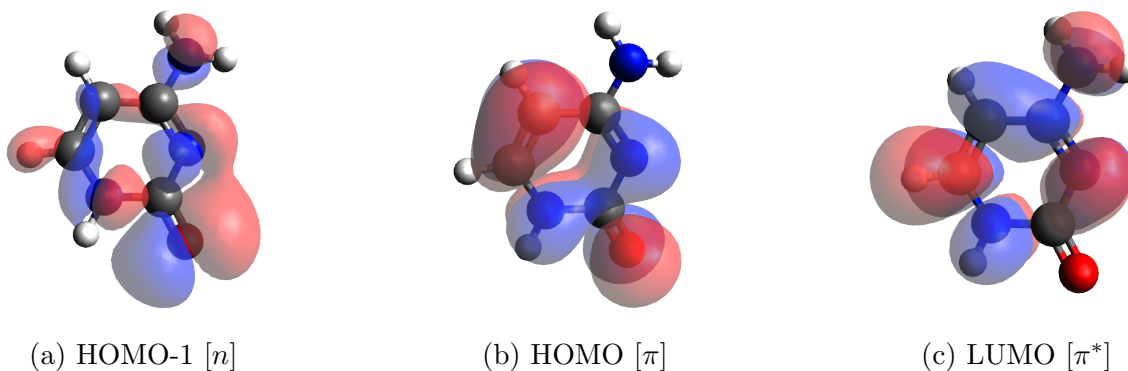


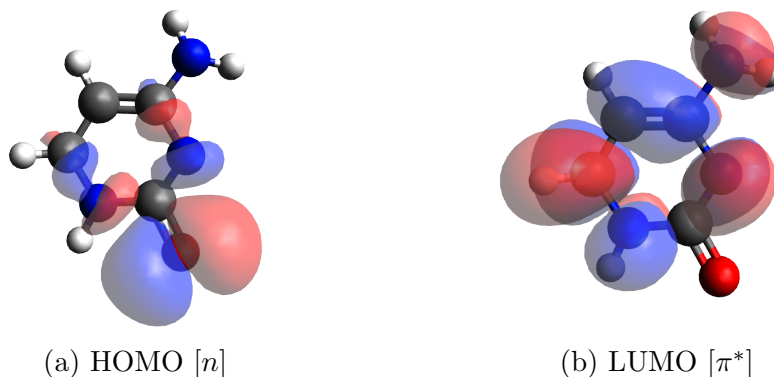
Figure 4.2: Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals in the ground state optimized geometry of cytosine.

state following algorithm. However, without using state following, the S_3 state would not converge using the same initial geometries.

In contrast, the S_2 state has a significantly distorted structure.[?] The NH_2 functional group twists and the ring also puckers. ?? shows the S_2 excited state geometries with state following (color) and without (dark gray). It is readily apparent that in this case different final states are obtained. Comparing the optimized structures and energies of the S_1 and S_2 states without state following, it is apparent that they actually converge to the same final state (????).

State	Absolute Energy (E_h)	Excitation Energy (eV)	Oscillator Strength	Dominant Contribution (occ→virt)
S_0	-394.950	—	—	—
S_1	-394.7732	4.8013	0.0503	HOMO → LUMO = 0.9590
S_2	-394.7731	4.8049	0.0006	HOMO-1 → LUMO = 0.9442

Table 4.3: Energies, oscillator strengths and molecular orbital contributions for ground-state geometry with and without state following

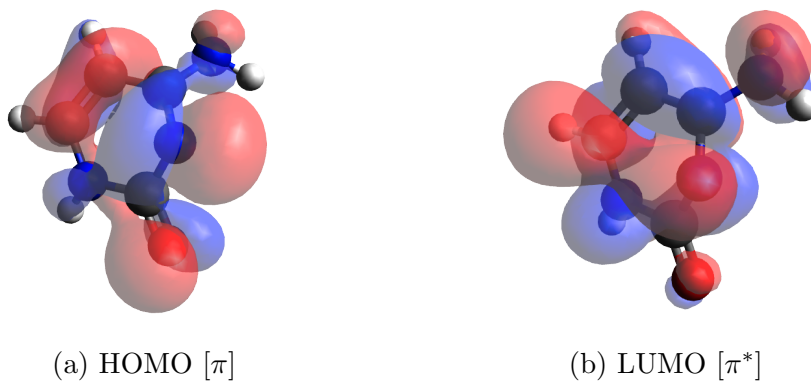
Figure 4.3: Important molecular orbitals for the S_1 optimized geometry

The two highest occupied molecular orbitals (HOMO, HOMO-1) and lowest unoccupied molecular orbital (LUMO) for the ground state geometry are pictured in ???. The dominant contribution to the first singlet excited state, S_1 is the HOMO $\rightarrow$ LUMO transition, which is $\pi \rightarrow \pi^*$. The second is dominated by the HOMO-1 $\rightarrow$ LUMO or $n_O \rightarrow \pi^*$ transition (??)

State	Absolute Energy (E_h)	Excitation Energy (eV)	Oscillator Strength	Dominant Contribution (occ $\rightarrow$ virt)
S_1 & S_1^{sf}	-394.812	3.746	0.0000	HOMO $\rightarrow$ LUMO = 0.9983
S_2	-394.811	3.773	0.0000	HOMO $\rightarrow$ LUMO = 0.9995
S_2^{sf}	-394.795	4.208	0.0044	HOMO $\rightarrow$ LUMO = 0.9278

Table 4.4: Energies, oscillator strengths and molecular orbital contributions for optimized geometries with and without state following

The effect of the $S_1 \rightarrow S_2$ state crossing and the proper qualitative energy ordering are obtained at the B3LYP/6-31+G* level of theory, however for quantitatively more accurate

Figure 4.4: Important molecular orbitals for the S_2 optimized geometry (with state following)

results it is necessary to use a larger basis set.[?]

In this situation, our state following algorithm allows for geometrical optimization of states that are not otherwise readily accessible and prevents collapse to local minima which are not of the same character as the initial state. Using conventional geometry optimization techniques it would be necessary to begin with a structure quite close to the optimal one. In the case of cytosine where this information can be corroborated with results gas phase measurements it may be somewhat intuitive, however, this is not always the case. Using state-following it is not as necessary to start close to the optimized solution, and this method could prove very useful for studying novel chemical systems.

4.3.2 *Ab initio* molecular dynamics: Helium clusters, He₇

Helium clusters have generated significant interest due to their unique properties.^{??} In addition to the well known properties such as their extremely low temperatures and superfluidity,^{???}, they have high excitation energies, and can be doped quite easily for use in very fundamental studies of solvent-solute interactions.^{????}

In general, homogeneous cluster excited states provide a stringent test of this method due to their large number of energetically comparable excited states. For the 7-atom helium clusters, considering only the $n = 2$ manifold of states, there are 28 states that must be considered. The full results from the He₇ dynamics were recently published,[?] but here we focus on the use of the state-following algorithm as it was originally developed for this application.

The 7-atom cluster was chosen as bulk helium has 6 nearest neighbors and in an octahedral geometry this corresponds to one atom and its first solvation shell. The initial ground state geometry of 100 randomized clusters was generated by adding a random distance between 0 and 3 Å to each coordinate of the octahedral cluster and then optimizing using MP2/6-311G. Vertical excitation energies into the $n = 2$ manifold were then calculated using CIS with a customized Pople style 6-311(2+)G basis set, where the diffuse functions are of *sp* character, as this combination was previously shown to give good results for static excitations.[?]

The nuclear dynamics are computed using a standard velocity-Verlet algorithm[?] with no initial kinetic energy. The atoms in the excited cluster then move based solely on the forces generated by the vertical excitation. The trajectories are computed until the gradient drops below $< 1 \times 10^{-4} E_h/a_o$ and the energy change $< 1 \times 10^{-8} E_h$ or step-to-step atomic displacements $< 1.2 \times 10^{-4}$ Å. A minimum of 2000 and a maximum of 8000 time steps were computed using a step size of ≈ 0.1 fs.

In a majority of the trajectories (90%), due to the weak binding energy of ground state helium and high excitation energies, the excited clusters simply dissociate leaving behind a single excited atom. However, occasionally dimers and trimers can result in which excitation is carried away by two or three atoms respectively. Ultimately, 3% of the trajectories result in a dimer being formed and 0.3% result in trimers. The remaining trajectories (6%) stagnate as their initial excitations are very diffuse and do not exert significant forces on the clusters.[?]

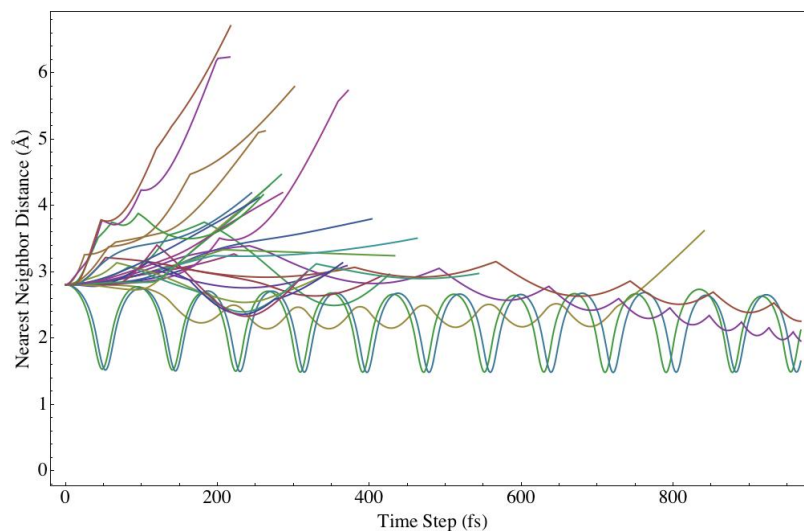
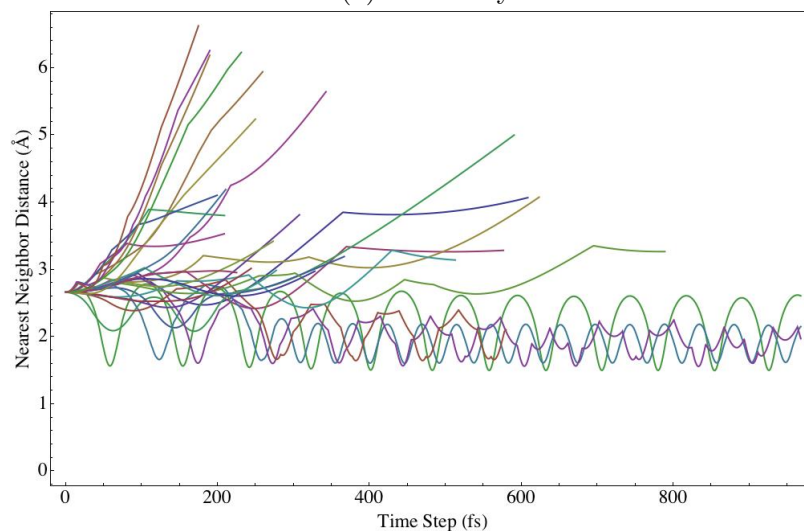
(a) Geometry *A*(b) Geometry *B*

Figure 4.5: Nearest neighbor distance throughout the trajectories for the 28 states associated with two initial geometries. Note the periodic oscillation of the dimers and discontinuities associated with the formation of double dimers from the nearest neighbor distance switching between different atoms.

Experimentally, clusters containing $> 10^6$ atoms are excited into the $n = 3$ manifold, and ionized with a time-delayed probe pulse.[?] Despite the differences in the systems, atomic ions are also the most frequently detected. These are followed by dimers, trimers and even larger ionized clusters which appear on a time scale remarkably similar to those computed using the state-following algorithm.[?]

First we consider the situation where there is no state following at the dynamics are fully adiabatic. ?? shows the absolute nearest neighbor distance as a function of time for each excited state of a single initial geometry, A . In this case, two stable dimers and two trimers are formed, and all other trajectories ultimately dissociate into atoms. There is also a single trajectory where a dimer is initially formed but then undergoes further interactions resulting in full dissociation. Trimers result from a slow approach of the atoms as they are unstable with respect to the excited dimers.^{???} The oscillatory behavior with sharp peaks results from changes of the nearest two atoms.

?? is also a plot of nearest neighbor distance vs. time for a different initial geometry, B . Here two dimers are again formed, and most fully dissociate, but there are also a couple trajectories which exhibit a more complex structure. These are the result of two sets of dimers, or “double dimers” being formed which occur when two mutually exclusive sets of atoms form excited dimers. These are unphysical as they require more energy than available from a single photon excitation. They arise during the course of adiabatic dynamics due to discontinuous potential surfaces and result in trajectories with very poor energy conservation. Using the diabatic states removes many of these hops by keeping the system in the desired state even if the relative energetic ordering of the states changes.

Turning on the state following algorithm and calculating the trajectories from these same initial states yields very different results. First the trajectories were recalculated using a small energy threshold of $\gamma_E = 0.001$ eV and a moderate overlap threshold of $\gamma_S = 0.5$. Overall significantly fewer excited dimers were formed, and the unphysical double dimers completely disappeared. Interestingly the number of trimers appeared to remain constant. The nearest neighbor distances are shown in ?? and ?? for geometries A and B respectively.

Using an energy threshold an order of magnitude larger, $\gamma_E = 0.01$ eV and the same overlap threshold of $\gamma_S = 0.5$ results in the diabatic state being more frequently selected. Ultimately the ratios of the final dissociation products were very similar to those using the preceding conditions, however, the individual trajectories did vary significantly. Varying the overlap threshold between 0.1 and 0.75 has essentially no effect on the outcomes and increasing the energy gap further also does not affect the outcomes. If γ_S is much larger than 0.75 or γ_E smaller than $\gamma_E = 0.001$ eV the diabatic states are predominantly rejected and pure adiabatic dynamics are recovered along with the unphysical double dimers.

State switching turns out to be a relatively rare event in He_7 , which is supported by the fact that the excited states are mostly parallel in the Franck-Condon regime, however it is crucial to account for the fact that they can cross for obtaining physically meaningful results. For the data generated with $\gamma_E = 0.01$ and $\gamma_S = 0.5$, which underwent the most diabatic transitions, a majority, 56%, of the trajectories never changed states, 87% had ≤ 5 and 90% had ≤ 10 state-switches. Thus, although the dynamics generated under these conditions are

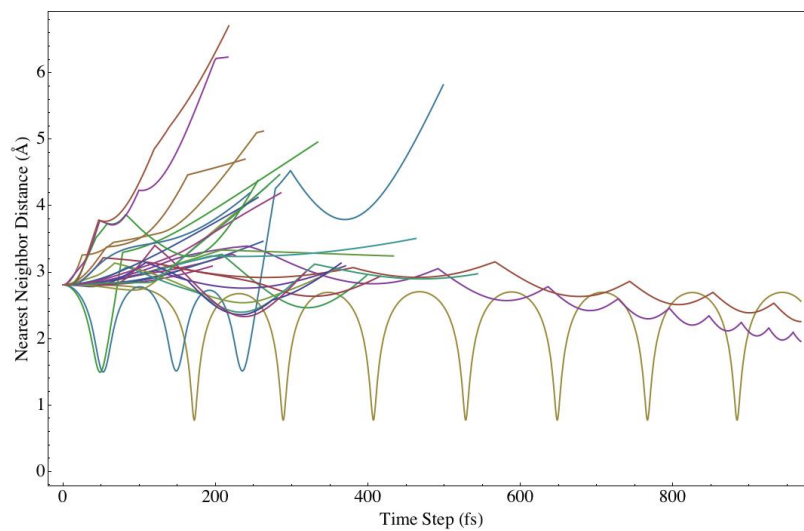
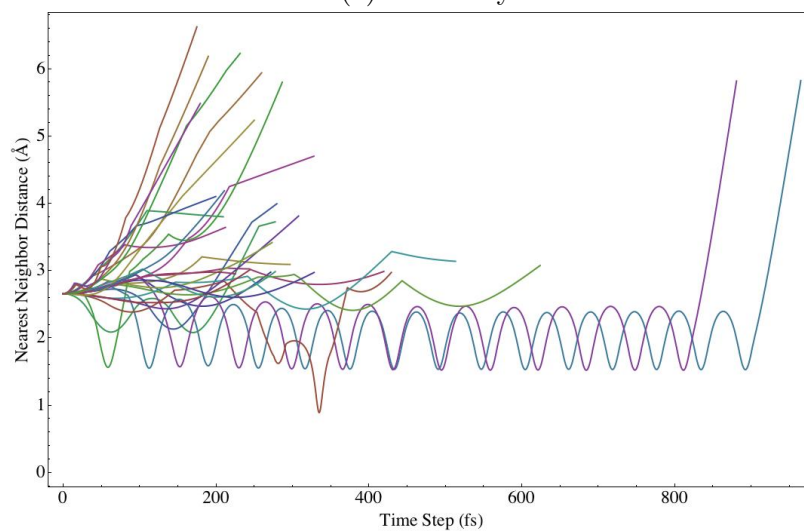
(a) Geometry *A*(b) Geometry *B*

Figure 4.6: Nearest neighbor distance throughout the trajectories for the 28 states associated with the same initial geometries for $\gamma_E = 0.001$ eV and $\gamma_S = 0.5$.

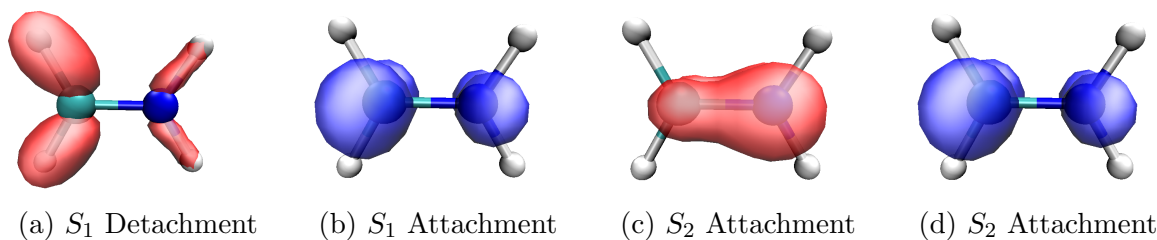


Figure 4.7: Detachment (red) and attachment (blue) densities for the first two excited states of the formaldimine cation at the ground state geometry

primarily adiabatic, changing states is allowed whenever nearly degenerate states exist.

The crudeness of these calculations, which use classical nuclear dynamics and CIS for the underlying electronic structure calculations, do not allow quantitative conclusions. However, it is clear that applying the state following algorithm yields dramatically different results. With the introduction of diabatic surface switching, the trajectories are better able to conserve energy and yield more physically accurate results, than what can be obtained using purely adiabatic dynamics. Thus, this is a very useful method of incorporating some diabatic effects into AIMD calculations without significant additional computational cost.

4.3.3 Minimum Energy Path: Formaldimine Cation, CH_2NH_2^+

The formaldimine cation is a popular model chromophore which is known to pass through a conical intersection between the S_1 and S_2 states as it relaxes following a vertical excitation into the $S_2(\pi \rightarrow \pi^*)$ state.^{???} The ground state is planar (C_{2v}), however, the relaxed $\pi \rightarrow \pi^*$ state is actually the first excited state at the perpendicular geometry (90° rotation about the C=N bond).

Although this is a well studied system, it is ideal for testing the combination of the state-following algorithm with GSM to determine the approximate conical intersection.

The ground and first excited state optimized geometries were determined using standard DFT/TD-DFT calculations with the ω -B97 functional and the 6-31G** basis set.[?] Vertically excited states were computed at the same level of theory with TD-DFT.

The minimal energy path (MEP) was computed using the growing string method with 11 nodes in combination with our state following algorithm with $\gamma_E = 0.5$ eV and $\gamma_S = 0.5$.

?? shows the attachment and detachment densities for the first two excited states of the formaldimine cation. It is readily apparent that the first state has $\sigma \rightarrow \pi^*$ character while the second state has $\pi \rightarrow \pi^*$ character. Both states have a particle density (??, ??) which is visually the same for both states. The hole density (??, ??) is very different with the first state losing an electron from the N-H and C-H σ bonds, and the second being removed from a π orbital.

?? shows the attachment/detachment densities for the optimized excited state geometry. Again, the attachment densities for the two states appear identical, but the detachment

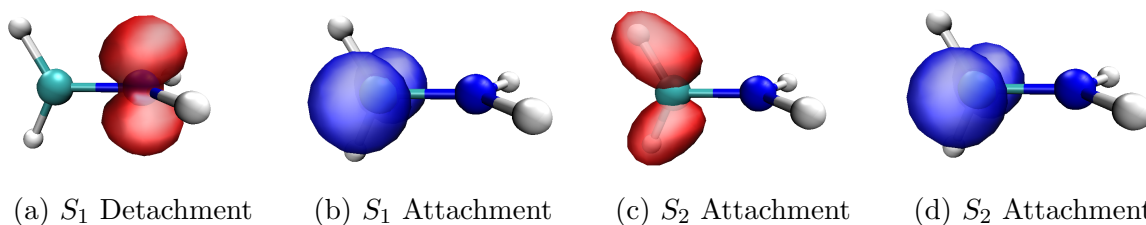


Figure 4.8: Detachment (red) and attachment (blue) densities for the first two excited states of the formaldimine cation at the perpendicular geometry

densities differ significantly. In this case, the first excited state ?? appears to be losing an electron from a p orbital, although lowering the isosurface value reveals that it is indeed a π orbital. ?? shows the hole density centered on the C-H bonds.

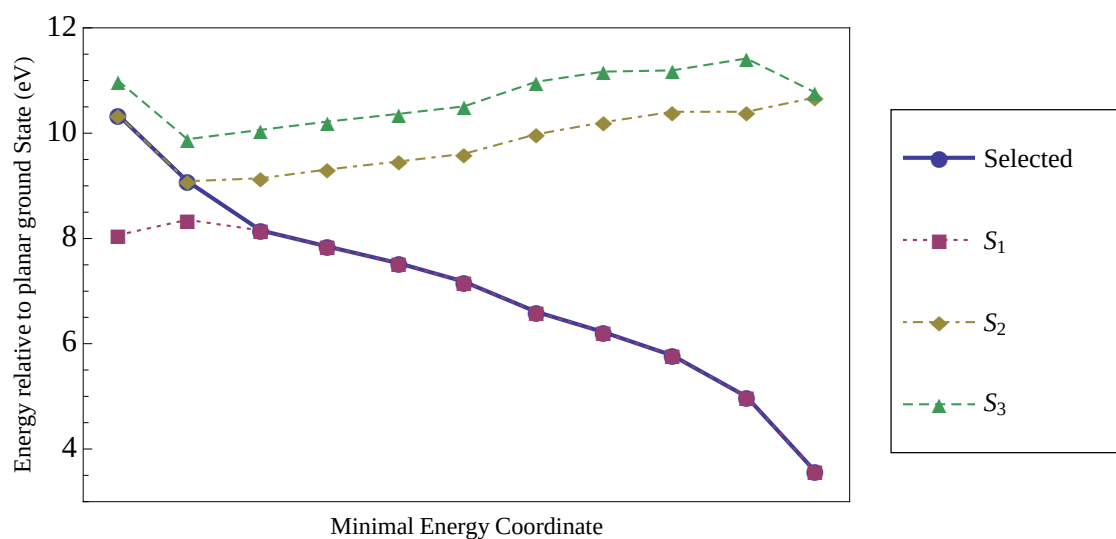


Figure 4.9: Growing string method for minimal energy path from S_2 at the ground state planar geometry to S_1 at the optimized perpendicular geometry. The state selected by the state following algorithm is marked by the solid blue line and has $\pi \rightarrow \pi^*$ character.

Thus, it is confirmed that there must some point where the character of these states changes. Applying the GSM with state-following reveals the minimal energy path between these states and the results are shown in ??. In this case the energy window is chosen to be quite large ($\gamma_E = 0.5$ eV), but considering the energy change from the ground state to the optimized excited state geometry is over 6 eV it is not unreasonable. The conical intersection between excited states S_1 and S_2 occurs fairly near to the ground state geometry. This is in agreement with the results by Tavernelli et. al.[?]

While using state-following does not determine the intersection point exactly, it does yield a guess, which can be further refined through other methods. Without state following or some other technique for determining the relevant state it is not possible to use the GSM in this manner.

4.4 Conclusion

This method of state-following, for multiple states occurring in a selected energy window, is based upon the attachment/detachment density overlap. After the initial excitation, subsequent states can be chosen adiabatically or diabatically depending on how the parameters γ_E and γ_S are chosen.

Generally large γ_E and small γ_S result in diabatic state following while small γ_E and large γ_S lead to adiabatic surface following. The values selected for these parameters are highly dependent upon the application, but as a general rule, the calculations are relatively insensitive to γ_S with only very high or very low values causing a significant change in the results. The energy window parameter should generally be made large if diabatic state-following is desired, but not so large that more than three or four states are ever captured. When more states appear in the window the risk of selecting a state with a similar density but dissimilar energy increases and often leads to undesired results. Another general rule of thumb is that γ_E should be larger for geometry optimizations and path finding applications than for AIMD. While the results presented use CIS or TD-DFT the algorithm is quite general and only requires the definition of an attachment/detachment density.

We have demonstrated the utility of this semi-classical and deterministic method for a diverse set of applications including geometry optimization, AIMD and minimal path finding calculations. In geometry optimization and MEP finding cases using the state-following algorithm expands the types of calculations that are possible, and in AIMD it provides more physically meaningful results than using only the adiabatic states.

Chapter 5

A local excited state method using single substitutions in the absolutely localized molecular orbital basis with application to spectra of large helium clusters

5.1 Introduction

Predicting the electronically excited states of large systems with reasonable accuracy is an ongoing challenge for quantum chemistry. The competing interests of accuracy and efficiency place significant limitations on the methods considered practically useful.^{??} By far the most widely used method for calculating excited states of medium-sized and larger molecules is time-dependent Kohn-Sham density functional theory (TD-DFT).^{??} This method involves computational effort per state which is formally similar to the effort necessary to treat the ground state by DFT. Formally, a quadratic number of variables, akin to single excitations, are involved, and the computational cost typically grows between the square and the cube of system size per state, and cannot be worse than the fourth power. Thus calculations of roughly 5-40 states are feasible if the ground state calculation is feasible. On the other hand, obtaining *all* excited states would require computational effort that rises with the asymptotically with sixth power of molecular size, which rapidly becomes unfeasible even when the ground state calculation is tractable. The accuracy of TDDFT calculations is limited by the well-known difficulty in systematically improving present-day density functionals. Incorrect asymptotic potentials cause errors in the position of Rydberg excited states, while self-interaction errors yield dramatic failures for charge transfer excited states, which can to some extent be remedied by using range-separated density functionals.^{????}

By contrast, wave function approaches to excited states are appealing in that they can

be improved straight-forwardly by successively incorporating additional degrees of freedom, typically in the form of higher substitutions in a trial configuration interaction (CI) wave function. Due to the Brillouin Theorem, the variationally optimized mean field Hartree-Fock wavefunction has zero matrix elements with all singly substituted configurations. Thus, the simplest CI wave function for excited states is CI in the space of single substitutions (CIS)^{??}:

$$|\Psi\rangle = \sum_s c_s |\Phi_s\rangle \quad (5.1)$$

CIS has half the number of degrees of freedom of TDDFT (it has the identical number of degrees of freedom as TDDFT in the Tamm-Dancoff approximation).[?] Thus its computational cost is roughly comparable to TDDFT. Relative to TDDFT with commonly available functionals, CIS has the advantage of a correct asymptotic potential and zero self-interaction error. However it has the disadvantage of complete neglect of dynamic electron correlation, which leads to errors in valence excitation energies that are on the order of 1 eV (the correlation energy of a pair of electrons).

More sophisticated wave function methods include additional complexity in the wave function to account for electron correlation effects through double and higher substitutions. The simplest methods are perturbative cousins such as the non-degenerate CIS(D) correction,[?] and its quasi-degenerate variants.[?] The latter are closely related to the second order coupled cluster approximation (CC2),[?] which is an approximation to full equation of motion coupled-cluster (EOM-CC) theory (e.g. EOM-CCSD, EOM-CCSD(T)).^{??} The cost of these correlation methods is as low as fourth order in system size for scaled opposite spin methods,^{??} while it is fifth order for the perturbative methods,[?] and sixth order with full iterative treatment of the doubles. Iterative triples methods scale with the eighth power of system size. Such steep increases in computational cost with system size places increasingly severe restrictions on the system sizes that can be successfully treated. Even so, the above methods fail for problems where the ground state is not a good single configuration, which must be addressed by active space methods such as the complete active space self-consistent field method (CAS-SCF), or spin-flipping methods,^{??} or the corresponding second order perturbative corrections.^{???}

There has been great interest in reducing the computational requirements of electronic structure theory calculations for the ground state from quadratic storage and cubic computation towards linear scaling. As argued by Kohn,[?] the 1-particle density matrix that controls the ground state energy is intrinsically “short-sighted” and therefore in the large system limit, only a linear number of variables are significant. While linear scaling methods for forming the effective Hamiltonian^{???} have been widely used since the early 1990’s, linear scaling replacements for diagonalization, though extensively developed,[?] are not widely applied, because very large systems are needed to realize adequate sparsity in real space,[?] and the situation is even more challenging in spectral representations.

Linear scaling methods for excited states are generally less thoroughly developed than for ground states, although there has been significant progress.[?] Specifically, there have been formulations of CIS and TDDFT which are appropriate for linear scaling,^{??} and some

proof-of-concept implementations and calculations have been reported.^{???} However, these methods are not widely used for production calculations at the moment, perhaps because excited states appear to exhibit substantially greater delocalization than ground states.

Therefore if one is interested in systems significantly larger than 100 atoms, but not large enough that rigorous linear scaling is possible, it is necessary to apply additional approximations.[?] Exploiting the intrinsic locality in certain types of chromophores has led to the development of incremental, multi-layer and fragmentation based approaches.^{?????} Biological systems often fall into this category and reports of heroic calculations with over 20,000 atoms have been reported.[?] However, even in these calculations the excited states were only computed on fragments containing no more than 103 atoms.

Grimme recently published a simplified method based on the Tamm-Dancoff approximation to TD-DFT (sTDA), where he reported results for a 483 atom/6879 basis function system^{??}. The two-pronged approach used a Löwdin-monopole basis for the two electron integrals and a bold truncation of the single excitations to make this feasible. The integral approximation leads to a preferential description of delocalized states and four global parameters are introduced to reduce some of the systematic error.

Current implementations of CIS and TDDFT are optimized for computing only a handful of the low-lying excited states, and both the linear scaling and fragment-based methods discussed above for treating larger systems are similar in this respect. However, when dealing with large homogeneous systems, such as atomic and molecular clusters, there are dense manifolds of states with similar energies to consider and thus many states (a full description of at least the bands of interest) are required to connect directly to experimental results. Part of the reason that non-covalently bound clusters have generated so much excitement is that they span the range between the gas phase and bulk limits, and are useful for investigating fundamental differences between bulk and surface properties^{???}.

As an example, consider the excitation energies of rare gas clusters such as helium atoms, which have been of great interest because of their superfluid properties[?] and as a spectroscopic medium they provide a unique environment yielding rotational resolution of dopant solutes.^{????} For the electronic spectrum of undoped clusters, the sharp atomic lines (e.g. 2p and 3p) of the helium atom give way to broad blue-shifted peaks in large clusters,[?] which correspond to bands of excited states. The photoionization dynamics of helium clusters have also been the subject of considerable recent interest.[?]

In this chapter, we report the development of a local excited state method that can adequately describe large numbers of electronic excited states (as needed to describe the bands) in large atomic and molecular clusters at greatly reduced computational cost. In a 1000 atom cluster, the $n=2$ band would require a minimum of 4000 states to describe correctly. This requirement of the number of desired states increasing with cluster size is one that conventional molecular excited state codes are quite unsuited to handle, and it introduces an enormous additional pre factor to the computational cost relative to the usual situation of requiring only a few excited states. Fundamentally it increases the scaling of the computational cost by at least one power of system size. At the same time, because each atom in a helium cluster is identical, there is no obvious locality to the excited states: in

general they may be fully delocalized through-out the cluster. Both of these factors make the development of a viable computational method potentially very challenging.

However there is one critically important physical advantage that we can exploit to make the problem tractable. We have previously reported on the electronically excited states of small helium clusters using standard configuration interaction singles (CIS).²² In the $n = 2$ manifold, we determined that the excited states could be interpreted in terms of superpositions of atomic-like excitations.²² This is perhaps not too surprising because of the very high ionization energy of He atoms, and the fact that the electron affinity is negative. This characteristic of the excited states suggests that the excited states associated with the $2p$ and $3p$ bands may be adequately described as superpositions of atomically localized excitations. Such a model will have storage requirements that grow linearly per state, and only quadratically for all states. The computational cost will grow no worse than the cube of the number of atoms to obtain all excitations.

The theory will be formulated for either atomic or molecular clusters (nitrogen clusters, or even water clusters, for example, may behave quite similarly). The ground state of a strongly localized molecular cluster can be quite accurately treated at greatly reduced computational cost through the use of absolutely localized molecular orbitals (ALMOs).²³ The ALMO approximation is that the MO coefficient matrix is defined as block diagonal in the molecules comprising the cluster.^{23,24,25} Thus each MO on a given molecule is a superposition of only AO's from that same molecule. In addition to accelerating SCF calculations for large molecules,²³ ALMO's have been used for calculating the contributions to intermolecular interactions.^{24,25} A direct result of the ALMO approximation is that ALMO's are non-orthogonal between fragments.

The ALMO's are an ideal basis within which to perform CIS with the approximation of superpositions of intra-fragment excitations. By allowing excitations only on fragments, charge-transfer between fragments is prohibited and the number of singly excited states that factor into the calculation grows only linearly with cluster size (for a homogeneous cluster). As a result, far larger clusters can be examined than would otherwise be possible. In this chapter we formulate the theory for this local ALMO-CIS method, and discuss an efficient cubic scaling implementation that yields all the ALMO-CIS states via direct diagonalization after building the effective Hamiltonian. We present benchmarks showing the extent to which ALMO-CIS calculations are faithful to full CIS calculations for helium clusters, with very satisfactory results. Timings for the algorithm are presented for helium clusters containing over 250 atoms. We then apply the ALMO-CIS method to model the size dependence of the excitation spectrum of helium clusters.

5.2 Theory

5.2.1 Notation

Tensors provide a convenient method for treating non-orthogonal functions, such as the ALMO's. Thus standard tensor notation is used,^{??} where subscripts indicate functions in the covariant (given) basis, and superscripts indicate functions in the (biorthogonal) contravariant space. The Einstein summation convention is employed, where an index that occurs once covariant and once contravariant, implies a sum.

Occupied molecular orbitals (MO's) are denoted as i, j, k , virtual orbitals as a, b, c and general orbitals as p, q, r . Orbitals that are well-defined occupied or virtual levels are represented by the greek letter ϕ . When it is important to distinguish ALMO's from MO's (such as for virtual levels), the ALMOs will be denoted by ψ . Atomic orbital (AO) functions are given by χ_μ , auxiliary basis functions (used in resolution of the identity fitting) by χ_Q , and fragments are indicated I, J or F_I, F_J .

Fragment-localized quantities will be made explicit through the use of connecting lines above or below: for instance 2 MO's p and q are constrained to a single fragment if their indexes are connected as $\overline{pq}$. Throughout the discussion of the algorithms, when discussing the scaling, capital letters will denote quantities that scale with the size of the system and lower case letters indicate the value only depends upon the identity of the fragments. In particular, in our analysis of homogeneous atomic or molecular clusters we shall consider them to contain M identical fragments, and thus the computational effort can be analyzed as a power of M .

5.2.2 Ground State Wavefunction with Absolutely Localized Molecular Orbitals

The ground-state Hartree-Fock wavefunction is a Slater determinant of one electron functions.

$$|\Phi_0\rangle = |\phi_1 \dots \phi_i \dots \phi_n\rangle. \quad (5.2)$$

For standard electronic structure calculations the ϕ_i are canonical MO's, which diagonalize the Fock operator, and are typically highly delocalized. The MO's are expanded in terms of atom-centered basis functions (AO's) as

$$|\phi_p\rangle = \sum_\mu |\chi_\mu\rangle c_p^\mu. \quad (5.3)$$

The AO's, χ_μ , are assumed to be contracted Gaussians.

The atom-centered AO's used in electronic structure theory calculations are naturally partitioned according to the fragment on which they reside. Absolutely localized molecular orbitals (ALMOs) arise by applying a constraint that the MO coefficient matrix should be fragment blocked, such that the ALMO's which describe a molecule in a cluster contain only

contributions from the AO's of that molecular in the cluster.[?] When using ALMOs, each molecular orbital is tagged to a fragment F_J and expanded only in the subset of basis set functions with centers on that fragment.

$$|\psi_p\rangle = \sum_{\mu \in F_J} c_{p,\mu}^\mu |\chi_\mu\rangle, \quad p \in F_J. \quad (5.4)$$

The resulting occupied ALMOs are nonorthogonal between fragments, although the occupied ALMO's on a single fragment can be chosen as orthogonal. The block-diagonal structure of the ALMO transformation leads to very high computational efficiency. It is highly desirable to maintain this local structure for excited state evaluation, as will be discussed further in ??.

In tensor notation, the overlap of non-orthogonal orbitals, such as the ALMO's, is defined by the covariant overlap metric

$$\langle \psi_p | \psi_q \rangle = \sigma_{pq} = S_{pq} \quad (5.5)$$

and likewise the contravariant metric is

$$\langle \psi^p | \psi^q \rangle = \sigma^{pq} = \sigma_{pq}^{-1} = S_{pq}^{-1}. \quad (5.6)$$

The biorthogonality of the covariant and contravariant subspaces implies

$$\langle \psi^p | \psi_q \rangle = \delta_{pq}^p. \quad (5.7)$$

The nonorthogonality of ALMO's on one fragment to another has the interesting implication that the so-called ‘‘virtual’’ ALMO's, ψ_α , are not strictly virtual, because they overlap occupied ALMO's on other fragments: $\langle \phi_l | \psi_\alpha \rangle \neq 0$. To have well-defined virtual functions, ϕ_a , it is necessary to remove contamination in ψ_α from the occupied subspace. Thus projecting the occupied ALMOs ψ_k from the virtual ALMOs ψ_α yields new (projected) ALMO virtuals ϕ_a . The ϕ_a are orthogonal to all occupied ALMO's by construction, but remain nonorthogonal amongst themselves.

$$\begin{aligned} |\phi_a\rangle &= \mathcal{N}_\alpha \left(|\psi_\alpha\rangle - \hat{P}_{occ} |\psi_\alpha\rangle \right) = \mathcal{N}_\alpha \left(|\psi_\alpha\rangle - |\phi_k\rangle \sigma^{kl} \langle \phi_l | \psi_\alpha \rangle \right) \\ &= \mathcal{N}_\alpha \left(|\psi_\alpha\rangle - |\phi_k\rangle \sigma^{kl} \sigma_{l\alpha} \right) = \mathcal{N}_\alpha \left(|\psi_\alpha\rangle - |\phi_k\rangle t_{\alpha}^k \right) \end{aligned} \quad (5.8)$$

Here $\mathcal{N}_\alpha$ is a normalization factor to ensure $\langle \phi_a | \phi_a \rangle = 1$.

5.2.3 Nonorthogonal CIS and the ALMO-CIS model

Singly substituted configurations are formed by promoting an electron from an occupied Hartree-Fock orbital to a virtual one.

$$|\Phi_{\cdot a}^i\rangle = |\phi_1 \phi_2 \dots \phi_a \phi_j \dots \phi_n\rangle \quad (5.9)$$

The CIS excited states are superpositions of all single substitutions, with amplitudes t_i^a :

$$|\Psi_{CIS}\rangle = a_a^\dagger a^i |\Phi_0\rangle t_i^a = |\Phi_{\cdot a}^i\rangle t_i^a \quad (5.10)$$

Substituting this wavefunction into the time-independent Schrödinger equation and projecting with each of the excited determinants according to the linear variational principle yields equations for the CIS excitation energies.

$$\langle \Phi_{\cdot j}^b | \hat{H} | \Phi_{\cdot a}^i \rangle t_i^a = \omega_{CIS} \langle \Phi_{\cdot j}^b | \Phi_{\cdot a}^i \rangle t_i^a \quad (5.11)$$

where $\omega_{CIS} = E_{CIS} - E_0$.

The choice of the natural representation[?] makes evaluation of the matrix elements isomorphic to the conventional orthonormal case, because biorthogonality of covariant and contravariant functions permits similar simplifications. Recalling ??, we see that:

$$\langle \Phi_{\cdot j}^b | \Phi_{\cdot a}^i \rangle = \delta_{\cdot j}^i \delta_{\cdot a}^b \quad (5.12)$$

Carefully evaluating the matrix elements leads to the following eigenvalue equation in the natural representation (this is a generalized version of the conventional result, where biorthogonality replaces orthogonality):

$$A_{\cdot j a}^{ib} t_i^a = \omega_{CIS} \delta_{\cdot a}^b \delta_{\cdot j}^i t_j^b \quad (5.13)$$

The matrix elements of the singles-singles block of the Hamiltonian are given in the biorthogonal representation as:

$$A_{\cdot j a}^{ib} = f_a^b \delta_{\cdot j}^i - f_{\cdot j}^i \delta_{\cdot a}^b + \langle \phi^i \phi^b | | \phi_a \phi_j \rangle \quad (5.14)$$

These equations can be transformed to the covariant integral representation (where the unknown amplitudes are fully contravariant, whilst the known matrix elements are fully covariant) using metric matrices to obtain

$$A_{ibja} t^{ai} = \omega_{CIS} S_{ab} S_{ij} t^{bj} \quad (5.15)$$

$$A_{ibja} = f_{ba} S_{ij} - f_{ij} S_{ba} + \langle \phi_i \phi_b | | \phi_a \phi_j \rangle \quad (5.16)$$

For closed shell wavefunctions, the spin-restricted form, with all dimensions collapsed to those of spatial orbitals rather than spin-orbitals, is:

$$A_{ibja} = f_{ba} S_{ij} - f_{ij} S_{ba} + 2 (\phi_i \phi_a | \phi_b \phi_j) - (\phi_i \phi_j | \phi_b \phi_a) \quad (5.17)$$

The spatial orbital two-electron integrals are written in the “chemist’s notation” where the first two indexes involve the coordinates of electron 1 and the last two indexes are those of electron 2.

The non-orthogonal CIS equations, as written, convey computational advantage only when the one and two-electron matrix elements become sufficiently sparse that the dimension of the problem can be greatly reduced. As argued in the introduction, this is very difficult

to exploit computationally except for truly enormous systems. For clusters on the order of 1000 atoms, as may be treated with this theory, there is very little effective sparsity because of the spatially extended basis sets that are needed to treat excited states (equivalent to at least doubly augmented basis sets, in terms of the Dunning hierarchy or the (2+) sets in terms of diffuse functions for Pople basis sets).

Instead, we shall make a physically-based model, akin to local correlation models, which restricts the single substitutions to only occur within fragments. By doing so, we prohibit charge transfer between fragments. In the limit of non-interacting fragments, such a model is exact. As we have argued in the introduction, it is also likely to be quite accurate for weakly interacting clusters if their constituent atoms or molecules have high ionization potentials and low (or negative) electron affinities. We shall use the notation that the single substitution of an occupied level i by a virtual level a , is constrained to a single fragment F_I if we connect their indexes as follows: $\underline{ia}$.

We shall refer to this model where the excited states are approximated as superpositions of intra-fragment single substitutions as the ALMO-CIS model. Considering homogeneous atomic or molecular clusters containing M fragments, it is evident that the ALMO-CIS model retains only $\mathcal{O}(M)$ of the original $\mathcal{O}(M^2)$ CIS amplitudes. Since the model has included locality at the design level, it will also be relatively easy to exploit this great reduction in the computational complexity. The ALMO-CIS equations follow from the non-orthogonal CIS equations in the covariant integral representation by deleting all rows and columns corresponding to single substitutions that transfer charge between fragments:

$$\mathcal{A}_{\underline{ia},\underline{jb}} t_{\underline{ia},\underline{jb}}^{\overline{ai}} = \omega_{CIS} \mathcal{S}_{\underline{ia},\underline{jb}} t_{\underline{ia},\underline{jb}}^{\overline{ai}} \quad (5.18)$$

with

$$\mathcal{A}_{\underline{ia},\underline{jb}} = A_{\underline{ibja}} \text{ and } \mathcal{S}_{\underline{ia},\underline{jb}} = S_{ij} S_{ab}. \quad (5.19)$$

5.2.4 ALMO-CIS Oscillator Strengths

The oscillator strength for a electronically excited state κ reflects the probability of a transition from the ground state into that state and is generally defined as

$$f_{\kappa} = \frac{2}{3} \omega_{\kappa} \left| \langle \Psi_0 | \hat{\mu} | \Psi_{\kappa} \rangle \right|^2 \quad (5.20)$$

The energy difference, ω_{κ} comes directly from the calculation of the ALMO-CIS eigenvalues, and the dipole expectation value is

$$\langle \Psi_0 | \hat{\mu} | \Psi_{\kappa} \rangle = \sum_J \sum_{i,a \in \{\Psi_J\}} t_{\kappa}^{\overline{ai}} \langle \phi_i | \hat{\mu} | \phi_a \rangle. \quad (5.21)$$

Expanding $\langle \phi_i | \hat{\mu} | \phi_a \rangle$ into the atomic orbital basis we obtain

$$\langle \phi_i | \hat{\mu} | \phi_a \rangle = (\phi_i | \chi^{\mu}) \langle \chi_{\mu} | \hat{\mu} | \chi_{\nu} \rangle (\chi^{\nu} | \phi_a). \quad (5.22)$$

Now substituting ?? back into ?? and defining dipole moment $\mu_{\mu\nu} = \langle \chi_\mu | \hat{\mu} | \chi_\nu \rangle$ and the transition density $P_\kappa^{\mu\nu}$

$$\begin{aligned} P_\kappa^{\nu\mu} &= (\chi^\nu | \phi_i) t_\kappa^{ia} (\phi_a | \chi^\mu) \\ \implies f_\kappa &= \frac{2}{3} (E_\kappa - E_0) |\mu_{\mu\nu} P_\kappa^{\nu\mu}|^2 \end{aligned} \quad (5.23)$$

5.3 Efficient Implementation and Scaling

5.3.1 Direct vs Iterative Diagonalization

The first key design decision is how the truncated Hamiltonian should be diagonalized: directly by dense linear algebra, or iteratively on the basis of matrix-vector multiplies.⁷ While iterative diagonalization is greatly preferred if only a few eigenvalues are desired, direct diagonalization is more efficient if a significant fraction of the eigenvalues are sought. Our first target application of ALMO-CIS is to compute the excited states of large homogeneous clusters. These typically have many excited states within a narrow energy window, corresponding to bands that broaden the discrete excitations of the spectrum of a single fragment, and thus a large percentage of the CIS eigenvalues are desired.

Therefore we choose direct diagonalization as the basis of this implementation. We note that this is not a serious limitation on the size of system that can be treated via ALMO-CIS, as the ALMO-CIS vectors are $\mathcal{O}(M)$ and thus construction of the ALMO-CIS Hamiltonian requires $\mathcal{O}(M^2)$ storage, and direct diagonalization is $\mathcal{O}(M^3)$ for the full spectrum. By contrast, conventional CIS involves eigenvectors of length $\mathcal{O}(M^2)$ and therefore requires $\mathcal{O}(M^4)$ storage and $\mathcal{O}(M^6)$ computational effort for direct diagonalization. The ALMO-CIS calculation thus involves storage and computation that is proportional to only the square root of that for conventional CIS. Or for equivalent computational resources, ALMO-CIS will be able to treat a system of $\mathcal{O}(M^2)$ size if conventional CIS can treat a system of size $\mathcal{O}(M)$.

5.3.2 Strategy for Two-Electron Integral Evaluation

Generally the most computationally demanding step in standard CIS is associated with formation and transformation of the two-electron repulsion integrals (ERI's). There are two basic issues that dictate our strategy. First, is the extent to which basis function overlaps become sparse in a large cluster. Second, is the question of how effective the resolution of the identity (or density fitting) approach is likely to be. We shall discuss these issues in turn, and then outline our chosen approach.

With regard to the first issue, AO-ERI calculation naïvely scales as $\mathcal{O}(M^4)$. In large molecules with compact basis sets, this can be reduced to quadratic cost by applying appropriate screening techniques, such as the Schwarz integrals, which yield a strict upper bound

to the size of the integrals.??

$$\left| (\mu\nu | \lambda\sigma) \right| \leq (\mu\nu | \mu\nu)^{1/2} (\lambda\sigma | \lambda\sigma)^{1/2} \quad (5.24)$$

The number of significant basis function pairs, with a threshold of 1×10^{-12} are shown in ?? as a function of cluster size for octahedral helium clusters using the cc-pVTZ basis, and a customized [5s2p] basis (consisting of the 3s functions of 6-311G and two sets of diffuse s and diffuse p exponents, often denoted 6-311(2+)G) that is suitable for describing the n=2 Rydberg manifold. It is evident that effective linear scaling is not obtained with the diffuse basis set until clusters of well over 1000 atoms. By contrast the more compact cc-pVTZ basis reaches linear scaling in its number of numerically significant basis function pairs much sooner. Therefore excited state calculations face growth in the number of significant AO-ERI's that remains close to $\mathcal{O}(M^4)$ into regimes as large as 1000 atoms. As a result, evaluation of the MO-ERI's by naïve transformation of AO-ERI's would be at least this demanding, and therefore will not be very computationally efficient.

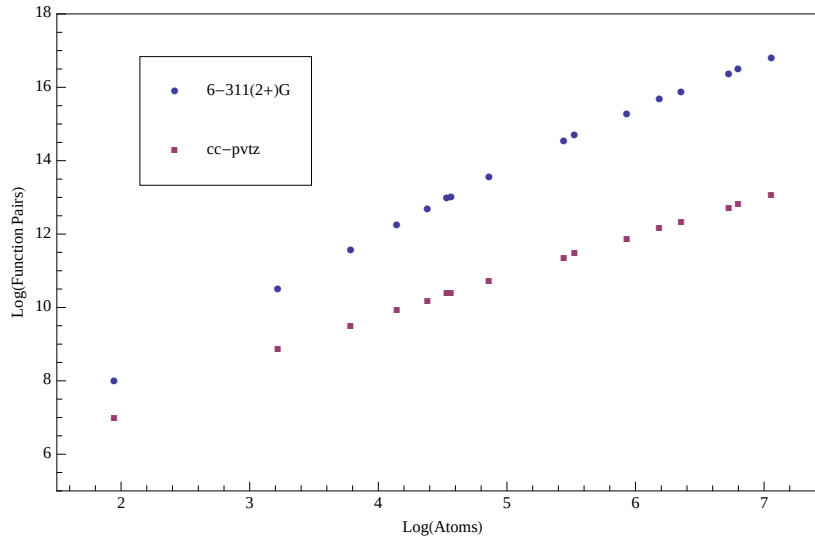


Figure 5.1: Scaling of the significant basis function pairs with system size (He₇ to He₁₁₅₉). A linear fit to the last five points on each curve gives slopes of 1.3 and 1.0 for the custom 6-311(2+)G (11 functions/atom) and for standard cc-pVTZ (14 functions/atom) basis sets respectively.

The ALMO-CIS model, however, offers crucial additional computational advantages. The ALMO occupied orbitals and the unprojected virtual orbitals are both fragment blocked, and as a result, *if we ignore the projection terms* the ALMO-CIS model rigorously requires only $\mathcal{O}(M^2)$ AO-ERI's. Let us begin by expanding the Coulomb-like term, $(\phi_i \underline{\phi}_a | \phi_j \underline{\phi}_b)$, of Eq.

(??), in terms of unprojected ALMO contributions and projection corrections:

$$\begin{aligned}
 (\phi_i \phi_a | \phi_j \phi_b) &= \mathcal{N}_\alpha \mathcal{N}_\beta \left\{ (\phi_i \psi_\alpha | \phi_j \psi_\beta) \right. \\
 &\quad \left. - 2 (\phi_i \psi_\alpha | \phi_j \phi_k) (\phi^k | \psi_\beta) + (\phi_i \phi_k | \phi_j \phi_\ell) (\phi^k | \psi_\alpha) (\phi^\ell | \psi_\beta) \right\} \\
 J &= N^2 (J1 - 2 \cdot J23 + J4)
 \end{aligned} \tag{5.25}$$

Due to the fragment-blocking of the ALMO MO coefficient matrix, the necessary AO-ERI's to evaluate the unprojected contribution, $(\phi_i \psi_\alpha | \phi_j \psi_\beta)$ (i.e. $J1$), will be just the $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma)$ subset. Similarly, the exchange term, $(\phi_i \psi_\alpha | \phi_j \psi_\beta)$, of Eq. (??) can be written as:

$$\begin{aligned}
 (\phi_i \phi_j | \phi_a \phi_b) &= \mathcal{N}_\alpha \mathcal{N}_\beta \left\{ (\phi_i \phi_j | \psi_\alpha \psi_\beta) \right. \\
 &\quad \left. - 2 (\phi_i \phi_j | \psi_\alpha \phi_k) (\phi^k | \psi_\beta) + (\phi_i \phi_j | \phi_k \phi_\ell) (\phi^k | \psi_\alpha) (\phi^\ell | \psi_\beta) \right\} \\
 K &= N^2 (K1 - 2 \cdot K23 + K4)
 \end{aligned} \tag{5.26}$$

Here the $(\mu\nu | \lambda\sigma)$ AO-ERI's are all that are needed for the unprojected ALMO contributions $((\phi_i \psi_\alpha | \phi_j \psi_\beta)$ or $K1$). This is true even if all $\mathcal{O}(M^4)$ AO-ERI's are non-zero.

These results suggest that we should evaluate the *unprojected* contributions to the ALMO-CIS Coulomb and exchange integrals by fragment-blocked transformation of the $\mathcal{O}(M^2)$ required AO-ERI's, and then correct separately. The unprojected ALMO-CIS integrals will therefore require only $\mathcal{O}(M^2)$ computational effort. The corrections for projection require evaluating ALMO integrals with 3 occupied indexes, $(\phi_i \psi_\alpha | \phi_j \psi_k)$, $(\phi_i \phi_j | \psi_\alpha \psi_k)$, and 4 occupied indexes, $(\phi_i \psi_k | \phi_j \psi_l)$. These corrections are significantly smaller in magnitude and can be evaluated using the resolution of the identity (RI) approximation without significant loss of accuracy.^{??} Doing these corrections via RI avoids the need for larger numbers of 4-center AO-ERI's and permits the efficiency of dense linear algebra.

5.3.3 ALMO Integral Evaluation

The half-transformed integrals $J_{\mu\nu}^{ia} = (\phi_i \psi_\alpha | \chi_\mu \chi_\nu)$ and $K_{\mu\nu}^{ia} = (\phi_i \chi_\mu | \psi_\alpha \chi_\nu)$ are computed within Q-Chem's AO-ERI evaluation code, which uses the PRISM algorithm for efficiency.^{???} We have added a customized ERI "digester" that carries out first two MO quarter-transformations on a batch of AO-ERI's. The batch size is determined by the integral code and does not scale with the size of the system. The fully-transformed integrals are then formed from the half-transformed integrals externally.

Only the integrals with ϕ_i and ψ_α on F_I , and χ_μ and χ_ν on F_J are required (corresponding to $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma)$ and $(\chi_\mu \chi_\nu | \chi_\lambda \chi_\sigma)$ as discussed in the previous subsection). No additional truncation is possible within the coulomb integrals, but for the exchange contributions, using the Schwarz integrals, only AO-ERI's with significant overlap need be computed. By

creating mini-lists of the required half-transformed integrals we avoid forming many of the AO integrals.??

The AO integrals are efficiently transformed using customized digester algorithms. The coulomb digester, is outlined in ?? and the exchange digester, is shown in ?. These algorithms are shown schematically rather than exactly as implemented in order to avoid undue complexity. In particular, the production code is organized into loops over different angular momentum classes for bras and kets, and then loops over the different shell quartets corresponding to the current bra and ket angular momentum. Finally batches of selected shell quartets are evaluated. By contrast, the simplified schematics shown in ?? and ?? show only loops over AO function pairs.

Algorithm 5.1: Coulomb digester for integrals, $J_{i\alpha\lambda\sigma} = (\psi_i\psi_\alpha | \chi_\lambda\chi_\sigma)$

```

for  $\mu\nu \in F_I$  do
  for  $\lambda\sigma$  batches do
    Make  $(\mu\nu | \lambda\sigma)$  for  $\mu\nu, \lambda\sigma$ 
    for  $\lambda\sigma \in \text{batch}$  do
       $F_J \leftarrow \lambda\sigma$ 
       $J_{i\alpha\lambda\sigma} += (\mu\nu | \lambda\sigma) P_{i\alpha}^{\mu\nu}, \forall i\alpha \in F_I$ 
       $J_{j\beta\mu\nu} += (\mu\nu | \lambda\sigma) P_{j\beta}^{\lambda\sigma}, \forall j\beta \in F_J$ 

```

For the coulomb integrals a batch of AO integrals $\mathbf{W}$ are contracted with the transition densities $P_{i\alpha}^{\mu\nu} = c_i^\mu c_\alpha^{\nu\dagger}$. Each batch corresponds to a single bra, $\langle \chi_\mu \chi_\nu |$, so each member of the batch can be identified with a specific ket, $|\chi_\lambda \chi_\sigma\rangle$. Here λ and σ must belong to the same fragment F_J . Thus, the loop over excitations jb only includes the those on F_J . The digester loops over the elements of the batch and identifies the corresponding fragment F_J . This is followed by gathering the relevant elements of the density matrix for the ket side belonging to F_J , $P_{j\beta}^{\lambda\sigma}$. Note that the density matrix is symmetrized and vectorized by fragment to further increase the efficiency. Then a matrix multiplication between the AO integrals and the density matrix is performed accounting for the symmetry of the integrals and the half-transformed integrals $J_{\mu\nu j\beta}$ are incremented.

The digester for the coulomb-like terms uses a symmetrized transition density and yields a half-transformed matrix that is also symmetrized. By contrast, the exchange terms (??) cannot accept a symmetrized density, and yield an unsymmetric half-transformed tensor. Thus all symmetries must be accounted for explicitly. It is also important to emphasize in

Algorithm 5.2: Exchange digestor for integrals, $K_{\underline{i}\alpha\nu\lambda} = (\overline{\phi_i\nu|\psi_\alpha\lambda})$

```

for  $\mu\nu$  do
  for  $\lambda\sigma$  exchange batches do
     $F_I \leftarrow \lambda, F_J \leftarrow \sigma$ 
    Make  $(\overline{\mu\nu|\lambda\sigma})$  for  $\mu\lambda \in F_I, \nu\sigma \in F_J$ 
    for  $\lambda\sigma \in \text{batch}$  do
       $K_{\underline{j}\beta\underline{\mu}\underline{\lambda}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{j}\beta}^{\nu\sigma}, \forall \underline{j}\beta \in F_J$ 
       $K_{\underline{j}\beta\underline{\lambda}\underline{\mu}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{j}\beta}^{\sigma\nu}, \forall \underline{j}\beta \in F_J$ 
       $K_{\underline{i}\alpha\underline{\nu}\underline{\sigma}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\mu\lambda}, \forall \underline{i}\alpha \in F_I$ 
       $K_{\underline{i}\alpha\underline{\sigma}\underline{\nu}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\lambda\mu}, \forall \underline{i}\alpha \in F_I$ 
    if  $F_I == F_J$  then
      for  $\lambda\sigma \in \text{batch}, \underline{i}\alpha \in F_I$  do
         $K_{\underline{i}\alpha\underline{\mu}\underline{\sigma}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\nu\lambda}$ 
         $K_{\underline{i}\alpha\underline{\sigma}\underline{\mu}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\lambda\nu}$ 
         $K_{\underline{i}\alpha\underline{\nu}\underline{\lambda}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\mu\sigma}$ 
         $K_{\underline{i}\alpha\underline{\lambda}\underline{\nu}} += (\overline{\mu\nu|\lambda\sigma}) P_{\underline{i}\alpha}^{\sigma\mu}$ 

```

addition to computational costs which only grow as $\mathcal{O}(M^2)$ even when there are as many as $\mathcal{O}(M^4)$ significant AO-ERI's, these routines are also designed to ensure at most $\mathcal{O}(M^2)$ storage requirements. Both the input transition densities and the output half-transformed matrices are stored in packed format keeping only the required values. Finally, while not shown explicitly, the final two quarter transformations are also done making use of the ALMO locality and scale no higher than $\mathcal{O}(M^2)$.

5.3.4 ALMO integral corrections

The smaller terms, which are still critical for accurate evaluation of the two electron integrals from Eqs. (??) and (??) include $J23$, $J4$, $K23$ and $K4$. These will be evaluated using the RI approximation, following algorithms which we describe below.

For compactness, the 3-center ERI integrals will be denoted as $v_{ijQ} = (\chi_Q | \phi_i \phi_j)$ and $v_{iaQ} = (\chi_Q | \phi_i \psi_\alpha)$. Similarly, the 2-center ERI's in the auxiliary basis will be denoted as $v_{PQ} = (\chi_P | \chi_Q)$, while elements of its inverse will be written as v^{PQ} . In this notation, the RI correction terms, first introduced in Eqs. (??) and (??) can be explicitly written as follows:

$$J23 = v_{i\alpha P} v^{PQ} v_{j\beta Q} \sigma_\beta^k \quad (5.27)$$

$$J4 = \sigma_\alpha^k v_{ikP} v^{PQ} v_{jlQ} \sigma_\beta^l \quad (5.28)$$

$$K23 = v_{ijP} v^{PQ} v_{\alpha\beta Q} \sigma_\beta^k \quad (5.29)$$

$$K4 = \sigma_\alpha^k \sigma_\beta^l v_{ijP} v^{PQ} v_{klQ} \quad (5.30)$$

There are two primary steps to determine these correction terms. First the RI integrals must be generated and then they are combined to form the final corrections. The RI integrals in the AO basis are formed in batches and subsequently transformed using a digester within AOints. Two types of integrals are needed, those with both indices occupied, $(\chi^Q | \phi_i \phi_j)$, and those with one occupied and one virtual. The number of occupied-occupied integrals that are required will grow linearly with respect to system size in large enough systems, since ϕ_i and ϕ_j are fragment-localized and therefore do not have a large spatial extent. The number of occupied-virtual integrals will be larger as the virtual orbitals are significantly more diffuse, however, they are still ALMOs and retain advantages in efficiency. The cost to form the transformed 3-center ERI's does not exceed $\mathcal{O}(M^3)$ with system size.

By only computing the significant occupied-occupied RI integrals the final combination of the integrals to form the correction terms can also be made to scale as $\mathcal{O}(M^3)$ with system size or lower.

?? shows the steps for computing the coulomb corrections. For transparency of computational cost, all multiplications are expanded as loops. Steps that grow in cost linearly with the size of the system are in blue, while purple loops are over sparse indices and scale quadratically for small systems but linearly for large systems. The exchange corrections are computed similarly (??). The intermediate V_{ijkl} is common to both the coulomb and exchange terms and is only computed once (??).

Algorithm 5.3: Coulomb RI Corrections

```

for  $ik = 1, N_{Oo}$  do
  for  $Q = 1, N_{aux}$  do
    for  $P = 1, N_{aux}$  do
       $b_{ikQ} += v_{ikP} \cdot v^{PQ}$ 
    for  $j\ell = 1, N_{Oo}$  do
       $\mathcal{V}_{ikj\ell} += b_{ikQ} \cdot v_{j\ell Q}$ 
    for  $ja = 1, N_{Ov}$  do
       $V_{ikja} += b_{ikQ} \cdot v_{jaQ}$ 
  for  $F_I = 1, N_F$  do
    for  $ia = 1, N_{ov}$  do
      for  $j\ell = 1, N_{Oo}$  do
        for  $k = 1, N_O$  do
           $\mathcal{V}_{iaj\ell} += V_{ikj\ell} \cdot \sigma_a^k$ 
        for  $jb = 1, N_{on_v}$  do
          for  $\ell = 1, N_O$  do
             $J23_{iajb} += V_{iaj\ell} \cdot \sigma_b^\ell$ 
             $J4_{iajb} += \mathcal{V}_{iaj\ell} \cdot \sigma_b^\ell$ 

```

5.4 Results

We will employ helium clusters as test systems to explore the accuracy and computational cost of the ALMO CIS method. With these results in hand, we are then able to use the ALMO-CIS method to examine the size-dependence of electronic spectrum associated with the $n = 2$ Rydberg levels. As already discussed, helium clusters appear likely to be suitable for the ALMO-CIS method because the high ionization potential and negative electron affinity make the discarded charge-transfer (CT) configurations high in energy relative to the retained atomic excitations. Therefore we expect CT effects to be secondary. Tests to explore this question are reported in ?? by comparing ALMO-CIS to standard CIS for medium sized He_{25} clusters. In ??, a detailed analysis of the computational performance of the code is reported, spanning clusters from 7 to 251 atoms. With these characterizations in hand, we turn in ?? to a pilot application of the ALMO-CIS method, which is reporting calculations on the size-dependence of the excitation spectrum.

Algorithm 5.4: Exchange RI Corrections

```

for  $ik = 1, N_{Oo}$  do
  for  $Q = 1, N_{aux}$  do
    for  $ja = 1, N_{Ov}$  do
       $V_{ijka} += b_{ijQ} \cdot v_{kaQ}$ 
    end for
  end for
  for  $F_I = 1, N_F$  do
    for  $ia = 1, N_{ov}$  do
      for  $j\ell = 1, N_{Oo}$  do
        for  $k = 1, N_O$  do
           $\mathcal{V}_{ijal} += V_{ijkl} \cdot \sigma_a^k$ 
        end for
        for  $jb = 1, N_{Ov}$  do
          for  $\ell = 1, N_O$  do
             $K23_{ijab} += V_{ijal} \cdot \sigma_b^\ell$ 
             $K4_{ijab} += \mathcal{V}_{ijal} \cdot \sigma_b^\ell$ 
          end for
        end for
      end for
    end for
  end for
end for

```

5.4.1 Accuracy

To determine how ALMO-CIS performs it was first applied to small 25-atom clusters which have previously been studied in depth using CIS.^{??} For the $n = 2$ manifold, 100 states are required to fully characterize the band, with the lowest 25 states having mostly superpositions of $2s$ -type orbitals and the remaining 75 being characterized as primarily $2p$ -type. In ??, we make a first comparison of the excitation spectrum calculated by full CIS against the simplified ALMO-CIS model, at a single local minimum of He_{25} . It is evident that the general form of the spectrum is entirely preserved by ALMO-CIS: a clear distinction remains between the 25 states of $2s$ character, and the 75 states of $2p$ character. This is an encouraging validation of the ALMO-CIS model.

In slightly more detail, one sees that the low energy part of the $2s$ and $2p$ state manifolds is systematically more accurately reproduced by ALMO-CIS than the high-energy part. The error, of course, is entirely due to charge transfer. It is therefore quite logical that the higher up we are in the manifold, the greater the error will be due to neglect of CT, because those discarded ionic configurations are gradually becoming separated by smaller energy differences from the state of interest. It is also reasonable that errors in the $2p$ manifold are larger than the $2s$ manifold simply because this is a higher energy window, and therefore CT corrections can contribute greater energy stabilization.

These conclusions are transferable to other geometries. As can be seen in ?? for five sample configurations of the He_{25} cluster, the ALMO-CIS errors, measured against CIS, are qualitatively consistent from geometry to geometry, and begin very small at the red end of both

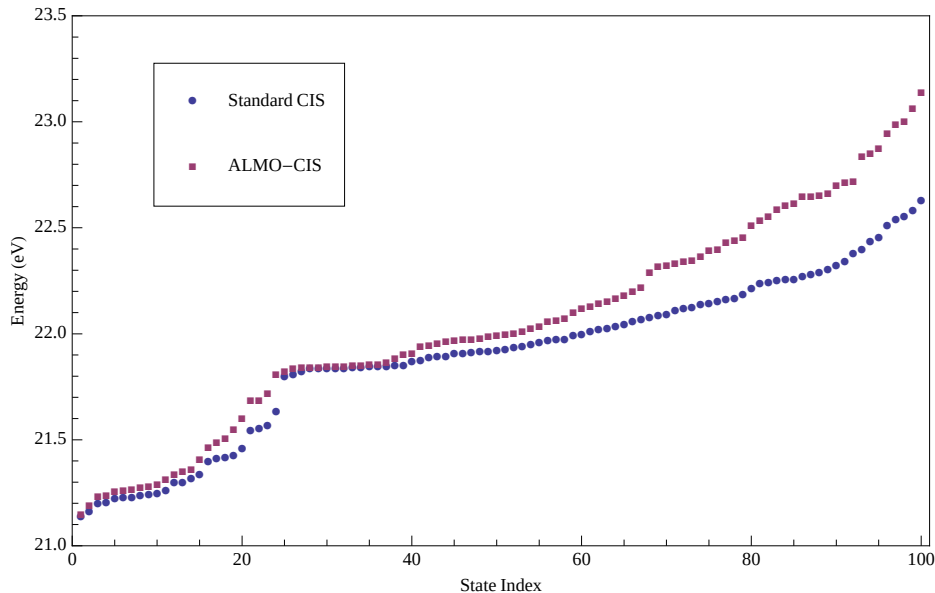


Figure 5.2: $E_{(ALMO-CIS)} - E_{(CIS)}$: This plot shows the excitation energy for a single geometry of He_{25} as a function of increasing state, evaluated by CIS and the ALMO-CIS model, for the 100 states in the $n = 2$ Rydberg manifold. He_{25} states 1-25 are predominantly of $2s$ character and states 26-100 are predominantly of p character. It is evident that ALMO-CIS is nearly identical to CIS for the lowest energy $2s$ and $2p$ states while the maximum error occurs for the states at the blue end of the excited $n = 2$ band.

the s - and p -manifolds and increase with increasing state number. The maximum error is 0.4-0.5 eV ($< 2.5\%$), which is non-negligible, but less than the standard CIS error of ≈ 1 eV. For applications, however, the most important point is that the errors all have the same sign, and increase gently and systematically from state to state. This suggests that a qualitatively correct spectrum will be obtained, with highest accuracy at the red edge, and will exaggerate the width of the blue tail of particularly the $2p$ manifold.

The spectrum for He_{25} at the CIS/6-311(2+)G level of theory was previously computed[?] using 100 randomized clusters with geometries optimized using Møller-Plesset perturbation theory (MP2/6-311G). As $1s \rightarrow 2s$ transitions are symmetry forbidden, the s states of the cluster only contribute weakly to the optical spectrum, which is dominated by a broad peak corresponding to the cluster p states. This peak has the atomic excitation energy as its lower bound, and spreads over a range of nearly 2 eV. Using these same structures for the ALMO-CIS/6-311(2+)G spectrum we obtain the results shown in ??, which are compared against the corresponding CIS spectrum.

Qualitatively, the results shown in ?? are exactly as we would have anticipated based on inspecting the CIS and ALMO-CIS excitation energies for a single configuration in ??, or the ALMO-CIS errors for 5 different configurations shown in ?. In the lowest excited states of the 25-atom clusters (red end of the spectrum), very little error is introduced by the ALMO-

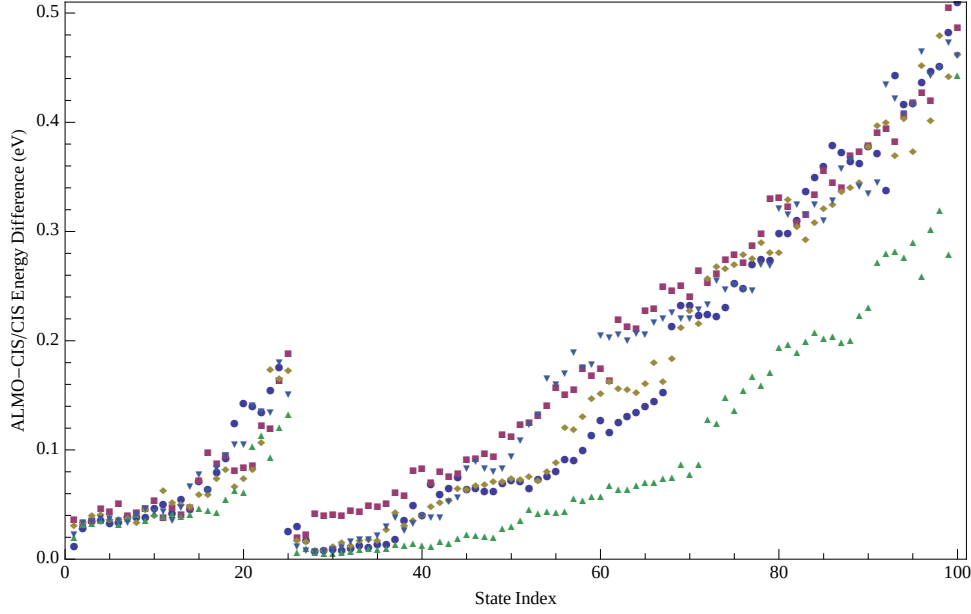


Figure 5.3: $E_{(ALMO-CIS)} - E_{(CIS)}$: This plot shows the excitation energy differences (eV) between ALMO-CIS and CIS as a function of state for 5 different He_{25} ground state geometries (ie. local minima). He_{25} states 1-25 are s -like and states 26-100 are p -like. ALMO-CIS is nearly identical to CIS for the lowest energy $2s$ and $2p$ states. The maximum errors occurs for the states at the blue end of the excited $2p$ manifold.

CIS approximation. On the other other hand, as anticipated, the blue tail of the ALMO-CIS spectrum is extended to higher energies relative to the CIS spectrum. Interestingly, there is a second effect also, which is that we see a loss of integrated oscillator strength in the $2p$ calculated by ALMO-CIS relative to CIS. It may be directly inferred that the neglected CT configurations do contribute non-negligibly to oscillator strength even in the low energy part of the $2p$ band where they contribute very little to the excitation energy.

A little more physical insight into the origin of the deviations can also be obtained from the detailed analysis of the CIS spectrum reported previously (??).[?] It was determined that the states at the higher energy edge of the spectrum tended to arise from excitations of atoms in the center of the cluster, while the low energy edge (at the atomic excitation energy) corresponded to atoms at the surface. This is primarily because the extended $2s$ and $2p$ Rydberg orbitals of a bulk atom overlap the ground state $1s$ orbital of their neighbors, giving a destabilizing Pauli repulsion. In addition to smaller energy gaps to CT states, it is reasonable to expect states dominated by these bulk contributions to be most affected by charge-transfer, because they better overlap other atoms to yield a significant matrix element for CT.

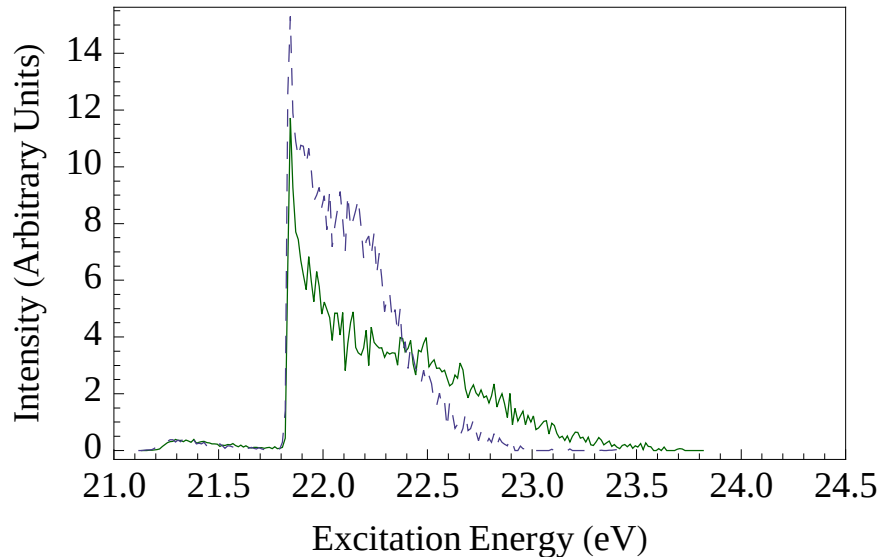


Figure 5.4: Absorption spectra calculated for a He_{25} cluster with CIS (dashed blue) and ALMO-CIS (solid green).

5.4.2 Timings

The main advantage of the ALMO-CIS method is that it can in principle have very low computational cost, $\mathcal{O}(M^3)$ as a function of cluster size for all its eigenvalues eigenstates, by contrast with the $\mathcal{O}(M^6)$ computational effort associated with obtaining all CIS eigenstates. As discussed in ?? the diagonalization step is straightforwardly third order in system size. By contrast, as already discussed in ??, quite significant effort is required to formulate an efficient algorithm for the evaluation of the matrix elements that can yield $\mathcal{O}(M^3)$ scaling of computational effort in practice. The purpose of this section is to discuss the computational effort for each component of the algorithm that is observed in practice, and thereby assess the present implementation. The timings reported in this section were obtained from calculations using an AMD Opteron 6300 series processor on a single core for helium clusters ranging in size from He_{44} to He_{251} consisting of regularly spaced atoms (4 Å).

Component	Scaling	
	Predicted	Observed
Diagonalization	M^3	3.03
Total	M^3	2.97

Table 5.1: Theoretical and actual scaling for total ALMO-CIS calculation and diagonalization

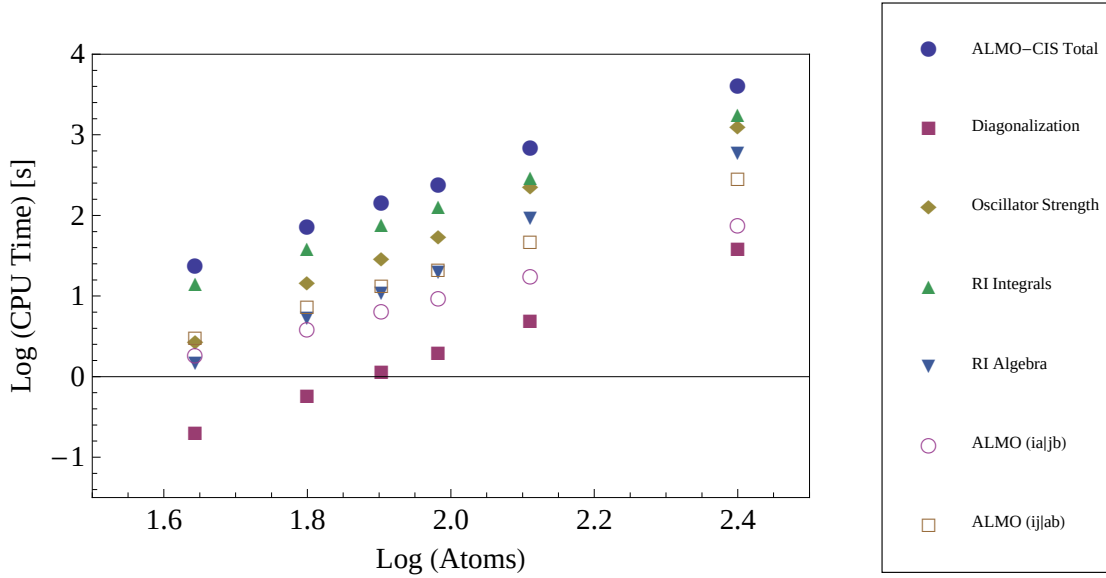


Figure 5.5: CPU timing data for ALMO-CIS. The clusters in this plot range from 44-251 atoms. The slope of the line corresponding to the total ALMO-CIS time is 2.97, indicating that the scaling is overall $\mathcal{O}(M^3)$ in computational effort, as a function of the number of atoms, M .

Overall the method is scaling as desired (??), revealing overall growth of computational effort just below $\mathcal{O}(M^3)$ in the size range from He₄₄ to He₂₅₁. In more detail, the results obtained for the relative magnitude of the ALMO-CIS components can be seen in ??. It is evident that while matrix diagonalization is strictly $\mathcal{O}(M^3)$, it has such a low prefactor that it is the least important of the major computational steps in this size regime. We will now explore some of the other components of the timings in more detail.

The costs of the formation of $J1$ and $K1$ (the unprojected direct and exchange integrals defined in Eqs. (??) and (??)) are summarized in ??. In principle, none of these steps should scale worse than $\mathcal{O}(M^2)$ with the system size, and we have designed our implementation to satisfy this criterion. $J1$ is evaluated most efficiently because selection of significant ERI's can be done already at the shell pair level, and, relative to $K1$, only one quarter as many floating point operations are required per significant ERI. On the other hand, $K1$ technically has (NN) sparsity (only a linear number significant matrix elements are required for large enough systems). However, our present shell quartet selection algorithm is based on all *fragment pairs* rather than also screening away fragment pairs that give vanishing $K1$ contributions, and therefore scales as $\mathcal{O}(M^2)$. From ??, we can see that the lower scaling implementation of the *unprojected* ALMO $J1$ and $K1$ integrals will clearly cross with diagonalization with another doubling of system size.

The costs associated with forming the RI integrals and subsequently assembling the

Component	Memory doubles	Scaling	
		Predicted	Observed
$(\phi_i \psi_\alpha \chi_\mu \chi_\nu)$	$NO nv$	$NO n^3$	2.21
$(\phi_i \psi_\alpha \phi_j \chi_\nu)$	$O^2 nv$	$O^2 n^2 v$	2.02
$(\phi_i \psi_\alpha \phi_j \psi_\beta)$	$O^2 v^2$	$O^2 nv^2$	2.00
J1 Total	M^2	M^2	2.12
$(\overline{\phi_i \chi_\mu} \psi_\alpha \chi_\nu)$	$(NO) nv$	$(NN) n^2 o$	2.78
$(\overline{\phi_i \phi_j} \psi_\alpha \chi_\nu)$	$(OO) nv$	$(OO) n^2 v$	1.95
$(\overline{\phi_i \chi_\mu} \psi_\alpha \chi_\nu)$	$(OO) v^2$	$(OO) nv^2$	2.06
K1 Total	(MM)	(MM)	2.61

Table 5.2: Theoretical and actual scaling for the formation of J1 and K1. Capital letters scale with the size of the system, lowercase letters are constant and based on the identity of the fragments, N , O , V and M are the number of basis functions, occupied orbitals, virtual orbital and system size respectively. Parentheses indicate sparse matrix scaling: these scale quadratically for small systems and linear otherwise.

correction terms are given in ???. All of these are third order steps, in our design, and most are implemented this way, as is observed in the timings. However, the exchange corrections $K23$ and $K4$ are not yet fully optimized and presently are scaling as $\mathcal{O}(M^4)$ due to an extra loop over the occupied orbitals in the current implementation. This will be optimized to $\mathcal{O}(M^3)$ scaling very shortly, because for larger systems than shown in ??, these $K23$ and $K4$ steps will surpass the most costly third order steps and dominate the computational cost. The mostly costly $\mathcal{O}(M^3)$ steps are the formation of the RI integral terms v_{ijP} and v_{ibP} as is clear from ??. Their cost could be reduced by approximately a factor of two, by reusing the $(\chi_\mu \chi_\nu | \chi_P)$ terms, and there may additional pre-factor reductions that are possible. These optimizations will not affect the overall scaling, however.

While there are still some sections of the code that can be optimized further (and this will be necessary for calculations on over 1000 atoms), we have created an algorithm which scales $\mathcal{O}(M^3)$. We have applied this code for timing purposes in calculations on as many as 251 atoms and 2761 basis functions, to obtain over 2511 excited states. We believe that excited state calculations of this scale have not been reported hitherto.

Component	Rate limiting step	Memory doubles	Scaling	
			Predicted	Observed
$(\chi^Q \chi^P)$	matrix inversion	X^2	X^3	2.84
$(\phi_i \phi_j \chi_P)$	$(\chi_\mu \chi_\nu \chi_P)$	$(NN)X$	$(NN)X$	2.74
$(\phi_i \psi_\beta \chi_P)$	$(\chi_\mu \chi_\nu \chi_P)$	$(NN)X$	$(NN)X$	2.78
$v^{PQ} v_{klQ}$		$(OO)X$	$(OO)X$	(with below)
$v_{ijP} v^{PQ} v_{klQ}$		$(OO)^2$	$(OO)^2 X$	3.37
$J23$	$v_{\underline{ia}P} v_{klP}$	$(OO)Ov$	$(OO)OvX$	3.24
$J4$	$\mathcal{V}_{\underline{iaj\ell}} \cdot \sigma_b^\ell$	$O^2 v^2$	$O^3 v^2$	3.04
$K23$	$v_{ibP} v_{\underline{j}lP}$	$(OO)Ov$	$(OO)OvX$	3.50
$K4$	$\mathcal{V}_{\underline{ijal}} \cdot \sigma_b^\ell$	$(OO)v^2$	$(OO)Ov^2$	3.90

Table 5.3: Theoretical and actual scaling for RI integrals and formation of correction terms $J23$, $J4$, $K23$, $K4$. Notation as in ??, with the addition of X for the number of auxiliary functions. Where multiple steps are involved the most costly step is indicated.

5.4.3 Size-dependence of the excitation spectrum of helium clusters

In the ground state, the superfluidic phase can be distinguished for clusters with greater than or equal to about 60 atoms,[?]. Additionally, it is predicted that clusters in the regime of ≈ 500 atoms begin displaying bulk-like properties.[?] Thus, this range of clusters containing $10^2 - 10^3$ atoms is particularly interesting as it spans this boundary region where the properties are likely to be changing. Previous theoretical studies of excited states of helium were only able to utilize clusters with ≤ 25 atoms due to the computational cost of calculating the large number of excited states required.^{???}

Therefore the size-dependence of the excitation spectrum of helium clusters is an ideal pilot application for the ALMO-CIS method. We have performed ALMO-CIS calculations on clusters of He_7 , He_{25} , and He_{63} , using the same 6-311(2+)G basis set and protocol of averaging over 100 different optimized low-energy ground state local minima of each size cluster that we used previously for CIS excitation spectra of He_7 and He_{25} .[?] The 63-atom

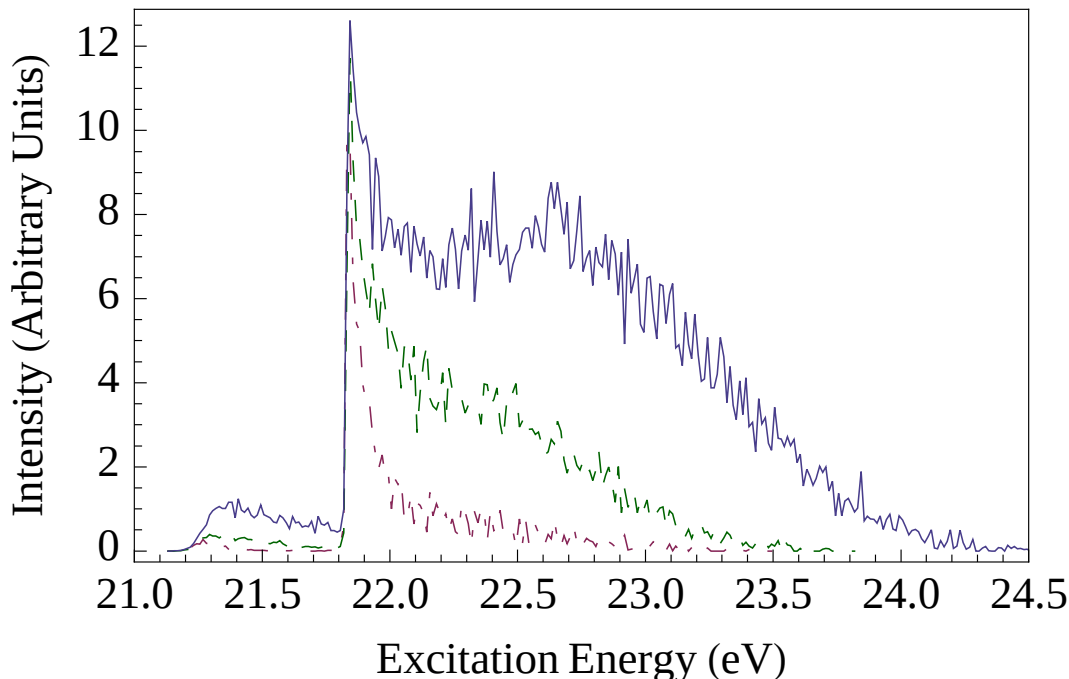


Figure 5.6: Calculated absorption spectra for He_{63} (blue solid), He_{25} (green dashed), and He_7 (purple dot-dash) with ALMO-CIS.

clusters have a diameter of roughly 20 Å, and contain 252 excited states in the $n = 2$ manifold.

The calculated spectra are shown in ???. It is immediately evident that there are indeed strong size-dependent effects on the absorption spectra. The first effect is an increase in oscillator strength contained in the band, which is simply a reflection of the number of states in the manifold increasing linearly with size of the cluster. The second effect, also related to oscillator strength, is the emergence of intensity borrowing in the $2s$ manifold as the cluster size increases. This reflects a small amount of $2p$ mixing which carries the oscillator strength.

The most interesting size-dependent effects on the absorption spectrum are in the $2p$ band where the width of the manifold increases noticeably with cluster size, and the center of gravity of the oscillator strength shifts from the red edge of the manifold in the small He_7 cluster towards the middle of the manifold by He_{63} . This is strong confirmation of the assignment of primarily “bulk” character to the states that lie towards the blue end of the manifold, versus “surface” character to the states that lie towards the red end of the manifold. Thus the effects of increasing the size of the cluster are primarily due to the increasing importance of the bulk-like states. In the 63-atom cluster, which contains the highest percentage of bulk states, a hump can be seen clearly forming near 22.7 eV that can therefore be attributed to states on the interior of the cluster.

Finally from the tests reported in ??, we recall that the main ALMO-CIS error is the

exaggerated bandwidth of the manifold, with states on the blue edge increasingly overestimated. It is possible that this effect increases with the size of the cluster, but since standard CIS cannot be reasonably run on the 63-atom clusters with enough states to explore the blue edge, we must leave this issue as an open question. The other result from our tests of ALMO-CIS vs CIS reported in ?? was that neglect of the short-range charge transfer terms certainly leads to an overall underestimate of oscillator strength, which likely becomes more important towards the blue edge as CT contributions become less negligible (though surely still small).

5.5 Conclusions

In computations on homogenous atomic and molecular clusters, large numbers of excited states are required to describe the broadening of atomic or molecular excitations into bands associated with cluster, which gradually evolve towards the bulk limit. This need for many states makes conventional excited state methods particularly costly for such applications. To address this problem, we have developed a physically motivated local variant of configuration interaction with single substitutions (CIS), which retains only intra-fragment singles. All inter-fragment singles are discarded. We use the absolutely localized molecular orbitals (ALMO's) to describe the occupied and virtual levels of the cluster, and thus term our fragment-localized method as ALMO-CIS. ALMO-CIS is physically appropriate for homogeneous clusters composed of atoms or molecules with high ionization potentials and low or negative electron affinities, as this combination minimizes the importance of the neglected charge-transfer terms.

The main conclusions of our work developing, implementing, testing and applying the ALMO-CIS model are as follows.

1. **Formal scaling.** Complete construction and diagonalization of the ALMO-CIS hamiltonian for all eigenvalues and eigenstates scales no worse than $\mathcal{O}(M^3)$ with the number of atoms or molecules, M , in the cluster. By contrast, conventional CIS for all states scales as $\mathcal{O}(M^6)$.
2. **Accuracy for helium cluster absorption spectra.** Testing against full CIS for He_{25} absorption spectra shows good qualitative agreement for the full spectrum, and excellent quantitative agreement at the red edge of the $2s$ and $2p$ manifolds. ALMO-CIS systematically overestimates the excitation energies, with the systematic error gradually increasing to its largest values at the blue edge of the $2p$ manifold.
3. **Numerical performance.** We have successfully formulated and implemented an algorithm that is operationally $\mathcal{O}(M^3)$ up to the largest cluster tested (251 atoms), and permits these calculations with over 2500 basis functions and over 10000 calculated states on workstation class computers. Further optimization is clearly possible and is underway.

4. **Application to helium cluster absorption spectra.** As a pilot application we evaluated the size-dependence of absorption spectra of helium clusters, and observed a variety of interesting effects that are qualitatively similar to trends seen experimentally.
5. **Further possibilities.** The ALMO-CIS model could benefit from a variety of improvements. Most important is some type of diagnostic or correction for the role of the neglected charge transfer configurations. Such differences also potentially yield physical insight into the role of CT in excited states. Also very interesting is the extension to non-homogenous clusters, and clusters that are open shell. Finally dynamic correlation is missing, and might be reincorporated either by extending the model to time-dependent density functional theory, or incorporating wave-function based correlation.

Appendix A

Additional Details for ALMO-CIS

A.1 Derivation of Matrix Elements

We consider each case on the right hand side of the ALMO-CIS equations.

$$\langle \Phi_{.j}^b | \hat{H} | \Phi_{.a}^i \rangle t_{.i}^a = \omega_{CIS} \langle \Phi_{.j}^b | \Phi_{.a}^i \rangle t_{.i}^a \quad (\text{A.1})$$

Using standard definitions of the Fock operator

$$f_{.q}^p = \langle \phi^p | \hat{f} | \phi_q \rangle = \langle \phi^p | \hat{h} | \phi_q \rangle + \sum_{k \in \{\Phi_0\}} \langle \phi^p \phi^k || \phi_q \phi_k \rangle \quad (\text{A.2})$$

and the ground state energy

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \sum_{k \in \{\Phi_0\}} \langle \phi^k | \hat{h} | \phi_k \rangle + \frac{1}{2} \sum_{k,l \in \{\Phi_0\}} \langle \phi^k \phi^l || \phi_k \phi_l \rangle \quad (\text{A.3})$$

1. $i \neq j$ and $a \neq b$

$$\langle \Phi_{.j}^b | \hat{H} | \Phi_{.a}^i \rangle = \langle \phi^i \phi^b || \phi_a \phi_j \rangle = \Pi_{.ja}^{ib} \quad (\text{A.4})$$

2. $i = j$ and $a \neq b$

$$\begin{aligned} \langle \Phi_{.i}^b | \hat{H} | \Phi_{.a}^i \rangle &= \langle \phi^b | \hat{h} | \phi_a \rangle + \sum_{k \in \{\Phi_0, \neg \phi_i\}} \langle \phi^b \phi^k || \phi_a \phi_k \rangle \\ &= \langle \phi^b | \hat{h} | \phi_a \rangle + \sum_{k \in \{\Phi_0\}} \langle \phi^b \phi^k || \phi_a \phi_k \rangle - \langle \phi^b \phi^i || \phi_a \phi_i \rangle \\ &= \langle \phi^b | \hat{f} | \phi_a \rangle - \langle \phi^b \phi^i || \phi_a \phi_i \rangle = f_{.a}^b - \Pi_{.ai}^{bi} \end{aligned} \quad (\text{A.5})$$

3. $i \neq j$ and $a = b$

$$\begin{aligned}
\langle \Phi_{.j}^a | \hat{H} | \Phi_{.a}^i \rangle &= -\langle \phi^i | \hat{h} | \phi_j \rangle - \sum_{k \in \{\Phi_0, a\}} \langle \phi^i \phi^k | | \phi_j \phi_k \rangle \\
&= -\langle \phi^i | \hat{h} | \phi_j \rangle - \sum_{k \in \{\Phi_0\}} \langle \phi^i \phi^k | | \phi_j \phi_k \rangle - \langle \phi^i \phi^a | | \phi_j \phi_a \rangle \\
&= -\langle \phi^i | \hat{f} | \phi_j \rangle - \langle \phi^i \phi^a | | \phi_j \phi_a \rangle = -f_{.j}^i - \Pi_{.ja}^{ia}
\end{aligned} \tag{A.6}$$

Note negative sign appears due to placing the determinants in maximum coincidence because of electron anti-symmetry:

$$\begin{aligned}
| \Phi_{.a}^i \rangle &= | \phi_1 \dots \phi_a \phi_j \dots \phi_n \rangle \\
\Rightarrow | \Phi_{.a}^j \rangle &= | \phi_1 \dots \phi_i \phi_a \dots \phi_n \rangle = - | \phi_1 \dots \phi_a \phi_i \dots \phi_n \rangle.
\end{aligned} \tag{A.7}$$

4. $i = j$ and $a = b$

$$\begin{aligned}
\langle \Phi_{.i}^a | \hat{H} | \Phi_{.a}^i \rangle &= \sum_{k \in \{\Phi_0, -i, a\}} \langle \phi^k | \hat{h} | \phi_k \rangle + \frac{1}{2} \sum_{k, l \in \{\Phi_0, -i, a\}} \langle \phi^k \phi^l | | \phi_k \phi_l \rangle \\
&= \sum_{k \in \{\Phi_0\}} \langle \phi^k | \hat{h} | \phi_k \rangle - \langle \phi^i | \hat{h} | \phi_i \rangle + \langle \phi^a | \hat{h} | \phi_a \rangle + \frac{1}{2} \sum_{k, l \in \{\Phi_0\}} \langle \phi^k \phi^l | | \phi_k \phi_l \rangle \\
&\quad + \sum_{k \in \{\Phi_0\}} \left(\langle \phi^a \phi^k | | \phi_a \phi_k \rangle - \langle \phi^i \phi^k | | \phi_i \phi_k \rangle \right) - \langle \phi^i \phi^a | | \phi_i \phi_a \rangle \\
&= \sum_{k \in \{\Phi_0\}} \left(\langle \phi^k | \hat{h} | \phi_k \rangle + \frac{1}{2} \langle \phi^k \phi^l | | \phi_k \phi_l \rangle \right) + \\
&\quad \langle \phi^a | \hat{h} | \phi_a \rangle + \sum_{k \in \{\Phi_0\}} \langle \phi^a \phi^k | | \phi_a \phi_k \rangle - \\
&\quad \langle \phi^i | \hat{h} | \phi_i \rangle - \sum_{k \in \{\Phi_0\}} \langle \phi^i \phi^k | | \phi_i \phi_k \rangle - \langle \phi^i \phi^a | | \phi_i \phi_a \rangle \\
&= E_0 + f_{.a}^a - f_{.i}^i - \Pi_{.ia}^{ia}
\end{aligned} \tag{A.8}$$

Combining all cases and making use of the two-electron integral permutational symmetry we obtain

$$\langle \Phi_{.j}^b | \hat{H} | \Phi_{.a}^i \rangle = E_0 \delta_{.a}^b \delta_{.j}^i + f_{.a}^b \delta_{.j}^i - f_{.j}^i \delta_{.a}^b + \Pi_{.aj}^{ib} \tag{A.9}$$

Noting that for real functions

$$\begin{aligned}
\langle \phi^p \phi^q | | \phi_r \phi_s \rangle &= \langle \phi^q \phi^p | | \phi_s \phi_r \rangle = -\langle \phi^q \phi^p | | \phi_r \phi_s \rangle = -\langle \phi^p \phi^q | | \phi_s \phi_r \rangle \\
&= \langle \phi^r \phi^s | | \phi_p \phi_q \rangle = \langle \phi^s \phi^r | | \phi_q \phi_p \rangle = -\langle \phi^r \phi^s | | \phi_q \phi_p \rangle = -\langle \phi^s \phi^r | | \phi_p \phi_q \rangle
\end{aligned} \tag{A.10}$$

A.2 Resolution of the Identity Corrections to the two electron integrals

While the primary components of the two electron integrals are evaluated exactly, they must be corrected due to the non-orthogonal ALMOs. Here the derivation of the integral corrections which are evaluated with using the RI approximation are shown for the coulomb-type integrals.

A.2.1 Coulomb integrals

$$(\phi_i \phi_a | \phi_j \phi_b) = N^2 \left\{ (\phi_i \psi_\alpha | \phi_j \psi_\beta) - 2 (\phi_i \psi_\alpha | \overline{\phi_j \phi_k}) (\phi^k | \psi_\beta) + (\overline{\phi_i \phi_k} | \overline{\phi_j \phi_l}) (\phi^k | \psi_\alpha) (\phi^l | \psi_\beta) \right\} \quad (\text{A.11})$$

$$J = N^2 (J1 - 2 \cdot J23 + J4) \quad (\text{A.12})$$

1. $J23$

$$(\phi_i \psi_\alpha | \overline{\phi_j \phi_k}) (\phi^k | \psi_\beta) = (\phi_i \psi_\alpha | \chi_P) (\chi^P | \chi^Q) (\chi_Q | \overline{\phi_j \phi_k}) (\phi^k | \psi_\beta) \\ \implies J23 = v_{i\alpha}^P S^{PQ} v_{jk}^Q \sigma_\beta^k \quad (\text{A.13})$$

2. $J4$

$$(\overline{\phi_i \phi_k} | \overline{\phi_j \phi_l}) (\phi^k | \psi_\alpha) (\phi^l | \psi_\beta) = (\phi^k | \psi_\alpha) (\overline{\phi_i \phi_k} | \chi_P) (\chi^P | \chi^Q) (\chi_Q | \overline{\phi_j \phi_l}) (\phi^k | \psi_\beta) \\ \implies J4 = \sigma_\alpha^k v_{ik}^P S^{PQ} v_{jl}^Q \sigma_\beta^l \quad (\text{A.14})$$

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