

**AN INVESTIGATION OF THE ENERGY LEVELS OF THE PT^{2+} ION USING
MULTI-REFERENCE SPIN-ORBIT CONFIGURATION
INTERACTION THEORY**

by

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THESIS

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DEDICATION

This thesis is dedicated to my parents, my teachers, and mentors who have brought me to this point over the course of 23 years, and The Almighty God above all else.

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This project sought to obtain more info for NIST's Atomic Spectra Database (ASD) by generating energies of the Pt^{2+} ion, whose current data is sparse. We used the COLUMBUS suite of codes to perform this task and calculated the energy levels and transition moments of Pt^{2+} under various symmetries using multi-reference spin-orbit configuration interaction calculations.

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CHAPTER ONE: INTRODUCTION

One aspect of atoms and ions that is important for computational and experimental chemists alike is their energetics. The energy levels and ionization energies can provide insight into the reactivity and stability of compounds of interest. A recent review of these theoretical and experimental properties is given by Safronova et al.¹ The National Institute of Standards and Technology (NIST) has an Atomic Spectra Database (ASD) providing spectral information about many atoms and their ions.² This gives us a record of the ground state and multiple excited state energies for these species, as well as the configuration, term symbol, J-value, % uncertainty, Landé-g factor, % leading contributing term, and reference for those states.

These values can be obtained via experimental methods or theoretical calculations. We have computational resources available to us to create codes and submit calculations to generate our own data. For this project, computational support was provided by the Texas Advanced Computing Center's Stampede2 supercomputer through The University of Texas at Austin, and the Arc (formerly Shamu) High Performance Computing cluster, provided by the University of Texas at San Antonio.

CHAPTER TWO: BACKGROUND

To understand platinum, its spectral fingerprint, and its interactions with other atoms to form complexes and catalyze reactions, we rely on databases for information about its states and energies. Currently, the Pt^{2+} ion has little data available to NIST, having only a ground state configuration and a theoretical ionization energy.

According to Ryabtsev³, there is a proposed table of configurations with associated energies for Pt^{2+} , but it has yet to be verified and released by the ASD. This can be seen in Table 1 of Appendix A. While Ryabtsev and their team generated that list by analyzing experimental spectra from spectrographs of hollow cathode emissions and cosmic observations, we intend to calculate a new list of configurations and energies via computational methods. Filling in this data would further highlight the energetic trends Group 10 transition metals have and possibly lend insight into platinum's catalytic behavior.

CHAPTER THREE: THEORY AND COMPUTATIONAL METHODS

When studying atoms and their ions, there are different ways to approach an understanding of the energies of these species and their electron shells. It is generally accepted that the energy of a quantum mechanical system is given by the *time-independent Schrödinger equation*,

$$\hat{H}\Psi = E\Psi \quad (1)$$

which tells us that if we know the *wavefunction* Ψ and an appropriate *Hamiltonian operator* \hat{H} to apply to it, we can get an energy eigenvalue E as an observable. For atoms and ions, the Hamiltonian operator has three component operators, seen as

$$\hat{H} = \hat{H}^0 + \hat{H}_{\text{rep}} + \hat{H}_{\text{S.O.}} \quad (2)$$

The first component, \hat{H}^0 , is the hydrogen-like Hamiltonian that describes the kinetic energy, given by the operator \hat{T} , of N electrons, and the potential energy, given by the operator \hat{V} , of Coulombic attraction between an electron and the nucleus of Z charge, where Z is the number of protons. Applying this component alone in a calculation yields the energy of the electron configuration for the species of interest in a *time-independent electron approximation*. These operators are defined below as

$$\hat{H}^0 = \hat{T} + \hat{V} \quad (3)$$

$$\hat{T} = \sum_{i=1}^N \frac{-\hbar^2}{2m_i} \nabla_i^2 = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (\text{in atomic units}) \quad (4)$$

$$\hat{V} = \sum_{i=1}^N \frac{-Ze^2}{4\pi\epsilon_0 r_i} = \sum_{i=1}^N \frac{-Z}{r_i} \quad (\text{in atomic units}) \quad (5)$$

The second component, \hat{H}_{rep} , describes the potential energy of repulsion between electrons.

Applying these first two components yields the energies designated by *term symbols* that can arise from a given configuration. This is written as

$$\hat{H}_{\text{rep}} = \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} = \sum_i \sum_{j>i} \frac{1}{r_{ij}} \text{ (in atomic units)} \quad (6)$$

The third component, $\hat{H}_{\text{S.O.}}$, includes relativistic spin-orbit coupling considerations for the electrons. Applying all three of these components yields the energies of the individual *levels* that arise from each term symbol. This is written as

$$\hat{H}_{\text{S.O.}} = \sum_{i=1}^N \frac{1}{2m_i^2 c^2 r_i} \frac{dV_i(r_i)}{dr_i} \hat{L}_i \cdot \hat{S}_i = \sum_{i=1}^N \xi_i(r_i) \hat{L}_i \cdot \hat{S}_i \quad (7)$$

where c is the speed of light, \hat{L}_i is the orbital angular momentum operator, and \hat{S}_i is the spin angular momentum operator. We can see the refinement of these energy calculations in the figure below

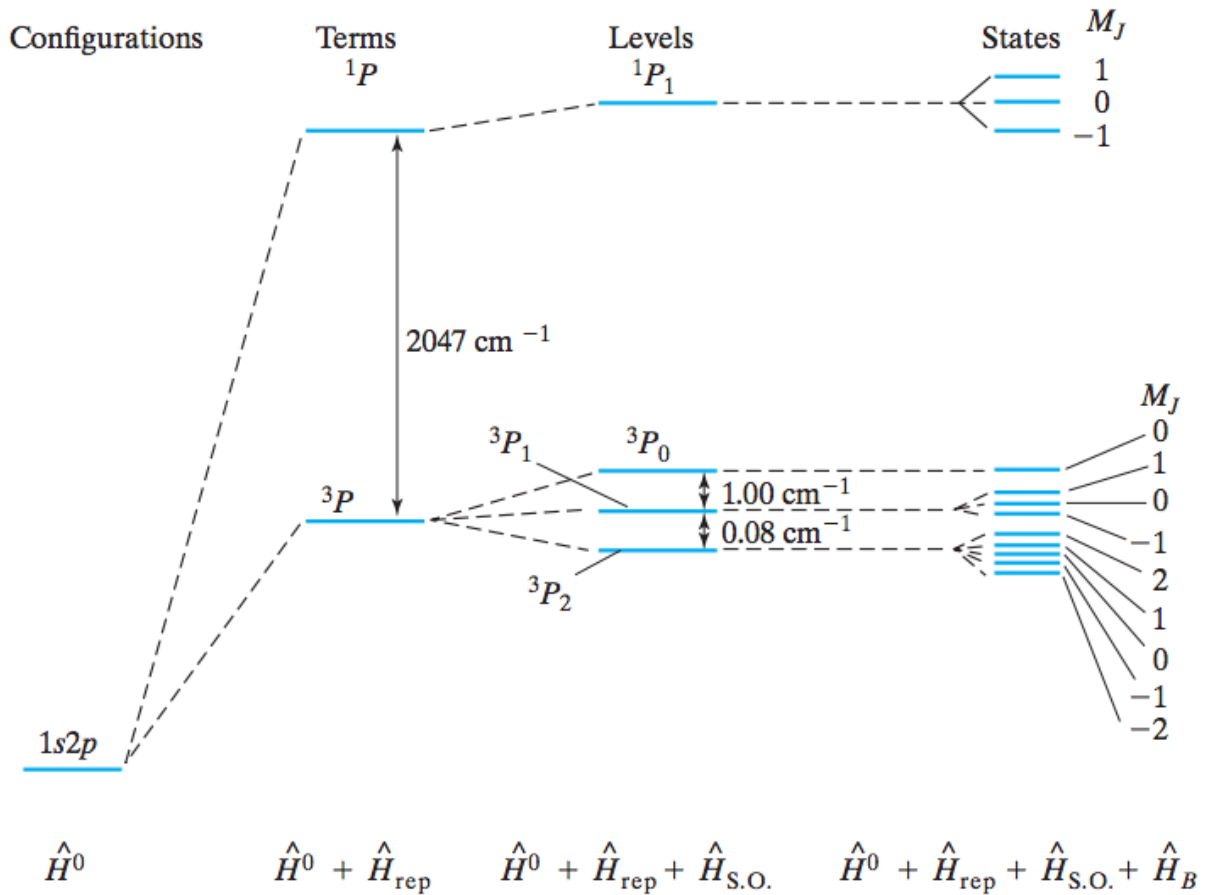


Figure 1: Energy Splitting of Helium 1s2p Configuration due to Inclusion of Hamiltonian Terms⁴

The *Zeeman* effects of \hat{H}_B , due to an applied magnetic field, are not considered it for this project. We generate term symbols by considering the four quantum numbers that each electron possesses. The first is the principal quantum number $n = 1, 2, \dots$, which describes the electron shell, given by the row number on the periodic table. The second is the angular quantum number $l = 0, 1, \dots, n-1$, which describes the electron subshell, and is given by the position on the periodic table. These correspond to orbital shapes, where $l = 0$ is an s orbital, $l = 1$ is a p orbital, and so on, indicating the number of angular nodes on the orbital. These two numbers make up the general form of an electron configuration $n l^x$. The third is the magnetic quantum number $m_l = -l, -(l-1), \dots, 0, \dots, (l-1), l$, which describes the specific orbital's Cartesian orientation in 3D space. The fourth is the spin quantum number $m_s = \pm 1/2$, which indicates the electron's spin ($1/2$ for "up" spin, $-1/2$ for "down" spin). Taking a vector sum of the last two quantum numbers yields **L** and **S** quantities that help define the term symbol. **L** is the total orbital angular momentum for the system and is defined as

$$\mathbf{L} = \sum_i l_i \quad (8)$$

where each **L** value has a specific corresponding letter, similar to the letter designations for the angular quantum number. **L** = 0 corresponds to S, **L** = 1 corresponds to P, and so on. **S** is the total spin angular momentum for the system and is defined as

$$\mathbf{S} = \sum_i s_i \quad (9)$$

This number is used in the expression $2\mathbf{S} + 1$ to define the *multiplicity* of the term. When this value is equal to 1, that is called a *singlet* term. When it is two, we call this a *doublet*, and so on.

The term symbol is of the form

$$^{2\mathbf{S}+1}\mathbf{L} \quad (10)$$

In a given configuration, the fully occupied “closed” shells will have $\mathbf{L} = 0$ and $\mathbf{S} = 1$ (yielding $2S + 1 = 0$) and thus will contribute $^1\mathbf{S}$ to the term. Therefore, we need only consider partially filled “open” shells for our term symbol. Since the electron(s) can be in orbitals of different orientations and of different spins, multiple term symbols are possible. The ground state term symbol will maximize the multiplicity, then maximize the \mathbf{L} value. We will use these angular momentum values from the term symbols to consider spin-orbit coupling.

The wavefunction contains all the spatial and spin information for the system. To be an eigenfunction of the equation, it is required to be single-valued, continuous, quadratically integrable, and its first derivative must be continuous. It is also expected to be antisymmetric with respect to an exchange of particles. A solution to this equation is thus considered to be a *well-behaved* wavefunction.

The mathematics behind solving for these solutions involves many complex integrals. To condense these expressions, we will use Dirac notation, which is written as

$$\int_{-\infty}^{\infty} \Psi^* \Psi d\tau = \langle \Psi | \Psi \rangle \quad (11)$$

$$\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau = \langle \Psi | \hat{A} | \Psi \rangle \quad (12)$$

The Ψ^* notation represents the complex conjugate of the wavefunction. The Hamiltonian operator is considered to be a *Hermitian* operator, which establishes that

$$\langle \Psi_i | \hat{H} | \Psi_j \rangle = \langle \Psi_j | \hat{H} | \Psi_i \rangle^* \quad (13)$$

A consequence of being Hermitian is that the eigenvalues of this operator are real-valued since the energy levels of chemical species are observables. To determine the energy from a given wavefunction and Hamiltonian, we calculate the integral

$$\langle E \rangle_k = \frac{\langle \Psi_k | \hat{H} | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle} = \langle \Psi_k | \hat{H} | \Psi_k \rangle \quad (\text{since } \Psi_k \text{ is normalized}) \quad (14)$$

This seems straightforward enough, but actually obeys the *Variational Principle*, which states that the integral above is an upper-bound approximation to the true energy of the system. Thus, we must fine tune the elements of this integral to obtain as low of an energy as possible. The Hamiltonian will typically be unaltered, since we have nearly all possible energy contributions considered. This leaves us with *trial* wavefunctions as the subject of optimization.

The trial wavefunction Φ can be represented as a linear combination of known eigenfunctions in the same space. This can be determined by computing a *Slater determinant*, which is a collection of hydrogen-like spatial functions (ϕ orbitals) and spin functions (α or β). For a system of N electrons, this is defined as

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \cdots & \phi_{N/2}(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \cdots & \phi_{N/2}(2)\alpha(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N)\alpha(N) & \phi_1(N)\beta(N) & \cdots & \phi_{N/2}(N)\alpha(N) \end{vmatrix} \quad (15)$$

However, each spatial function can be defined by a linear combination of *basis functions*

$$\phi_i = \sum_p c_{ip} \chi_p \quad (16)$$

where $\{c_{ip}\}$ is the set of coefficients for the set of basis functions $\{\chi_p\}$. Orthonormality is a condition for orbitals defined as

$$\langle \phi_i | \phi_j \rangle = 1 \text{ for } i = j \text{ and } \langle \phi_i | \phi_j \rangle = 0 \text{ for } i \neq j \quad (17)$$

While the coefficients can be solved for analytically, the basis functions can come from one of two assumed types of functions – Slater Type Orbitals (STOs) and Gaussian Type Orbitals or Functions (GTOs or GTFs). Slater Type Orbitals are of the form

$$\chi \propto r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi) \quad (18)$$

for electron-nucleus distance r , quantum numbers n , l , and m , and spherical harmonic functions $Y_{lm}(\theta, \phi)$. Gaussian Type Orbitals are of the form

$$\chi \propto r^{(2n-2-l)} e^{-\zeta r^2} Y_{lm}(\theta, \phi) \quad (19)$$

To calculate the energy of an atom or ion using these theoretical principles, we will use *ab initio* calculations as these do not rely on experimental data. The most basic of these types of calculations is the Hartree-Fock Self Consistent Field method (SCF). This is a neat and simple calculation, yet ineffective for the large Pt^{2+} system as it is nonrelativistic, meaning it does not include the $\widehat{H}_{\text{S.O.}}$ term in the Hamiltonian and does not account for *correlation* energy. This is defined as the difference between the exact nonrelativistic energy for the system and the calculated Hartree-Fock energy.⁴

$$E_{\text{corr}} \equiv E_{\text{nonrel}} - E_{\text{HF}} \quad (20)$$

To account for this and minimize the difference, configuration interaction (CI) calculations can be performed. The premise behind these is to choose a basis set $\{\chi_i\}$, solve for its coefficients to determine the one-electron occupied and unoccupied (virtual) orbitals (ϕ_i 's), compute Slater determinant(s) to generate many-electron Configuration State Functions (CSFs), written as Φ_i 's, express the true wavefunction as a linear combination of these CSFs,

$$\psi = \sum_i \varepsilon_i \Phi_i \quad (21)$$

solve for the energy, and solve for their coefficients variationally. The CSFs include excitations of electrons from occupied to virtual. The least computationally demanding of these CI calculations is to have only single excitations, known as CIS. To further simplify computations, we can construct the true wavefunction by optimizing the orbital coefficients for the CSFs as well. This means instead of separately solving for the basis set coefficients, we can variationally solve for all the coefficients by expanding the determinants and writing the orbitals as linear combinations of basis functions. This is known as the multiconfiguration SCF (MCSCF) method. We can use this method to construct the wavefunction used in our CI calculations, rather than

starting off with SCF wavefunctions.⁵ This wavefunction defines the reference CSFs, and we can perform single (or higher) excitations of electrons out of the occupied orbitals of this CSF into virtual orbitals to generate more CSFs, colloquially referred to as configs in our procedures. For single excitations, this method is known as multireference CIS (MRCIS). The supporting theory detailed here can be found in Levine's *Quantum Chemistry*.⁴ We shall now explore the different codes that use MRCIS and other methods and theories to calculate energies and electric dipole transition moments for Pt^{2+} .

“atomic” program

One of the programs employed in generating energetic data is the **atomic** code. This program uses Russell-Saunders coupling, often called LS-coupling. LS-coupling refers to the combination of the orbital angular momentum and spin angular momentum values that we obtained from (8) and (9) for term symbols. Under this, the energy from electron repulsion is assumed to be greater than the energy from electrons’ spin-orbit interaction⁶, so we take a vector sum of the total orbital and spin angular momenta, as seen in the figure below, to obtain a **J** value that splits the term symbol into levels.

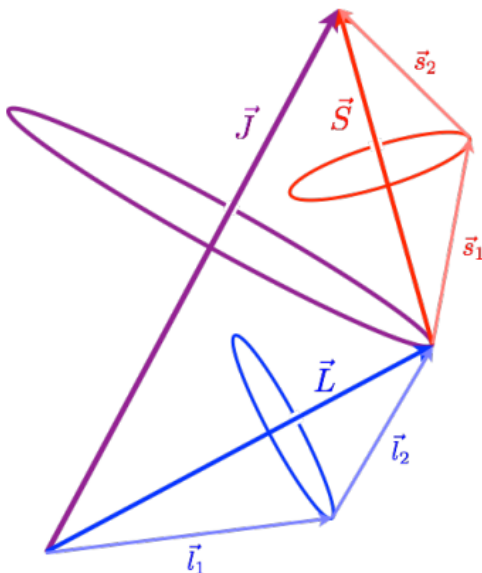


Figure 2: LS-coupling Vector Diagram

Mathematically, $\mathbf{J} = \mathbf{L} + \mathbf{S}, \mathbf{L} + \mathbf{S} - 1, \dots, |\mathbf{L} - \mathbf{S}|$. Ground state levels will minimize this **J**. This approximation is most valid with lighter systems. The program runs iterations of SCF calculations on basis sets of our choosing.⁷ It has options for STO or GTO basis inputs, retrieved from a library file called **basis.lib**. Although the Hamiltonian is nonrelativistic, the code for **atomic** introduces relativistic effects by including averaged relativistic effective core potentials

(ARECPs) retrieved from a library file called **potent.lib**. The purpose of these is to further reduce the complexity of the calculation by treating the core electrons with the nucleus as an *effective core* that the valence electrons can “feel”. This is done by defining the relativistic effective core potential as

$$U^{\text{RECP}} = U_{\text{LJ}}^{\text{RECP}}(r) + \sum_{l=0}^L \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} \sum_{m=-j}^j [U_{\text{lj}}^{\text{RECP}}(r) - U_{\text{Lj}}^{\text{RECP}}(r)] |ljm\rangle\langle ljm| \quad (22)$$

for the projection operator $|ljm\rangle\langle ljm|$.⁸ $U_{\text{Lj}}^{\text{RECP}}(r)$ is considered to be a *residual* potential with L and J ideally being at least 1 greater than the largest angular quantum number l for the core electrons^{8,9}, and $U_{\text{lj}}^{\text{RECP}}(r)$ is the nonrelativistic core potential derived from individual pseudospinors with quantum numbers l and j . From this, an averaged relativistic effective core potential can be defined as

$$U^{\text{ARECP}} = U_{\text{L}}^{\text{ARECP}}(r) + \sum_{l=0}^L \sum_{m=-l}^l [U_{\text{l}}^{\text{ARECP}}(r) - U_{\text{L}}^{\text{ARECP}}(r)] |lm\rangle\langle lm| \quad (23)$$

$$U_{\text{l}}^{\text{ARECP}} = \frac{1}{2l+1} [lU_{\text{l},l-1/2}^{\text{RECP}}(r) + (l+1)U_{\text{l},l+1/2}^{\text{RECP}}(r)] \quad (24)$$

These potentials introduce the relativistic effects not associated with spin-orbit coupling, namely the so-called mass-velocity and Darwin relativistic effects. The inclusion of this into the Hamiltonian can be written as a spin-orbit-like term that leads to the spin-orbit operator of the form seen in Eq. (7).

$$\hat{H}^{\text{SO}} = U^{\text{RECP}} - U^{\text{ARECP}} \quad (25)$$

The use of U^{ARECP} reduces the amount of basis functions needed for the calculation. One final component that goes into the input is a set of vector coupling coefficients required to identify the pure state corresponding to the term symbol for the given configuration, retrieved from a library file called **atosym.lib**. This makes for a typically quick calculation on valence electrons that

yields an energy approximation of our system under purely LS-coupling considerations. This program was run on Arc using GTOs.⁹ Example input can be seen in Appendix B.

“jjatom” program

The **jjatom** program has an algorithm similar to that of **atomic** but has the primary distinction of using jj-coupling for its spin-orbit considerations. Under this theory, the energy from the electrons’ spin-orbit interactions greater than or equal to the energy from their repulsion⁶, so we must first couple their individual orbital and spin angular momenta to obtain *j-values*. From there, we can take a vector sum of all the *j-values*, as depicted below, to obtain the aforementioned **J** value.

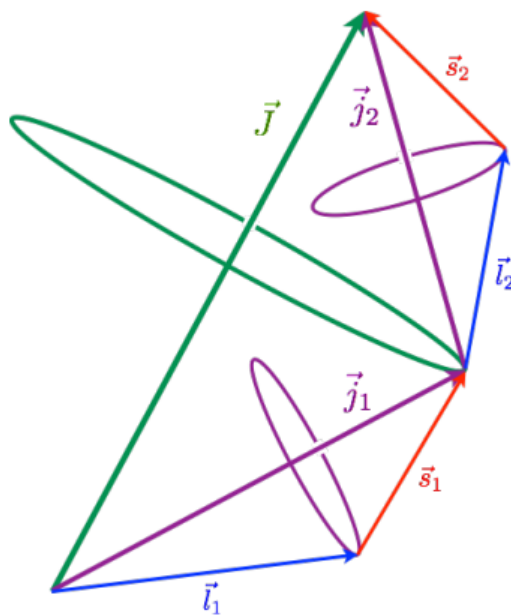


Figure 3: jj-coupling Vector Diagram

This approximation is more accurate for heavier atoms and is inherently relativistic. Due to higher nuclear charges for heavier elements, core electrons become more tightly bound, increasing their velocity and imposing relativistic effects on valence electrons.¹⁰ The effects considered in these calculations include *radial contraction and energetic stabilization of j*, where $j = l - \frac{1}{2}$ for $l > 0$, and *radial expansion and energetic destabilization of j*, where $j = l + \frac{1}{2}$.¹⁰ This induces relativistic spin-orbit splitting of the $l > 0$ orbitals into sublevels with higher energies.

The basis functions used for this program are called two-component atomic spinor (TCAS) basis functions. They too can be STOs or GTOs, retrieved from a library file called **BASIS.dat**. Their relativistic form is based on the splitting of the nonrelativistic orbital-like basis functions. This is determined from the relativistic quantum number k , defined as $k = l$ for $0 < l = j - \frac{1}{2}$ and $k = -(l + 1)$ for $l = j + \frac{1}{2}$, yielding l_j orbitals. The basis functions with positive k -values are lower in energy and written with * superscripts (e.g., $p_{1/2}^*$) and those with negative k -values are higher in energy and written without * superscripts (e.g., $p_{1/2}$). This program also uses relativistic effective core potentials (RECPs), retrieved from a library file called **RECP.dat**. Another difference from **atomic** is that the vector coupling coefficients are either generated by the code based on open-shell/closed-shell occupancies in the electron configuration or are placed in for specific **J** states. Running this program applies the calculations to valence electrons to obtain an energy approximation of our system under purely jj-coupling considerations. This program was also run on Arc using GTOs. Example input can be found in Appendix B.

COLUMBUS

To implement MRCIS calculations with spin-orbit effects, a sequence of programs is implemented in order to perform the optimization described in theory. The Hamiltonian used for this procedure includes not only the $\hat{H}_{\text{S.O.}}$ operator for spin-orbit effects, but also ARECPs. The spin-orbit operator includes the RECPs of the form¹¹

$$\hat{H}_{\text{S.O.}} = \sum_l \hat{O}_l \xi_l(r) \hat{\mathbf{l}} \cdot \hat{\mathbf{s}} \hat{O}_l \quad (26)$$

$$\hat{O}_l = \sum_{m_l} |lm_l\rangle \langle lm_l| \quad (27)$$

$$\xi_l(r) = 2\Delta U_l^{\text{RECP}}(r)/(2l + 1) \quad (28)$$

Once we include this into our Hamiltonian, spatial symmetry and spin angular momentum operators no longer commute with it and we do not obtain pure \mathbf{J} states. However, the symmetry operators acting on space and spin coordinates do commute, forming a mathematical group called the *double group*.¹¹ This is similar to a point-group, except it defines the operation R as a non-identity 2π rotation, thus doubling the number of operations and providing representations for electronic states with half-integral momenta (e.g. $\mathbf{J} = n + 1/2$ for integer n).¹² We then use basis functions that transform according to the irreducible representations (irreps) of these double groups. The Pt^{2+} system has an even number of electrons, so the Hamiltonian can be reduced over the four irreps A_1' , A_2' , B_1' , and B_2' , which are of the C_{2v}' double group. These are the symmetry types we will use for these calculations, with the exception of B_1' , as it is degenerate with B_2' in atoms. The codes also include factors to make the elements of the Hamiltonian matrix real-valued, further simplifying the complexity of the calculations.¹¹

The basis functions used are *generally contracted valence-core/valence* (gcv-c/v) GTOs, formed by using RECPs to distinguish inner-core electrons from outer core & valence electrons⁹

Next in the MRCIS procedure is to run **argos**, which calculates the Hamiltonian integrals of our basis set

$$\{\langle \hat{H} \rangle\} = \cup_{p=1}^m \langle \chi_p | \hat{H} | \chi_p \rangle \quad (29)$$

and yields an output file called **aoints1** for 1-electron atomic orbitals (AOs) and **aoints2** for 2-electron atomic orbitals. Afterwards, the **mcdrft** and **mcuft** programs prepare for the MCSCF step by generating coefficients $\{c_p\}$ for the basis set (configs) and coupling coefficients for the occupied atomic orbitals.

Then, we perform an MCSCF calculation on our basis functions to generate molecular orbitals (MOs) by running the **mcscf** program

$$\phi_i = \sum_{p=1}^m c_{ip} \chi_p \quad (30)$$

where $\{\phi_i\}_{i=1}^p$ represents the set of occupied MOs and $\{\phi_i\}_{i=p+1}^m$ represents set of virtual MOs.

This program also optimizes the coefficients from **mcdrft** and **mcuft**. The program **mofmt** formats the MOs and generates their coefficients, placing that output in a file called **mocoef**.

Next, a code called **tran** takes the atomic orbital integrals from **aoints** and transforms them into molecular orbital integrals using the molecular orbitals from **mcscf**. This is done piecewise for 1-electron and 2-electron AOs, applying the 1-electron Hamiltonian, $\hat{H}^{(1)}$, which includes all components but the \hat{H}_{rep} term, to the **aoints1** data, and applying the \hat{H}_{rep} term to the **aoints2** data. This is seen mathematically as

$$\langle \phi_i | \hat{H}^{(1)} | \phi_j \rangle = \sum_p \sum_q c_{ip} c_{jq} \langle \chi_p | \hat{H}^{(1)} | \chi_q \rangle \quad (31)$$

$$\left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_k \phi_l \right\rangle = \sum_p \sum_q \sum_r \sum_s c_{ip} c_{jq} c_{kr} c_{ls} \left\langle \chi_p \chi_q \left| \frac{1}{r_{12}} \right| \chi_r \chi_s \right\rangle \quad (32)$$

producing an **moaints** file as output. Then, we create our preliminary **configs** file. This is done by running the **cgdbg** program, which identifies the occupancy of outer core and valence shells to be treated and uses a reference CSF to generate single excitations consistent with the chosen

symmetry, yielding our $\{\chi_p\}$. We then perform more single excitations from the original **configs** list and append them to the original **cgdbg** input file, running **cgdbg** again to obtain an even larger set of double-group adapted functions used in our MRCIS calculation.

The program that performs this calculation is **cidbg**, which compute a CI wavefunction and corresponding energies, often referred to as *roots* or *eigenstates*.

With the output from our CI calculation, we perform the calculation of *electric dipole transition moments* μ_{nm}

$$\mu_{nm} = \langle \psi_n | \hat{\mu} | \psi_m \rangle \quad (33)$$

obtained by the electric dipole operator

$$\hat{\mu} = \sum_i Q_i \hat{r}_i \quad (34)$$

for charge Q_i . We use these to calculate the intensity of the transition between states n and m , which indicates to us its lifetime and allowedness. The intensity, given in terms of radiative lifetime τ_{nm} , is calculated in seconds by¹⁴

$$\tau_{nm} = \frac{3hc^3}{64\pi^4(\Delta E_{nm})^3 \mu_{nm}^2} \quad (35)$$

This is done by running the **tranmom** code.¹⁵ The Arc HPC held a single-node version of the **cidbg** code and the **tranmom** code. The Stampede2 supercomputer held a parallel version of the **cidbg** code, requiring multiple nodes. This is often referred to as parallel spin-orbit configuration interaction (PSOCI). Example input for all of these programs can be found in Appendix B.

CHAPTER FOUR: RESULTS

After performing calculations using the aforementioned codes, we obtained a series of energies at the spin-orbit MRCI level of theory. The table of values can be seen in Appendix A. In Tables 2 and 3, we observe that the ground state energy of Pt^{2+} is -3206 eV under both pure LS-coupling and pure jj-coupling considerations. After the MRCI procedure is complete, we recorded the ground state and configs information across all three symmetries and observe that the ground state energy of Pt^{2+} is -3214 eV. This is about 0.25% lower in energy than that of the previous two codes and corresponds to a combination of electron correlation and intermediate angular momentum coupling, the latter being a variational mixing of LS- and jj-coupling. Taking these roots to **tranmom** for electric dipole transition moment calculations, we observed five short-lived transitions on the order of microseconds (μs) and three long-lived transitions on the order of milliseconds (ms). These longer transitions indicate a degree of forbiddenness, often attributed to phosphorescence, whereas the short transitions indicate electric dipole allowed transitions, often attributed to fluorescence.

CHAPTER FIVE: CONCLUSIONS

From the data we have collected, we observed that spin-orbit MRCI calculations offer a higher degree of optimization not seen when considering only LS- or jj-coupling. The energies obtained are much lower than what is predicted by purely LS- or jj-coupling, indicating that Row 6 atoms and ions experience extensive intermediate angular momentum coupling. This set of data also shows a finer splitting of the electron configuration energies than what was observed by Ryabtsev and their team. While they had three unique energy levels over the span of ~ 1.21 eV, we were able to generate ten unique energy levels over a similar span of ~ 1.36 eV. However, these calculations did not have an overall large energy profile that can be extrapolated to the ionization energy of Pt^{2+} . Pure LS- and jj-coupling calculations estimate the ionization energy to range from 27.9 to 28.8 eV for this species, yet our calculations did not have enough roots to span that energy difference. In summary, this project further highlighted the effects of spin-orbit coupling that many-electron systems experience depending on atomic size and the magnitude of relativistic effects. The data generated also provides insight into the energy profile of the previously lesser studied Pt^{2+} ion.

APPENDIX A: TABLES

Table 1: Preliminary Table of Energies for Pt²⁺ (Ryabtsev)

Configuration	Term	J	Level (cm ⁻¹)	Energy (eV)
5d(8)	³ F	4	0	0
5d(8)	¹ D	2	5293.1	0.65626
5d(8)	³ F	3	9751.7	1.20906
5d(8)	³ F	2	14171.9	1.75709
5d(8)	³ P	0	14939.0	1.85220
5d(8)	³ P	1	16781.6	2.08065
5d(8)	¹ G	4	21330.8	2.64468
5d(7)(⁴ F)6s(1)	⁵ F	5	21836.7	2.70741
5d(8)	¹ D	2	24541.1	3.04271
5d(7)(⁴ F)6s(1)	⁵ F	4	27888.2	3.45770
5d(7)(⁴ F)6s(1)	⁵ F	3	32266.6	4.00055
5d(7)(⁴ F)6s(1)	⁵ F	2	33949.6	4.20921
5d(7)(⁴ F)6s(1)	⁵ F	1	34912.5	4.32860
5d(7)(⁴ P)6s(1)	⁵ P	2	36291.5	4.49957
5d(7)(⁴ F)6s(1)	³ F	4	36530.1	4.52915
5d(7)(⁴ P)6s(1)	⁵ P	3	36970.2	4.58372
5d(7)(⁴ P)6s(1)	⁵ P	1	40963.8	5.07886

Table 1: Continued

5d(7)(²G)6s(1)	³ G	5	42532.1	5.27331
5d(7)(⁴F)6s(1)	³ F	3	43057.2	5.33841
5d(7)(⁴F)6s(1)	³ F	2	45177.2	5.60126
5d(7)(²G)6s(1)	³ G	4	45438.7	5.63368
5d(7)(⁴P)6s(1)	³ P	2	46322.7	5.74328
5d(7)(²P)6s(1)	¹ P	1	46329.2	5.74409
5d(7)(²H)6s(1)	³ H	6	48134.2	5.96788
5d(7)(²G)6s(1)	³ G	3	49962.7	6.19459
5d(7)(²H)6s(1)	³ H	5	51466.0	6.38097
5d(7)(²G)6s(1)	¹ G	4	52013.6	6.44886
5d(7)(³D)6s(1)	³ D	3	54095.7	6.70701
5d(7)(⁴P)6s(1)	³ P	1	54503.7	6.75760
5d(7)(⁴P)6s(1)	³ P	2	54623.8	6.77249
5d(7)(²F)6s(1)	³ F	2	56908.6	7.05577
5d(7)(²F)6s(1)	³ F	2	57772.3	7.16285
5d(7)(²F)6s(1)	³ F	3	58410.1	7.24193
5d(7)(²P)6s(1)	³ P	1	59763.9	7.40978
5d(7)(²H)6s(1)	³ H	4	60041.4	7.44418
5d(7)(²H)6s(1)	¹ H	5	61332.2	7.60422

Table 1: Continued

5d(7)(3²D)6s(1)	¹ D	2	65958.7	8.17784
5d(7)(2¹P)6s(1)	¹ P	1	66521.4	8.24760
5d(7)(2¹F)6s(1)	¹ F	3	66700.9	8.26986
5d(6)6s(2)	⁵ D	2	74340 (th.)	9.21698 (th.)
5d(6)6s(2)	⁵ D	3	74493 (th.)	9.23595 (th.)
5d(6)6s(2)	⁵ D	0	78417 (th.)	9.72247 (th.)
5d(7)(1²D)6s(1)	³ D	2	79248 (th.)	9.82550 (th.)
5d(7)(1²D)6s(1)	³ D	3	80402 (th.)	9.96858 (th.)
5d(6)6s(2)	³ H	4	83740 (th.)	10.38244 (th.)
5d(6)6s(2)	³ G	5	87819 (th.)	10.88817 (th.)
5d(6)6s(2)	³ H	6	87922 (th.)	10.90094 (th.)

Table 2: Ground State and Ionization Energies from **atomic** (in eV)

	Configuration	Term	Energy	1st IE
Pt I (Pt)	5d(9)6s(1)	³ D	-3230.688	7.93
Pt II (Pt+)	5d(9)	² D	-3223.055	19.456
Pt III (Pt2+)	5d(8)	³ F	-3206.138	27.912

Table 3: Ground State and Ionization Energies from **jjatom** (in eV)

	Configuration	Energy	1st IE
Pt I (Pt)	5d*(4)5d(5)6s(1)	-3228.685	6.685
Pt III (Pt2+)	5d*(2)5d(6)	-3206.252	31.442
Pt III (Pt2+)	5d*(3)5d(5)	-3195.504	28.732
Pt III (Pt2+)	5d*(4)5d(3)6s(1)	-3203.259	25.389
Pt III (Pt2+)	5d*(4)5d(4)	-3206.390	29.574

Table 4: Summary of CI calculations (in eV)

Symmetry	A1	A2	B2
MCSCF energy	-3209.601	-3210.045	-3210.104
VCI energy w/ B2moints	-3211.054	-3211.070	-3210.104
Configs #	670614	700165	700165
DG Functions #	5948574	9820588	9820588
MRS ground energy	-3214.589	-3214.485	-3214.485

Table 5: CI Roots For All Symmetries

Eigenstate	Energy (eV)
A1E1	0
A1E2	0.00159
A1E3	0.01063
B2E1	0.10374
A2E1	0.10374
B2E2	0.11078
A2E2	0.11078
A1E4	0.87399
A1E5	0.89181
B2E3	0.97449
A2E3	0.97449
B2E4	1.35581
A2E4	1.35581
B2E5	1.35749
A2E5	1.35749

Table 6: Transition Moments

Transition	Moment (in a.u.)	Lifetime (s)
A2E1uA2E3	-0.00797510	4.6243E-07
A2E1uA2E5	-0.00414240	1.6856E-06
A1E1uA1E4	-0.00088440	6.6857E-05
A1E1uA1E3	-0.00045101	0.00025814
A1E1uA1E2	-0.00012534	0.00334839
A1E1uA1E5	0.00008810	0.00655538
A2E1uA2E4	0.00110209	2.3978E-05
A2E1uA2E2	0.00281696	3.7124E-06

APPENDIX B: SAMPLE INPUT FILES

atomic sample input file

```
1
Pt2+ AREP 18 5s(2)5p(6)5d(8) 3F
1
YES
0
0
NO
3
78
5 5 4
1 1 0
0 0 1
0 0 8
NO
0 0 0 0 0 0 0 0 0 0 0 0 0 0
2.3654 1.8045 0.5083 0.1484 0.05148
3.3722 2.5328 1.2740 0.6238 0.2210
1.4463 0.8898 0.3387 0.1320
NO
NO
0.0 0.0 0.0 1.0 0.0 /
0.0 0.0 0.0 1.0 0.0 /
0.0 0.0 0.0 1.0 /
NO
0.000000000000 0.000000000000 0.000000000000 0.000000000000
0.000000000000
0.000000000000 0.000000000000 -0.050000000000 -0.006632653061
0.002295918367
0.000000000000 /
PLATINUM GTF AREP 18
 5 60 0 0 0 0 0
14
      2      2.6091001034      -26.6245231628
      2      3.0292000771      90.0141220093
      2      4.0429000854      -193.8634033203
      2      6.0763001442      432.6285095215
      2      9.8383998871      -343.0379333496
      2      16.7040996552      387.9856872559
      1      47.6231002808      29.7609481812
      0      40.0689010620      6.7787342072
      2      1.8647999763      -0.8125420213
      2      4.8308000565      -13.0529289246
      2      12.3044996262      -73.7209854126
      2      34.8681983948      -141.1714477539
      2      110.9464035034      -412.5782470703
```

atomic sample input file continued

14	1	378.4443054199	-52.7245254517
	2	2.3127999306	-30.3742008209
	2	2.6816999912	102.4953002930
	2	3.5011999607	-205.2801513672
	2	5.1349000931	412.8767700195
	2	8.0055999756	-373.5076904297
	2	12.8712997437	355.2335205078
	1	35.5367012024	34.3938102722
	0	36.6483001709	5.9013581276
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
14	2	1.3830000162	-3.0278799534
	2	2.0704998970	64.2114944458
	2	2.4904999733	-146.1029968262
	2	3.6737000942	266.6141357422
	2	5.4851999283	-301.4702758789
	2	8.2098999023	278.5104370117
	1	18.5718002319	29.7185230255
	0	25.4209995270	7.8689160347
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
14	2	1.8671000004	-63.3894348145
	2	2.2018001080	215.7241973877
	2	2.9521000385	-333.9588012695
	2	4.3723998070	368.0679626465
	2	6.7848000526	-242.7938690186
	2	11.0228004456	233.0248413086
	1	27.7359008789	43.5935516357
	0	54.8493003845	4.5326499939
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
6	2	1.8647999763	-0.8125420213

atomic sample input file continued

2	4.8308000565	-13.0529289246
2	12.3044996262	-73.7209854126
2	34.8681983948	-141.1714477539
2	110.9464035034	-412.5782470703
1	378.4443054199	-52.7245254517 /

jjatom sample input file

```

1
Pt2+ SC REP 18 5s2 5p*2 5p4 5d*4 5d4 6s0
1 0 5 0 0 0 0 0 0 1 /
5 5 5 4 4 /
1 1 1 1 0 /
0 0 0 0 1 /
0 0 0 0 4 /
78.0 0.0 /
0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 /
    2.3654 1.8045 0.5083 0.1484 0.05148
    3.3722 2.5328 1.2740 0.6238 0.2210
    3.3722 2.5328 1.2740 0.6238 0.2210
    1.4463 0.8898 0.3387 0.1320
    1.4463 0.8898 0.3387 0.1320
0 0 /
    2.62289666      -3.02587326      -0.42755953      0.01582069      -
0.00609848
    -0.91756193      1.11624932      0.32694964      0.42292562
0.01834103
    0.44958015      -0.37549479      -0.55859657      -0.42518612      -
0.07782488
    -0.27747003      -0.35167561      -0.41577082      -0.15849640
    -0.22112325      -0.36867688      -0.41476868      -0.20784663
PLATINUM GTF REP 18
 9   60   0   1   0   0   0
14
    2      2.6091001034      -26.6245231628
    2      3.0292000771      90.0141220093
    2      4.0429000854      -193.8634033203
    2      6.0763001442      432.6285095215
    2      9.8383998871      -343.0379333496
    2      16.7040996552      387.9856872559
    1      47.6231002808      29.7609481812
    0      40.0689010620      6.7787342072
    2      1.8647999763      -0.8125420213
    2      4.8308000565      -13.0529289246
    2      12.3044996262      -73.7209854126
    2      34.8681983948      -141.1714477539
    2      110.9464035034      -412.5782470703
    1      378.4443054199      -52.7245254517
14
    2      2.3127999306      -36.6626586914
    2      2.6816999912      115.3814010620
    2      3.5011999607      -204.5491027832
    2      5.1349000931      344.9700012207
    2      8.0055999756      -261.0182495117
    2      12.8712997437      330.8809509277
    1      35.5367012024      47.9107551575

```

jjatom sample input file continued

	0	36.6483001709	5.8779220581
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
14			
	2	2.3127999306	-27.2299728394
	2	2.6816999912	96.0522537231
	2	3.5011999607	-205.6456756592
	2	5.1349000931	446.8301696777
	2	8.0055999756	-429.7524108887
	2	12.8712997437	367.4098205566
	1	35.5367012024	27.6353378296
	0	36.6483001709	5.9130759239
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
14			
	2	1.3830000162	-3.0468609333
	2	2.0704998970	62.3591613770
	2	2.4904999733	-139.4977111816
	2	3.6737000942	245.8525238037
	2	5.4851999283	-268.4549560547
	2	8.2098999023	259.6022338867
	1	18.5718002319	30.9752922058
	0	25.4209995270	7.8028273582
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
	1	378.4443054199	-52.7245254517
14			
	2	1.3830000162	-3.0152258873
	2	2.0704998970	65.4463882446
	2	2.4904999733	-150.5065155029
	2	3.6737000942	280.4552001953
	2	5.4851999283	-323.4804687500
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	1	18.5718002319	28.8806762695
	0	25.4209995270	7.9129748344
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246

jjatom sample input file continued

	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
14	1	378.4443054199	-52.7245254517
	2	1.8671000004	-59.6408653259
	2	2.2018001080	203.5800933838
	2	2.9521000385	-316.2478942871
	2	4.3723998070	353.2010498047
	2	6.7848000526	-234.7706451416
	2	11.0228004456	230.4700012207
	1	27.7359008789	43.7312545776
	0	54.8493003845	4.5268778801
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
14	1	378.4443054199	-52.7245254517
	2	1.8671000004	-66.2008590698
	2	2.2018001080	224.8322753906
	2	2.9521000385	-347.2419738770
	2	4.3723998070	379.2181396484
	2	6.7848000526	-248.8112945557
	2	11.0228004456	234.9409790039
	1	27.7359008789	43.4902763367
	0	54.8493003845	4.5369791985
	2	1.8647999763	-0.8125420213
	2	4.8308000565	-13.0529289246
	2	12.3044996262	-73.7209854126
	2	34.8681983948	-141.1714477539
	2	110.9464035034	-412.5782470703
6	1	378.4443054199	-52.7245254517
	2	1.8647999763	-0.7995695472
	2	4.8308000565	-12.9499073029
	2	12.3044996262	-73.9838256836
	2	34.8681983948	-142.6203613281
	2	110.9464035034	-415.9997863770
6	1	378.4443054199	-58.7785911560
	2	1.8647999763	-0.8229200244
	2	4.8308000565	-13.1353454590
	2	12.3044996262	-73.5107116699
	2	34.8681983948	-140.0123138428
	2	110.9464035034	-409.8410339355
	1	378.4443054199	-47.8812713623

cgdbg sample input file

```
Pt2+ C2v gcv-cv - Frozen 5s and 5p - B2 VCI
64 16 4 1 1 0 1 10 4 2
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
1 1 1 1 1 1 1 1 1 1 1 2 2 2 2
2 2 3 3 3 3 3 3 3 3 3 3 3 3 3
3 4 4 4 4 4 4 4 4 4 4 4 4 4 4
4 8 8
1 2 35 50
9 8 8
3 4 5 6 28 36 37 51 52
222100000000000000000000000000000000200000022000000000000002100000000000000
222100000000000000000000000000000000200000022000000000000002100000000000008
```

argos sample input file

```
Pt atom - C2v crenbl ecp/so gcv-c/v
1 1 4 4 4 0 0 0 0 1 1 /
4 1a1 1a2 1b1 1b2 /
1 /
4 3 2 /Irrep product
1 1 /Pt s
3 1 3 4 /Pt p
5 1 1 2 3 4 /Pt d
7 1 1 2 3 3 4 4 /Pt f
1 1 1 /S function
1 /s : a1
3 3 2 /P functions
0 0 1 /p z : a1
1 0 0 /p x : b1
0 1 0 /p y : b2
5 6 3 /D functions
1 1 -4 0 0 0 /d sigma : a1
1 -1 0 0 0 0 /d del+ : a1
0 0 0 1 0 0 /d xy : a2
0 0 0 0 1 0 /d xz : b1
0 0 0 0 0 1 /d yz : b2
7 10 4 /F functions
0 0 4 0 -9 0 -9 0 0 0 / z(5z^2-3r^2) : a1
0 0 0 0 1 0 -1 0 0 0 / z(x^2-y^2) : a1
0 0 0 0 0 0 0 0 0 1 / xyz : a2
1 0 0 0 0 -9 0 0 0 0 / x(x^2-3y^2) : b1
-1 0 0 0 0 -1 0 16 0 0 / x(5z^2-r^2) : b1
0 1 0 -9 0 0 0 0 0 0 / y(y^2-3x^2) : b2
0 -1 0 -1 0 0 0 0 16 0 / y(5z^2-r^2) : b2
14 1 7 / Pt S basis CRENB + aug-cc-pVDZ-PP
2.36540000 3.09201982 -0.89719413 5*0.0 /
1.80450000 -5.21828656 1.63394691 5*0.0 /
0.50830000 1.78717875 -0.92776836 5*0.0 /
0.14840000 -72.18545169 60.26196028 5*0.0 /
0.05148000 3.27000322 -1.03459945 5*0.0 /
```

argos sample input file continued

```

37.37500000  -0.03015128    0.00995068 5*0.0 /
23.36850000   0.12637293   -0.04250472 5*0.0 /
14.61640000  -0.19334173    0.06829292 5*0.0 /
 5.22096200   0.24678979   -0.13226573 5*0.0 /
 1.32673200   2.27449513   -0.64933047 1.0 4*0.0 /
 0.61632100  -2.73225417    1.35666409 0.0 1.0 3*0.0 /
 0.14806800  72.13309320  -60.83044485 0.0 0.0 1.0 2*0.0 /
 0.05239100  -3.37125122    0.53270349 0.0 0.0 0.0 1.0 0.0 /
 0.01850000  -0.01106157   -0.03168582 4*0.0 1.0 /
13  2  6 / Pt P basis CRENB + aug-cc-pVDZ-PP
 3.37220000   1.45706047 5*0.0 /
 2.53280000  -2.12616747 5*0.0 /
 1.27400000  -3.16573068 5*0.0 /
 0.62380000  -1.65560356 5*0.0 /
 0.22100000  -0.13017902 5*0.0 /
 9.99268000   0.04404942 5*0.0 /
 6.38317000  -0.16459392 5*0.0 /
 1.56965000   2.80300102 5*0.0 /
 0.74277900   1.78100967 1.0 4*0.0 /
 0.31802000   0.16479936 0.0 1.0 0.0 0.0 0.0 /
 0.11414600   0.01666296 0.0 0.0 1.0 0.0 0.0 /
 0.03986300  -0.00350675 0.0 0.0 0.0 1.0 0.0 /
 0.01390000   0.00085847 4*0.0 1.0 /
11  3  5 / Pt D basis CRENB + aug-cc-pVDZ-PP
 1.44630000  -0.53775991 4*0.0 /
 0.88980000   0.46900878 4*0.0 /
 0.33870000   0.10613240 4*0.0 /
 0.13200000  -0.05847563 4*0.0 /
10.41260000   0.00833887 4*0.0 /
 6.52266000   0.00859866 4*0.0 /
 1.66430000   0.08980539 4*0.0 /
 0.73420800  -0.79599221 1.0 3*0.0 /
 0.29740700  -0.41071901 0.0 1.0 0.0 0.0 /
 0.10759900  -0.06749129 0.0 0.0 1.0 0.0 /
 0.03890000  -0.00832928 0.0 3*1.0 /
 2  4  2 / Pt F pure aug-cc-pVDZ-PP
 0.8018000   1.0  0.0
 0.3357000   0.0  1.0
4  4 / Pt nelect 60 CRENB ECP
6 / Pt ul
 2  1.8648  -0.812542
 2  4.8308  -13.052929
 2 12.3045  -73.720985
 2 34.8682  -141.171448
 2 110.9464 -412.578247
 1 378.4443 -52.724525
8 / Pt S
 2  2.6091  -26.624523

```

argos sample input file continued

	2	3.0292	90.014122
	2	4.0429	-193.863403
	2	6.0763	432.628510
	2	9.8384	-343.037933
	2	16.7041	387.985687
	1	47.6231	29.760948
	0	40.0689	6.778734
8 / Pt P			
	2	2.3128	-30.374201
	2	2.6817	102.495300
	2	3.5012	-205.280151
	2	5.1349	412.876801
	2	8.0056	-373.507690
	2	12.8713	355.233521
	1	35.5367	34.393810
	0	36.6483	5.901358
8 / Pt D			
	2	1.3830	-3.027880
	2	2.0705	64.211502
	2	2.4905	-146.102997
	2	3.6737	266.614136
	2	5.4852	-301.470276
	2	8.2099	278.510437
	1	18.5718	29.718525
	0	25.4210	7.868916
8 / Pt F			
	2	1.8671	-63.389431
	2	2.2018	215.724197
	2	2.9521	-333.958771
	2	4.3724	368.067932
	2	6.7848	-242.793869
	2	11.0228	233.024857
	1	27.7359	43.593548
	0	54.8493	4.532650
8 / Pt P			
	2	2.3128	6.288457
	2	2.6817	-12.886098
	2	3.5012	-0.731049
	2	5.1349	67.906776
	2	8.0056	-112.489441
	2	12.8713	24.352579
	1	35.5367	-13.516945
	0	36.6483	0.023436
8 / Pt D			
	2	1.3830	0.012654
	2	2.0705	1.234891
	2	2.4905	-4.403522
	2	3.6737	13.841070

	2	5.4852	-22.010204
	2	8.2099	12.605469
	1	18.5718	-0.837846
	0	25.4210	0.044059
8 / Pt F			
	2	1.8671	-1.874284
	2	2.2018	6.072052
	2	2.9521	-8.855452
	2	4.3724	7.433455
	2	6.7848	-4.011614
	2	11.0228	1.277422
	1	27.7359	-0.068851
	0	54.8493	0.002886
6 / Pt G			
	2	1.8648	-0.005189
	2	4.8308	-0.041208
	2	12.3045	0.105136
	2	34.8682	0.579566
	2	110.9464	1.368612
	1	378.4443	2.421627
Pt	4	1 18. /	
	0.0	0.0	0.0 / CARTESIAN
1	1 /		
2	2 /		
3	3 /		
4	4 /		
	1		/ INDEX OF Pt CORE POTENTIAL AND SPIN-ORBIT SET

mcdrt sample input file

```
3 /input the spin multiplicity
16/input the total number of electrons
4 /input the number of irreps (1-8)
Y /enter symmetry labels:
a1
a2
b1
b2
4 /input the molecular spatial symmetry (irrep 1:nsym)
1 1 1 2 3 1 4 1
/input the list of doubly-occupied orbitals (sym(i),rmo(i),i=1,ndot)
1 3 1 4 1 5 2 1 3 2 4 2
/input the active orbitals (sym(i),rmo(i),i=1,nact)
0 0 0 0 0 0
8 8 8 8 8 8
/bmin
/bmax
/step masks
0 /input the number of vertices to be deleted
N /are any arcs to be manually removed?
/
y /keep all of these walks?
/
0/input walk number (0 to end)
Pt+2 (3B2)

Y /write the drt file?
Y /include step(*) vectors?
```

mcsf sample input file

```
&input
  niter=200, ncol=1,
  npath=1,-2,3,4,5,-9,-10,11,-12,13,-14,-15,-16,19,17
/&end
```

tran sample input file

```
&input
  freeze(1)=64*1,
&end
```

cidbg sample input file

```
Pt2+
 5   0  22   0   0   1   1   0
800   0
 0 .000001
 0 .000001
 0 .000001
 0 .000001
 0 .000001
 0 .000001
 1.D-12   1
```

tranmom sample input file

```
transition moments
 5   0  20   0   0   0   0   0
 5   0  21   0   0   0   0   0
```

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VITA

Jacob Belmares is from Laredo, Texas. He earned his Bachelor of Science in Chemistry and Mathematics from Saint Edward's University in Austin, Texas. He then completed his Master of Science in Chemistry at the University of Texas at San Antonio. His future endeavors include gaining some work experience in industry and pursuing a Ph.D. program.