

*Desarrollo de métodos de Coupled Cluster en el marco de la
teoría de orbital molecular para cualquier partícula
(APMO) y su implementación en LOWDIN*

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Abstract: In this work, a theoretical development of a Coupled Cluster method including singles and doubles excitations (CCSD) under the Any Particle Molecular Orbital (APMO) frame is presented. The method was implemented in the computational package LOWDIN. An application of this new methodology is presented in a system that contains one positron. The results show that the inclusion of interparticle correlation electron-positron at a CCSD level of theory allows to recover a higher percentage of this energy than other available methods. In this way, the APMO/CCSD method becomes the first CC scheme capable of performing calculations for systems with two or more different quantum species

Resumen: En este trabajo se presenta el desarrollo teórico de métodos de *Coupled Cluster* (CC) incluyendo excitaciones sencillas y dobles bajo el marco de la teoría de orbitales moleculares para cualquier partícula (APMO) para incluir correlación a este nivel de teoría entre partículas de diferente especie. Este método fue implementado en el paquete computacional LOWDIN. Se presenta una aplicación de esta nueva metodología a un sistema que contiene un positrón. Los resultados muestran que la inclusión de correlación interpartícula electrón-positrón a un nivel de teoría CCSD permite recuperar un mayor porcentaje de ésta energía que con otros métodos disponibles. Siendo el método APMO/CCSD el primer esquema de CC capaz de realizar cálculos que incluyan más de dos partículas de especies cuánticas diferentes.

Keywords: any particle molecular orbital, coupled cluster, positronic chemistry, LOWDIN code

Palabras clave: orbital molecular para cualquier partícula, coupled cluster, química positrónica, código LOWDIN

“Try not. Do... or do not. There is no try” - Yoda

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Nomenclature

APMO Any Particle Molecular Orbital

APMO/CCSD Any Particle Molecular Orbital at Coupled Cluster Singles Doubles Level

APMO/HF Any Particle Molecular Orbital at Hartree Fock level

APMO/MBPT(2) Any Particle Molecular Orbital at second order Many Body Perturbation Theory Level

BOA Born-Oppenheimer Approximation

CC Coupled Cluster

CCSD Coupled Cluster Singles Doubles

CI Configuration Interaction

GTO Gaussian Type Orbital

HF Hartree-Fock

MBPT Many-Body Perturbation Theory

MCMO Multi-Component Molecular Orbital

NEO Nuclear-Electronic Orbital

NOMO Nuclear Orbital plus Molecular Orbital

NQE Nuclear Quantum Effects

OOP Object Oriented Programming

PBE Positron Binding Energy

PES Potential Energy Surface

SCF Self Consistent Field

SE Schrödinger Equation

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CHAPTER 1

Introduction

1.1 Correlation Energy

Quantum chemistry has proved to be one of the best tools used to obtain and analyze a great amount of valuable information about molecular systems, such as structural data, reaction properties and description of many phenomena that a molecule can undergo [1–3]. For this, several methods have been developed in the last century, where the Hartree-Fock (HF) method stands out as one of the first methods that offered a qualitatively correct description of most closed-shell molecules, and in general, of systems with a large energy difference between the ground and excited states [4]. One of its limitations comes from the use of a mean-field approximation, since it neglects the correlated motion of electrons due to the electrostatic repulsion, failing to describe correctly systems where this correlation plays a key role in the properties of the system. To recover this correlation energy, which is the energy difference between the HF limit and the exact solution of the non-relativistic Schrödinger equation, more accurate theories have emerged. Some of the well-known methods that recover certain amount of this energy are: Many-body perturbation theory (MBPT), Configuration Interaction (CI) and Coupled Cluster (CC).

We will focus on the latter, which was initially developed by Fritz Coester and Hermann Kümmel in the late 1950s in order to study nuclear physics phenomena [5], and later becoming the most reliable, although computationally expensive method for the approximate solution of the electronic Schrödinger equation (SE) since its introduction into quantum chemistry made by Jiří Čížek in 1966, when he included electronic correlation in atoms and molecules [6]. After the reformulation, the method has been used to study a great number of phenomena, such as excited states [7], chemical and spectroscopic properties [8], molecular structures, among others. The reason behind the accuracy and prevalence of CC methods relies in the mathematical description, the corresponding equations will be presented in chapter 2.

1.2 Born-Oppenheimer Approximation

The above mentioned methods generally make use of one of the most fundamental approximations used in theoretical physics and chemistry to explore molecular properties, this

is, the Born-Oppernheimer Approximation (BOA), which simplifies the hamiltonian in the SE by considering nuclei as point charges, uncoupling the electronic and nuclear degrees of freedom [9]. Although this consideration has its implications, the approximation has been succesfully applied to evaluate a wide variety of properties in systems with a large amount of atoms (e.g. proteins), opening up the fields of research in quantum chemistry.

However, methods based on the BOA fail to describe some nuclear quantum effects (NQEs), such as tunneling or isotope effects, which can be very important for systems where there are delocalized nuclei. From this, an interest in developing a non-BOA methodology emerges to be able to study NQEs in the electronic structure of atoms and molecules.

1.3 Exotic Chemistry

The idea of developing a non-BOA methodology does not only comes from the need to evaluate NQEs, it is also intended to consider different quantum species (e.g., positrons and muons) in electronic structure calculations. The inclusion of quantum species (apart from electrons) in a chemical system form what it is commonly known as exotic atoms and molecules. The interest regarding the study of these exotic systems has been increasing in the past few decades, due primarily to advances in the manipulation of the exotic particles, especially in the particles charged positively. The positronic complexes have received most of the attention from different fields, such as solid state physics [10, 11], astrophysics [12], chemistry [13] and medicine, where advances in techniques such as positron emission tomography have proved to be a useful tool for medical applications [14].

On the other hand, several authors have studied theoretically and experimentally the consequences of attaching a positron to atoms and molecules, where a wide variety of properties such as the bound states of the positron with atoms and molecules [15–17], annihilation rates [18, 19], positronium formation [20], effects of the dipole moment [21], among others, have been examined using different methods. However, up to our knowledge, none of the methods proposed so far include a CCSD correlation between the exotic particles and electrons, which is necessary to obtain a better description of the interaction of the subatomic particle with the rest of the system.

In our research group we have studied the binding energy of positrons to aminoacids [22] and to other systems [23], in addition to studies including other kind of particle, such as negative muons [24].

1.4 Beyond BOA

Proposing a method that goes beyond the BOA is not an innovating idea, considering that several methods already exist. Some examples are the Nuclear-Electronic Orbital method (NEO) [31], the Nuclear Orbital plus Molecular Orbital method (NOMO) [32, 33] and the Multi-Component Molecular Orbital method (MCMO) [34]. These approaches have been used mostly to include NQE on the electronic structure and molecular geometries [35–37].

Our research group developed the Any Particle Molecular Orbital approach (APMO)[38] as an extension of NMO methods to any kind of quantum particle. At the APMO Hartree-Fock (APMO/HF) level of theory, the total wave function is constructed as a product of wave functions for each type of quantum particle, described as Slater deter-

minants for fermionic species and symmetric products for bosonic species. The APMO/HF method does not include interparticle correlation, necessary to describe the interaction between the electrons and the other quantum particles. Therefore, it has been extended to the second-order perturbation theory (APMO/MBPT(2)) level[39]. But in view that MBPT approaches do not recover enough interparticle correlation[40], the need to implement a method that recovers a higher percentage of that correlation arises.

1.5 This thesis

In this work, we have developed the theoretical expressions of the Coupled Cluster (including singles and doubles excitations) under the APMO framework, so that it is possible to include a high level correlation between particles of different species. The equations were implemented in the LOWDIN software, developed in our research group[41]. We will refer to this method as APMO/CCSD for the rest of the document.

This work is organized as follows: In chapter 2 we provide the basic expressions of the CCSD method and its extension to the APMO methodology. In chapter 3 we describe the implementation of the APMO/CCSD method in LOWDIN and we provide some examples of the input and output files. In chapter 4 we present the validation of the method as well as a study of the chemistry of one exotic system at the APMO/CCSD level of theory. Finally in chapter 5 we provide concluding remarks and perspectives for future work.

Coupled Cluster theory and APMO

In this chapter, we present a brief theoretical background of the CC methods as well as the expressions from the APMO methodology. We also present the extension of the CCSD equations under the APMO framework using diagrammatic derivation.

2.1 Coupled Cluster theory

The wave function from CC theory is written as an exponential ansatz:

$$|\Psi\rangle = e^{\hat{T}}|\Phi_0\rangle \quad (2.1)$$

where $|\Phi_0\rangle$ is a Slater determinant that is usually built using molecular orbitals (MOs) from HF, and the cluster operator \hat{T} , is an excitation operator that acts on $|\Phi_0\rangle$ to produce a linear combination of excited Slater determinants. The choice of the exponential ansatz is appropriate since, unlike other methods (e.g. CI), guarantees the size-consistency and size-extensivity properties of the solution.

The cluster operator is defined as:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N \quad (2.2)$$

For a system with N electrons, it ends with the \hat{T}_N operator, but in practice, it must be truncated. The main reason is that the contribution of the high level operators (\hat{T}_5 or \hat{T}_6) to the solution is small, while the computational cost is considerably higher. In this work the method was truncated to double excitations (CCSD), where the one-body (\hat{T}_1) and two-body (\hat{T}_2) operators are given by:

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}^\dagger \hat{i} = \sum_{ia} t_i^a \{\hat{a}^\dagger \hat{i}\} \quad (2.3)$$

$$\hat{T}_2 = \frac{1}{2!^2} \sum_{ijab} t_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \quad (2.4)$$

The equation for the m th cluster operator can be constructed by generalizing

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{ij\dots ab\dots} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j} \dots\} \quad (2.5)$$

Here, the terms $t_{ij\dots}^{ab\dots}$ are coefficients to be determined, from now on, we will refer to them as the amplitudes of the corresponding operator, and the creation and annihilation operators are in normal form (The brackets $\{ \}$ indicate normalization).

We have m pairs of creation and annihilation operators, which produce m excitations, where $m \leq N$, being N the number of electrons. The factor $(m!)^{-2}$ is introduced in the equation to cancel repeated terms, given that the index exchange produces equal contributions.

These \hat{T}_m contributions cannot be reduced, and they are referred to as connected contributions. In addition to these terms, we also have the disconnected components of the exact wave function that arise from the nonlinear exponential expansion.

$$\frac{1}{2} \hat{T}_2^2 = \sum_{\substack{ijab \\ klcd}} t_{ij}^{ab} t_{kl}^{cd} \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i} \hat{c}^\dagger \hat{d}^\dagger \hat{k} \hat{l} \quad (2.6)$$

$$\frac{1}{2} \hat{T}_1^2 = \sum_{\substack{ia \\ jb}} t_i^a t_j^b \hat{a}^\dagger \hat{b}^\dagger \hat{j} \hat{i} \quad (2.7)$$

$$\hat{T}_1 \hat{T}_2 = \sum_{\substack{ia \\ klcd}} t_i^a t_{kl}^{cd} \hat{a}^\dagger \hat{i} \hat{c}^\dagger \hat{d}^\dagger \hat{k} \hat{l} \quad (2.8)$$

It is very interesting to note that even though the equation 2.6 introduces quadruple excitations into the wave function, the amplitudes composing it are double excitation coefficients. Meaning that truncating the method up to doubles excitations, includes triples and quadruples terms due to the nature of the exponential ansatz. And these disconnected terms are the responsible of providing size-extensivity to the method, property that other correlated methods such as CI do not have.

In essence, the basic equations of CC theory can be deceptively simple, as we can write the energy equation for the CCSD method (for electrons) as:

$$E_{CCSD} = \sum_{i,a} t_i^a \{\hat{a}^\dagger \hat{i}\} + \frac{1}{4} \sum_{i,a,j,b} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{j}^\dagger \hat{b}\} + \frac{1}{2} \sum_{i,a,j,b} t_i^a t_j^b \{\hat{a}^\dagger \hat{i}\} \{\hat{j}^\dagger \hat{b}\} \quad (2.9)$$

The next step is to obtain the equation for the amplitudes, which are the only unknown quantities (apart from the total energy). This is done inserting the inverse of the exponential operator (i.e. $e^{-\hat{T}}$) to the left in the Schrödinger equation [25].

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E | \Phi_0 \rangle \quad (2.10)$$

followed by a projection of the reference determinant to obtain the correlation energy, and the projection of the excited determinant provides the equation for the amplitudes

$$\langle \Phi_0 | \bar{H} | \Phi_0 \rangle = E \quad (2.11)$$

$$\langle \Phi_i^a | \bar{H} | \Phi_0 \rangle = 0 \quad (2.12)$$

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle = 0 \quad (2.13)$$

Where \bar{H} is the similarity transformed hamiltonian

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad (2.14)$$

That leads to a linear combination of commutators between \hat{H} and \hat{T} through the use of the Campbell-Baker-Hausdorff formula[26–28]

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] \quad (2.15)$$

Inserting each term in the equation above into equations 2.11, 2.12 and 2.13 and evaluating the resulting matrix elements gives us the second-quantized expressions for each term. This algebraic treatment can be seen in more detail in Ref. [29]

2.1.1 Normal-Ordered Second-Quantized Operators

To simplify the derivation of the CC equations, the generalized Wick's theorem is used [30]. If we apply this theorem to the commutator $[\hat{H}, \hat{T}]$, we obtain

$$\begin{aligned} [\hat{H}, \hat{T}] &= \hat{H}\hat{T} - \hat{T}\hat{H} \\ &= \{\hat{H}\hat{T}\} + \{\overline{\hat{H}\hat{T}}\} - \{\hat{T}\hat{H}\} - \{\overline{\hat{T}\hat{H}}\} \end{aligned} \quad (2.16)$$

where the brackets $\{\}$ indicate a normal product and $\{\overline{\hat{H}\hat{T}}\}$ is the sum of all normal products were there are one or more contractions between the creation and annihilation operators in both \hat{H} and \hat{T} . And since both operators contain an even number of operators, the non-contracted terms cancel and the commutator is left as

$$[\hat{H}, \hat{T}] = \{\overline{\hat{H}\hat{T}}\} - \{\overline{\hat{T}\hat{H}}\} \quad (2.17)$$

And as we have seen, the cluster operators (\hat{T}_m) contain the operators $\hat{a}^\dagger, \hat{b}^\dagger, \dots$ and \hat{i}, \hat{j}, \dots , which refer to particle creation and hole annihilation respectively. We can define the non-zero contractions

$$\overline{ab^\dagger} = \delta_{ab} \quad (2.18)$$

and

$$\overline{i^\dagger j} = \delta_{ij} \quad (2.19)$$

and the contractions equal to zero appear from the different \hat{T}_m commutators,

$$[\hat{T}_m, \hat{T}_n] = 0 \quad (2.20)$$

As a result, the only surviving elements in the expansion 2.15 are those where the \hat{H} operator is on the left

$$\bar{H} = \hat{H} + \frac{1}{2} \overline{\hat{H}\hat{T}\hat{T}} + \frac{1}{3!} \overline{\hat{H}\hat{T}\hat{T}\hat{T}} + \frac{1}{4!} \overline{\hat{H}\hat{T}\hat{T}\hat{T}\hat{T}} \quad (2.21)$$

This is what is commonly known as the connected terms in the CC expansion, which can be expressed as

$$\bar{H} = (\hat{H}e^{\hat{T}})_C \quad (2.22)$$

With this expansion we can rewrite the projection of the reference and the excitation determinants as

$$\langle \Phi_0 | \hat{H}e^{\hat{T}} | \Phi_0 \rangle_C = E \quad (2.23)$$

$$\langle \Phi_i^a | \hat{H}e^{\hat{T}} | \Phi_0 \rangle_C = 0 \quad (2.24)$$

$$\langle \Phi_{ij}^{ab} | \hat{H}e^{\hat{T}} | \Phi_0 \rangle_C = 0 \quad (2.25)$$

So now the amplitude equations do not include the energy, which simplifies the further derivation.

So far, we have tried to clarify the foundations of the theory behind coupled cluster, but since the mathematical treatment is very extensive, we are showing the pertinent expressions for the reader to understand the extension of the method under the APMO framework, which we will explain below.

2.2 APMO Methodology

The main idea behind this approach is that the methods that had been developed to treat electronic wavefunctions in molecular systems under the BOA can be used to treat a system comprising several type of particles (i.e, different quantum species).

At the APMO/HF level, classical and quantum particles contribute to the molecular hamiltonian, that has the form:

$$H = - \sum_{i=1}^{N^q} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{N^q} \sum_{i>j}^{N^q} \frac{Z_i^q Z_j^q}{r_{ij}} + \sum_{i=1}^{N^q} \sum_{j=1}^{N^c} \frac{Z_i^q Z_j^c}{r_{ij}} + \sum_{i=1}^{N^c} \sum_{i>j}^{N^c} \frac{Z_i^c Z_j^c}{r_{ij}} \quad (2.26)$$

Here, the first term corresponds to the kinetic energy of the quantum particles (N^q), the second term refers to the interaction between pairs of quantum particles of charge Z_i^q and Z_j^q , the third term corresponds to the interaction between a quantum particle with charge Z_i^q and a classical particle with charge Z_j^c , and the last term refers to the interaction between classical particles with charges Z_i^c and Z_j^c .

At this level of theory (APMO-HF) the molecular wave function, Ψ_0 , is approximated by a product of single configurational wave functions, that we represent as Φ^α [31–33, 42], for the different quantum species α (i.e. electrons, nuclei, positrons)

$$\Psi_0 = \prod_{\alpha}^{N^Q} \Phi^\alpha \quad (2.27)$$

Each Φ^α is represented as either a Slater determinant or a symmetrized Hartree product of molecular orbitals (MO), ψ_i^α , depending on the fermionic or bosonic nature of the quantum species α . The APMO-HF equations are written in terms of effective one-particle operators

$$f^\alpha(i) \psi_i^\alpha = \epsilon_i^\alpha \psi_i^\alpha, \quad i = 1, \dots, N^\alpha, \quad \alpha = 1, \dots, N^{\text{species}} \quad (2.28)$$

For fermionic species each f^α can be written as

$$f^\alpha(i) = t^\alpha(i) + \sum_j^{N^\alpha} q_\alpha^2 [J_j^\alpha - K_j^\alpha] + \sum_{\beta \neq \alpha}^{N^{\text{types}}} \sum_j^{N^\beta} q^\alpha q^\beta J_j^\beta \quad (2.29)$$

where $t^\alpha(i)$ is the kinetic energy operator for particle i from species α , α and β are labels for the quantum species of charge q^α and q^β , and J^α and K^α are Coulomb and exchange operators defined as

$$J_j^\alpha(1) \psi_i^\alpha(1) = \left[\int d\mathbf{r}_2 \psi_j^{\alpha*}(2) \frac{1}{r_{12}} \psi_j^\alpha(2) \right] \psi_i^\alpha(1), \quad (2.30)$$

$$K_j^\alpha(1) \psi_i^\alpha(1) = \left[\int d\mathbf{r}_2 \psi_j^{\alpha*}(2) \frac{1}{r_{12}} \psi_i^\alpha(2) \right] \psi_j^\alpha(1). \quad (2.31)$$

2.3 APMO/CCSD

Having discussed the basics of the CC method and the APMO methodology, we can continue to the extension of the method.

For the construction of the APMO/CCSD equations we will follow the notation where the indices i, j, a, b, \dots correspond to the quantum species α and the capitalized indices I, J, A, B, \dots correspond to the quantum species β .

The corresponding extension for equation 2.9 to different quantum species is proposed as:

$$\begin{aligned}
E_{APMO/CCSD} = & \sum_{i,a \in \alpha}^{N^\alpha} t_i^a \{\hat{a}^\dagger \hat{i}\} + \frac{1}{4} \sum_{i,a,j,b}^{N^\alpha} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{j}^\dagger \hat{b}\} \\
& + \sum_{i,a \in \alpha} \sum_{I,A \in \beta} t_{iI}^{aA} N \{\hat{a}^\dagger \hat{i} \hat{A}^\dagger \hat{I}\} + \frac{1}{2} \sum_{i,a,j,b}^{N^\alpha} t_i^a t_j^b \{\hat{a}^\dagger \hat{i}\} \{\hat{j}^\dagger \hat{b}\} \\
& + \sum_{i,a \in \alpha} \sum_{I,A \in \beta} t_i^a t_I^A N \{\hat{a}^\dagger \hat{i}\} \{\hat{A}^\dagger \hat{I}\} \tag{2.32}
\end{aligned}$$

In this equation, the first, second and fourth terms are the same as the terms found in equation 2.9 with the addition of a sum that runs over the total number of different quantum species (N^α), and the third and fifth terms correspond to double excitations (connected and disconnected respectively) between different quantum species. The N factor in these new terms arises from the possible N -product operators.

The connected terms arise from the projection of the reference and excited determinants just like shown in section 2.1.1, taking into account that we now have different quantum species

$$\langle \Phi_0 | \hat{H}(\hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2) | \Phi_0 \rangle_C = E \tag{2.33}$$

$$\langle \Phi_i^a | \hat{H}(1 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3) | \Phi_0 \rangle_C \tag{2.34}$$

$$\langle \Phi_I^A | \hat{H}(1 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3) | \Phi_0 \rangle_C \tag{2.35}$$

$$\langle \Phi_{ij}^{ab} | \hat{H}(1 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2 \hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle_C \tag{2.36}$$

$$\langle \Phi_{IJ}^{AB} | \hat{H}(1 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2 \hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle_C \tag{2.37}$$

$$\langle \Phi_{iI}^{aA} | \hat{H}(1 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2 \hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4) | \Phi_0 \rangle_C \tag{2.38}$$

We need to note that if we are treating a system with many electrons and only one different quantum specie (e.g. quantum nuclei, muon, positron), many of the terms listed

vanish from the expansion, considering that we could only have one particle creation and one hole annihilation operator for the other particle, resulting in a significant simplification of the resulting matrix elements.

To obtain the final energy the amplitudes must be determined. To do so, we need to extend the equations for the amplitudes, for this, we need to define the possible commutators, for electrons

$$[\hat{i}^\dagger, \hat{j}] = \delta_{pq} \quad (2.39)$$

$$[\hat{i}^\dagger, \hat{j}^\dagger] = 0 \quad (2.40)$$

For a different quantum species

$$[\hat{I}^\dagger, \hat{J}] = \delta_{IJ} \quad (2.41)$$

$$[\hat{I}^\dagger, \hat{J}^\dagger] = 0 \quad (2.42)$$

And the interparticle commutator is defined as

$$[\hat{i}^\dagger, \hat{J}] = [\hat{i}^\dagger, \hat{J}^\dagger] = [\hat{i}, \hat{J}] = 0 \quad (2.43)$$

These definitions will be helpful in the construction of the amplitudes, we have that the t_1 amplitude equation is given by

$$\begin{aligned} 0 = & f_{ai} + \sum_c f_{ac} t_i^c - \sum_k f_{ki} t_k^a + \sum_{kc} \langle ka || ci \rangle t_k^c + \sum_{kc} f_{kc} t_{ik}^{ac} + \frac{1}{2} \sum_{kcd} \langle ka || cd \rangle t_{ki}^{cd} \\ & - \frac{1}{2} \sum_{klc} \langle kl || ci \rangle t_{kl}^{ca} - \sum_{kc} f_{kc} t_i^c t_k^a - \sum_{klc} \langle kl || ci \rangle t_k^c t_l^a + \sum_{kcd} \langle ka || cd \rangle t_k^c t_i^d \\ & - \sum_{klcd} \langle kl || cd \rangle t_k^c t_i^d t_l^a + \sum_{klcd} \langle kl || cd \rangle t_k^c t_{li}^{da} - \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{ki}^{cd} t_l^a - \frac{1}{2} \sum_{klcd} \langle kl || cd \rangle t_{kl}^{ca} t_i^d \end{aligned} \quad (2.44)$$

We have to note that equation 2.44 works for any type of quantum species if there is more than one in the system, otherwise most of the terms will vanish from the equation. On the other hand, the t_2 expression for one species has the form:

$$\begin{aligned}
0 = & \langle ab || ij \rangle + \sum_c \left(f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc} \right) - \sum_k \left(f_{kj} t_{ik}^{ab} - f_{ki} t_{jk}^{ab} \right) \\
& + \frac{1}{2} \sum_{kl} \langle kl || ij \rangle t_{kl}^{ab} + \frac{1}{2} \sum_{cd} \langle ab || cd \rangle t_{cd}^{ij} + P(ij) P(ab) \sum_{kc} \langle kb || cj \rangle t_{ac}^{ik} \\
& + P(ij) \sum_c \langle ab || cj \rangle t_i^c - P(ab) \sum_k \langle kb || ij \rangle t_k^a + \frac{1}{2} P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ac} t_{lj}^{db} \\
& + \frac{1}{4} \sum_{klcd} \langle kl || cd \rangle t_{ij}^{cd} t_{kl}^{ab} - \frac{1}{2} P(ab) \sum_{klcd} \langle kl || cd \rangle t_{ij}^{ac} t_{kl}^{bd} - \frac{1}{2} P(ij) \sum_{klcd} \langle kl || cd \rangle t_{ik}^{ab} t_{jl}^{cd} \\
& + \frac{1}{2} P(ab) \sum_{kl} \langle kl || ij \rangle t_k^a t_l^b + \frac{1}{2} P(ij) \sum_{cd} \langle ab || cd \rangle t_i^c t_j^d - P(ij) P(ab) \sum_{kc} \langle kb || ic \rangle t_k^a t_j^c \\
& + P(ab) \sum_{kc} f_{kc} t_k^a t_{ij}^{ab} + P(ij) \sum_{kc} f_{kc} t_i^c t_{jk}^{ab} - P(ij) \sum_{klc} \langle kl || ci \rangle t_k^c t_{lj}^{ab} \\
& + P(ab) \sum_{kcd} \langle ka || cd \rangle t_k^c t_{ij}^{db} + P(ij) P(ab) \sum_{kcd} \langle ak || dc \rangle t_i^d t_{jk}^{bc} \\
& + P(ij) P(ab) \sum_{klc} \langle kl || ic \rangle t_l^a t_{jk}^{bc} + \frac{1}{2} P(ij) \sum_{klc} \langle kl || ck \rangle t_i^c t_{kl}^{ab} - \frac{1}{2} P(ab) \sum_{kcd} \langle kb || cd \rangle t_k^a t_{ij}^{cd} \\
& - \frac{1}{2} P(ij) P(ab) \sum_{kcd} \langle kb || cd \rangle t_i^c t_k^a t_j^d + \frac{1}{2} P(ij) P(ab) \sum_{klc} \langle kl || cj \rangle t_i^c t_k^a t_l^b \\
& - P(ij) \sum_{klcd} \langle kl || cd \rangle t_k^c t_l^d t_{ij}^{ab} - P(ab) \sum_{klcd} \langle kl || cd \rangle t_k^c t_l^a t_{ij}^{db} + \frac{1}{4} P(ij) \sum_{klcd} \langle kl || cd \rangle t_i^c t_j^d t_{kl}^{ab} \\
& + \frac{1}{4} P(ab) \sum_{klcd} \langle kl || cd \rangle t_k^a t_l^b t_{ij}^{cd} + P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_i^c t_l^b t_{kj}^{ad} \\
& + \frac{1}{4} P(ij) P(ab) \sum_{klcd} \langle kl || cd \rangle t_i^c t_k^a t_j^d t_l^b \tag{2.45}
\end{aligned}$$

where the notation $P(ij)$ indicates the permutation operator whose function is given by

$$P(ij)f(i, j) = f(i, j) - f(j, i) \tag{2.46}$$

For the construction of the inter-particle t_2 equation, which starts with the integral $\langle aA || iI \rangle$, several inter-species permutation operators arise, for example, taking one of the terms from equation 2.45 to express it for two different quantum species

$$P(aA) \sum_k \langle kA || iI \rangle t_k^a = \sum_k (\langle kA || iI \rangle t_k^a - \langle ka || iI \rangle t_k^A) \tag{2.47}$$

$$P(aA) \sum_k \langle kA || iI \rangle t_k^a = \sum_k \langle kA || iI \rangle t_k^a \tag{2.48}$$

where it can be seen that the last term in the permutation vanishes due to the presence of a t_k^A amplitude. Performing the same procedure for each term in the equation results in

a similar expression for treating more than one type of quantum species, with some terms vanishing and others arising due to the distinction of species.

However, the algebraic notation is not usually chosen to visualize these expressions since the introduction of diagrammatic notation to this field. We will use the latter for a clear understanding of the terms in the APMO/CCSD equation.

2.3.1 Diagrammatic APMO/CCSD

Diagrammatic notation was originated in quantum field theory in the form of Feynman diagrams, in an explicit time-dependent format, which then were modified for non-relativistic fermionic systems and renamed as Goldstone diagrams[43]. The antisymmetrized Goldstone diagram formalism was later adapted and popularized by Kucharski and Bartlett[44]. Some of the advantages of using diagrammatic notation are: to make it easy to list all non-vanishing distinct terms in CC equations, to bring out certain cancellation in these sums, to provide certain systematics for manipulation of the various surviving terms and to construct the CC energy and amplitude equations far more quickly than by direct application of Wick's theorem.

A brief summary of the rules for the interpretations for the APMO/CCSD diagrams is presented below.

- The reference state $|\Phi_0\rangle$ is represented by an empty space.
- Upward and downward directed lines identify the orbitals that differ from those in the reference determinant.
- Upward directed lines represent hole states (orbitals occupied in the reference), and downward directed lines represent particle states (orbitals unoccupied in the reference).
- To discriminate between hole and particle states of different quantum species lowercase and uppercase indices will be used in the same way that in the previous section. In addition, we will use the vertices \bullet and \circ to refer to different species.

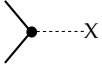

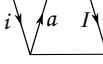
$$\Phi_i^a = \begin{array}{c} | \\ | \\ \downarrow i \\ \uparrow a \\ | \\ | \end{array} \quad \Phi_{ii}^{a\mathcal{A}} = \begin{array}{c} | \\ | \\ \downarrow i \\ \uparrow a \\ | \\ | \end{array} \quad I \begin{array}{c} | \\ | \\ \downarrow I \\ \uparrow \mathcal{A} \\ | \\ | \end{array}$$

- Dashed lines indicate components of the hamiltonian
- Solid lines indicate cluster operators \hat{T}_1 and \hat{T}_2
- Creation operators lie above the interaction line, and annihilation operators lie below.

We can have different types of vertices in CC diagrams, in table 2.1 we show the interpretation of each one.

There are two categories for the CC diagrams, the closed ones, which occur in the energy equation and the open ones, which appear in the amplitude equations. For electrons, there are only three distinct CC energy diagrams which we can associate with equation 2.9.

TABLE 2.1. Association of CC diagram vertices

Vertex	Diagram	Meaning
One-particle interaction		Associate a factor $f_{out,in}$
Two-particle interaction		Associate an antisymmetric inter-particle integral $\langle \text{left-out right-out} \text{left-in right-in} \rangle$
\hat{T}_m		Associate an amplitude t_{iI}^{aA}

$$\sum_{i,a} t_i^a \{ \hat{a}^\dagger \hat{i} \} = \text{Diagram: a solid black dot at the top with a dashed line to the right labeled X. Two lines enter from the left (labeled i and a) and two lines exit to the right, forming a loop structure.$$

$$\frac{1}{4} \sum_{i,a,j,b} t_{ij}^{ab} \{ \hat{a}^\dagger \hat{i} \hat{j}^\dagger \hat{b} \} = \text{Diagram: two solid black dots at the top, connected by a horizontal dashed line labeled X. Two lines enter from the left (labeled i and a) and two lines exit to the right (labeled j and b), forming two loops.$$

$$\frac{1}{2} \sum_{i,a,j,b} t_i^a t_j^b \{ \hat{a}^\dagger \hat{i} \} \{ \hat{j}^\dagger \hat{b} \} = \text{Diagram: two solid black dots at the top, connected by a horizontal dashed line labeled X. Two lines enter from the left (labeled i and a) and two lines exit to the right (labeled j and b), forming two separate loops.$$

With this information, we can rewrite the equation 2.32 in diagrammatic form, having not three, but eight terms, as can be seen in figure 2.1

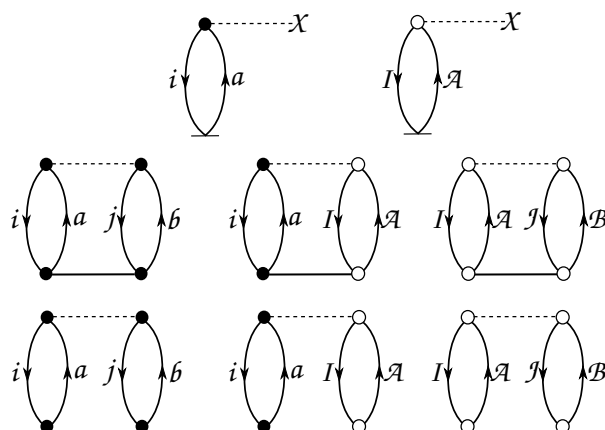


FIGURE 2.1. Diagrammatic terms for the APMO/CCSD energy, the vertices \bullet and \circ to refer to different species.

We can assign each diagram to each term in the equation, such as

$$\begin{aligned}
\langle \Phi_0 | \hat{H} + [\hat{H}\hat{T}_2] | \Phi_0 \rangle_C &= \sum_{i,a \in \alpha} \sum_{I,A \in \beta} \sum_{p,q \in \alpha} \sum_{P,Q \in \beta} \langle pP || qQ \rangle t_{iI}^{aA} \\
&\langle \Phi_0 | \{ \{ p^\dagger P^\dagger Qq \} \{ a^\dagger i A^\dagger I \} + \{ p^\dagger P^\dagger Qq \} \{ a^\dagger i A^\dagger I \} + \{ p^\dagger P^\dagger Qq \} \{ a^\dagger i A^\dagger I \} + \{ p^\dagger P^\dagger Qq \} \{ a^\dagger i A^\dagger I \} | \Phi_0 \rangle \\
&= \sum_{i,a \in \alpha} \sum_{I,A \in \beta} \langle iI || aA \rangle t_{iI}^{aA} = i \begin{array}{c} \bullet \text{---} \bullet \\ \uparrow \quad \downarrow \\ \bullet \text{---} \bullet \end{array} \begin{array}{c} \bullet \text{---} \bullet \\ \uparrow \quad \downarrow \\ \bullet \text{---} \bullet \end{array} \quad (2.49)
\end{aligned}$$

If we perform the same procedure for particles of the same species, we will see that a $\frac{1}{4}$ factor appears before the sum because we end up adding operator products that are equivalent. In this case we do not need the factor because equivalent products do not appear solving the equation.

To obtain the diagram for each of the terms included in the amplitudes equation, we need to break down the inter-particle interaction diagram into all the possible combinations, an example is show in Figure 2.2

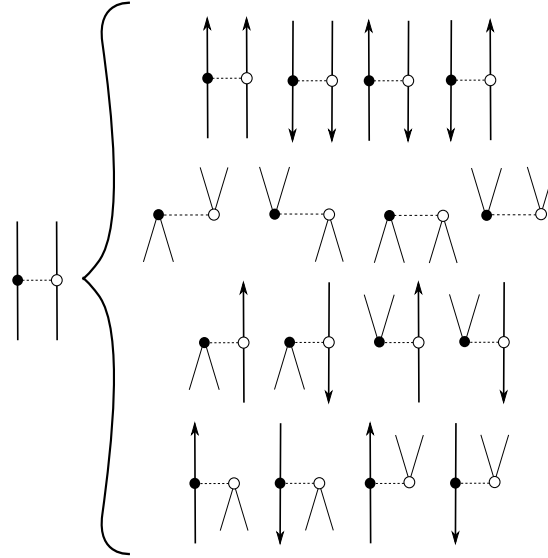


FIGURE 2.2. Combination of diagrams to construct the $\langle aA || iI \rangle \{ a^\dagger A^\dagger Ii \}$ operator

The corresponding diagrams for $\langle ab || ij \rangle \{ a^\dagger b^\dagger ji \}$ and $\langle AB || IJ \rangle \{ A^\dagger B^\dagger JI \}$ have the same form. Meaning that we end up with three times the number of diagrams shown in Figure 2.2 to obtain the full expression for that particular term.

Constructing all antisymmetrized and Goldstone diagrams for the model is not an easy task. Due to the large number of possible combinations, more than 200 diagrams (i.e. terms) are obtained. However, not all of them contribute to the total energy, but they are necessary to have a better understanding of the method.

The next logical step, which is the programming of all the terms and the calculation of the correlation energy, remained for a long time as the bottleneck of the CC methods, because the expressions obtained were not designed to implement them. In the next chapter we will address that matter.

Computational details

So far, we have presented the theory surrounding the CCSD and the APMO/CCSD methods, however, one of the biggest challenges in CC methods is the computational implementation, being one of the most discussed topics regarding this subject[45–47]. In order to facilitate the programming task the equations written in chapter 2 need to be reformulated, which can be done by the algebraic manipulation of the creation and annihilation operators through the use of Wick’s theorem[30], or using the diagrammatic derivation.

In this chapter, we will provide the implemented expressions as well as the structure of the code.

3.1 The program: LOWDIN

As mentioned in chapter 1, LOWDIN [41] is a platform that implements the APMO method. It is coded in the Fortran 2003 standard programming language, with some external libraries coded in C/C++. The published version is able to perform Hartree-Fock, second order Møller-Plesset, configuration interaction, second order propagator and DFT calculations, however, the software is in constant development, and is constructed in an object oriented programming (OOP) way, to facilitate the addition of methods to the code.

LOWDIN has a central structure, in this case named CORE, that is in charge of reading the input file, generate the molecular system and run the tasks requested by the user. The other essential parts of the structure are found as separated modules, these are the self consistent field (SCF) and the INTEGRALS programs. The latter evaluates the one- and two- particle integrals for the Gaussian Type Orbitals (GTOs) basis set functions, where the one-particle integrals have been implemented following the Head-Gordon-Pople[49] and Obara-Saika[50] schemes, and the two-particle integrals are calculated with the LIBINT library.[51]

In the SCF module, the minimization of the energy is carried out, ensuring the convergence in multi-species calculation. Furthermore, acceleration methods such as level shifting[52], DIIS[53] and optimal damping[54] have been succesfully tested in the code.

3.2 Implementation of the APMO/CCSD method

The APMO/CCSD method was implemented as an extra module called “*CC*”. All the code was written using the Fortran 2003 programming language. At this point, around 3000 lines of code were added to the software, following the LOWDIN programming philosophy.

3.2.1 Implemented expressions

Stanton proposed explicit equations for the CCSD method in a fully factored spin-orbital form[48]

T_1 equation:

$$\begin{aligned} t_i^a D_i^a = & f_{ia} + \sum_e t_i^e \mathcal{F}_{ae} - \sum_m t_m^a \mathcal{F}_{mi} + \sum_{me} t_{im}^{ae} \mathcal{F}_{me} - \sum_{nf} t_n^f \langle na || if \rangle \\ & - \frac{1}{2} \sum_{mef} t_{im}^{ef} \langle ma || ef \rangle - \frac{1}{2} \sum_{men} t_{mn}^{ae} \langle nm || ei \rangle \end{aligned} \quad (3.1)$$

T_2 equation:

$$\begin{aligned} t_{ij}^{ab} D_{ij}^{ab} = & \langle ij || ab \rangle + P_{(ab)} \sum_e t_{ij}^{ae} (\mathcal{F}_{be} - \frac{1}{2} \sum_m t_m^b \mathcal{F}_{me}) - + P_{(ij)} \sum_m t_{im}^{ab} (\mathcal{F}_{mj} - \frac{1}{2} \sum_e t_j^e \mathcal{F}_{me}) \\ & + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} \mathcal{W}_{mnij} + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \mathcal{W}_{abef} + P_{(ij)} P_{(ab)} \sum_{me} (t_{im}^{ae} \mathcal{W}_{mbej} - t_i^e t_m^a \langle mb || ej \rangle) \\ & + P_{(ij)} \sum_e t_i^e \langle ab || ej \rangle - P_{(ab)} \sum_m t_m^a \langle mb || ij \rangle \end{aligned} \quad (3.2)$$

Here, the one and two particle intermediates (\mathcal{F} and \mathcal{W} respectively) are needed to compute equations above

$$\mathcal{F}_{ae} = (1 - \delta_{ae}) f_{ae} - \frac{1}{2} \sum_m f_{me} t_m^a + \sum_{mf} t_m^f \langle ma || fe \rangle - \frac{1}{2} \sum_{mnf} \tilde{\tau}_{mn}^{af} \langle mn || ef \rangle \quad (3.3)$$

$$\mathcal{F}_{mi} = (1 - \delta_{mi}) f_{mi} - \frac{1}{2} \sum_e t_i^e f_{me} + \sum_{en} t_n^e \langle mn || ie \rangle - \frac{1}{2} \sum_{nef} \tilde{\tau}_{in}^{ef} \langle mn || ef \rangle \quad (3.4)$$

$$\mathcal{F}_{me} = f_{me} + \sum_{nf} t_n^f \langle mn || ef \rangle \quad (3.5)$$

$$\mathcal{W}_{mnij} = \langle mn || ij \rangle + P_{(ij)} \sum_e t_j^e \langle mn || ie \rangle + \frac{1}{4} \sum_{ef} \tau_{ij}^{ef} \langle mn || ef \rangle \quad (3.6)$$

$$\mathcal{W}_{abef} = \langle ab || ef \rangle - P_{(ab)} \sum_m t_m^b \langle am || ef \rangle + \frac{1}{4} \sum_{mn} \tau_{mn}^{ab} \langle mn || ef \rangle \quad (3.7)$$

$$\mathcal{W}_{mbej} = \langle mb || ej \rangle + \sum_f t_j^f \langle mb || ef \rangle - \sum_n t_n^b \langle mn || ej \rangle - \sum_{nf} \left(\frac{1}{2} t_{jn}^{fb} + t_j^f t_n^b \right) \langle mn || ef \rangle \quad (3.8)$$

where $P_{\pm(pq)}$ corresponds to the operator

$$P_{\pm(pq)} = 1 \pm \mathcal{P}_{(pq)} \quad (3.9)$$

And $\mathcal{P}_{(pq)}$ permutes the indices p and q , δ_{pq} is the Kronecker delta and the arrays (D) are defined as

$$D_i^a = f_{ii} - f_{aa} \quad (3.10)$$

and

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \quad (3.11)$$

The effective two-particle excitation operators τ γ $\tilde{\tau}$ have the form

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \quad (3.12)$$

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2} (t_i^a t_j^b - t_j^b t_i^a) \quad (3.13)$$

This set of equations corresponds to the initial part of the implemented code, it was used to test the CCSD method (for electrons) and as reference to build the inter-particle denominator, operators and intermediates:

$$D_{iI}^{aA} = f_{ii} + f_{II} - f_{aa} - f_{AA} \quad (3.14)$$

The effective inter-particle excitation operators are defined as

$$\tau_{iI}^{aA} = t_{iI}^{aA} + t_i^a t_I^A \quad (3.15)$$

$$\tilde{\tau}_{iI}^{aA} = t_{iI}^{aA} + \frac{1}{2} t_i^a t_I^A \quad (3.16)$$

The two-particle intermediates (\mathcal{W}) take the form

$$\mathcal{W}_{mMiI} = \langle mM || iI \rangle + \sum_e t_i^e \langle mM || eI \rangle + \sum_E t_I^E \langle mM || iE \rangle + \sum_{eE} \tau_{iI}^{eE} \langle mM || eE \rangle \quad (3.17)$$

$$\mathcal{W}_{aAeE} = \langle aA || eE \rangle - \sum_m t_m^a \langle mA || eE \rangle - \sum_M t_M^A \langle aM || eE \rangle + \sum_{mM} \tau_{mM}^{aA} \langle mM || eE \rangle \quad (3.18)$$

$$\begin{aligned} \mathcal{W}_{mMeE} = & \langle mM| |eE\rangle + \sum_f t_e^f \langle mM| |fE\rangle + \sum_F t_E^F \langle mM| |eF\rangle \\ & - \sum_n t_n^m \langle nM| |eE\rangle - \sum_N t_N^M \langle mN| |eE\rangle \end{aligned} \quad (3.19)$$

All of the equations above are expressed in a matricial form. Evaluating each term we can obtain the amplitudes t_i^a , t_I^A and t_{iI}^{aA} to compute the final energy as presented in equation 2.32

3.2.2 The CC module in LOWDIN

The implemented algorithm takes information from previous calculations in LOWDIN to obtain the final energy, as can be seen in figure 3.1. We summarize the code below.

1. An APMO/HF calculation is performed, to extract the molecular eigenvalues and the different species properties.
2. The new module asks for molecular integrals, which are obtained after passing through another module that transforms the atomic integrals into molecular integrals.
3. Once inside the APMO/CCSD module we can build the initial guesses for T_1 and T_2 as well as the array denominators.
4. The recursive calculation of the intermediates starts, as well as the computation of the APMO/CCSD energy, this iteration goes until convergence is achieved. The convergence criteria can be defined by the user in the input file, by default the calculation stops when the energy difference is less than 1×10^{-8} Hartree.

3.2.3 Running calculations at APMO/CCSD level of theory

To run an APMO/CCSD calculation in LOWDIN the job must be specified in the input file, an example is shown in figure 3.2. We present a brief explanation of the blocks that the input contains.

- The GEOMETRY block contains the information of the names, basis sets and positions of each particle.
- The TASKS block is where the desired type of calculation must be specified, in this particular case, a restricted Hartree-Fock calculation is requested, followed by a keyword framed in a blue box (coupledClusterLevel="CCSD") which tells the program to perform the post-HF calculation.
- The CONTROL block is other type of requests are made, in the example, we are telling the program to use one processor for the calculation and to build an output file for molden.

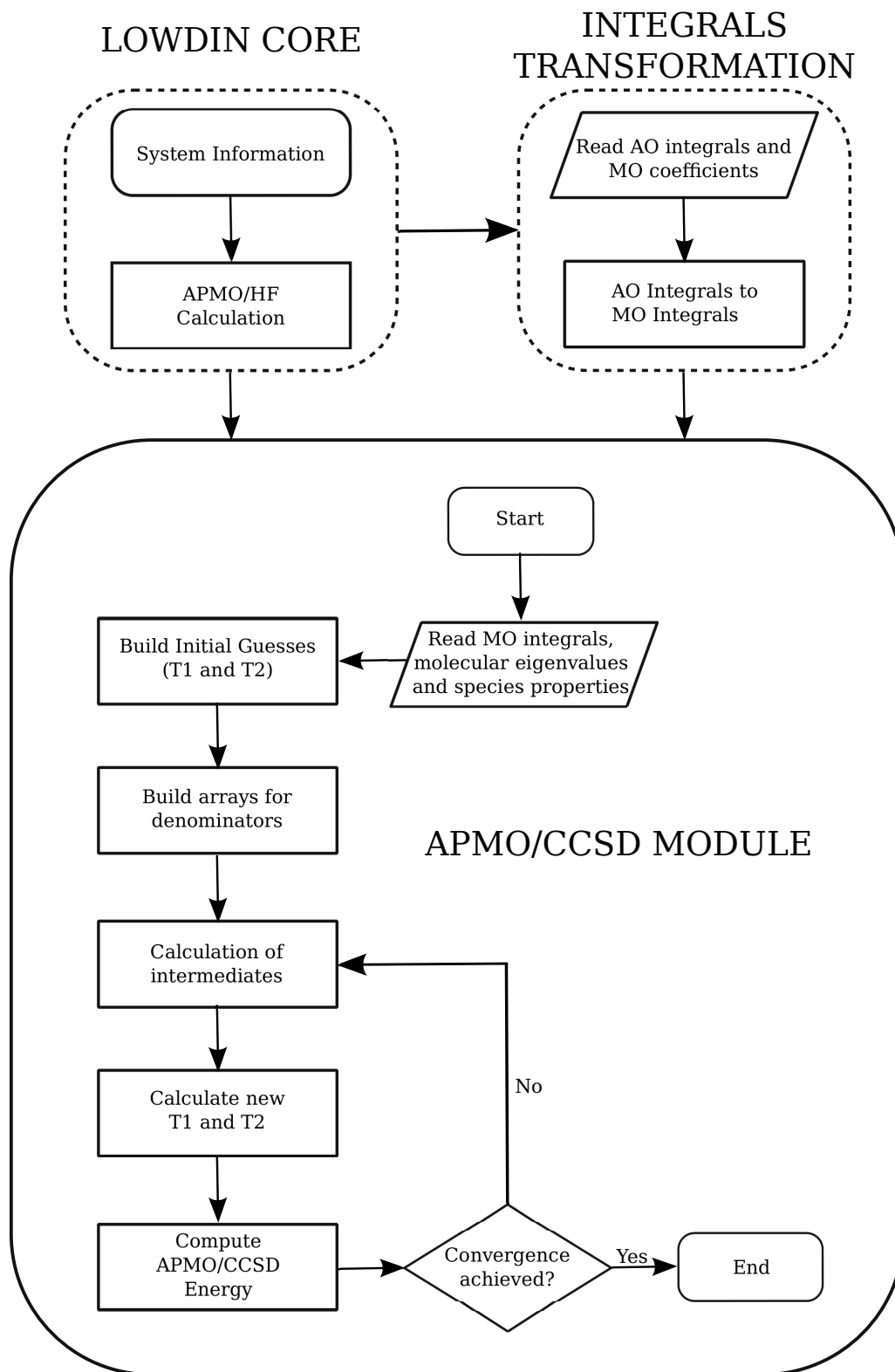


FIGURE 3.1. Flow chart of the APMO/CCSD code. The continuous line box frames the new code in LOWDIN.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Test APMO/CCSD
% Glycine/e+ Single Point
% Basis sets used:
%   6-31g for electrons
%   7s7p for positron
% Author: APT - 2015
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
GEOMETRY
e-(N)  6-31G  0.9291383829  0.6515863130  0.2579553587
e-(C)  6-31G  0.0897330453 -0.4420214032  0.8211560822
e-(C)  6-31G  0.0941630536 -0.3960959565  2.3553658057
e-(O)  6-31G  0.7921511128  0.4743116205  2.8734664606
e-(O)  6-31G -0.6077827204 -1.2484312025  2.8949479550
e-(H)  6-31G  1.8944763517  0.5362658862  0.5203576903
e-(H)  6-31G  0.4880613243 -1.3824615466  0.4704031433
e-(H)  6-31G -0.9147755436 -0.3205815874  0.4454496489
e-(H)  6-31G  0.8817574455  0.6779467470 -0.7468863001
e-(H)  6-31G  0.6329625479  1.5491921294  0.6056721554
N      dirac  0.9291383829  0.6515863130  0.2579553587
C      dirac  0.0897330453 -0.4420214032  0.8211560822
C      dirac  0.0941630536 -0.3960959565  2.3553658057
O      dirac  0.7921511128  0.4743116205  2.8734664606
O      dirac -0.6077827204 -1.2484312025  2.8949479550
H      dirac  1.8944763517  0.5362658862  0.5203576903
H      dirac  0.4880613243 -1.3824615466  0.4704031433
H      dirac -0.9147755436 -0.3205815874  0.4454496489
H      dirac  0.8817574455  0.6779467470 -0.7468863001
H      dirac  0.6329625479  1.5491921294  0.6056721554
e+    e+-0-7SP-aug-cc-pVDZ -0.6077827204 -1.2484312025  2.8949479550
END GEOMETRY
TASKS
      method = "RHF"
      coupledClusterLevel="CCSD"
END TASKS

CONTROL
      molderFile
      numberOfCores=1
END CONTROL

```

FIGURE 3.2. Basic LOWDIN input file for an APMO/CCSD calculation for the glycine molecule with one positron. In this example the nuclei are treated as classical particles, and the electrons and the positron are treated as quantum particles. The keyword inside the blue box indicates the instruction for LOWDIN to perform a CCSD calculation. The geometry for the glycine molecule, as well as the position of the positron in the input were taken from Ref [22]

At the end of the output file the results of the calculation are found, as shown in figure 3.3. The file displays the reference energy (HF), and the CCSD electronic correlation energy (red box) and the inter-particle correlation energy (blue box). The second order perturbation theory corrections are also printed, since they are the starting point for the CC calculation.

```
POST HARTREE-FOCK CALCULATION
COUPLED CLUSTER THEORY:
=====

                LEVEL = CCSD
                HF ENERGY =      -282.664487423972
                MP2 CORR. ENERGY =    -0.537891170424
                CCSD CORR. ENERGY =    -0.559860607141
=====
                Total Energy (HF+CCSD) =    -283.224348031113

COUPLED CLUSTER THEORY FOR DIFF. SPECIES
=====

                MP2 Corr.E-/POSIT =    -4.93427113E-03
                CCSD Corr.E-/POSIT =    -5.96413659E-03

=====
                MP2 Total Energy =    -283.20731287
                CCSD Total Energy =    -283.23031217
```

FIGURE 3.3. Output for the glycine single point calculation. The red box marks the CCSD electronic correlation and the blue box frames the interparticle correlation, in this case, the e^+/e^- correlation

Applications of the APMO/CCSD method

In this chapter we present the validation of the method calculating the electronic CCSD correlation for a set of 50 molecules followed by the study of the system comprising two hydrogen anions and one positron, referred throughout the rest of the document as $[\text{H}_2^{2-}; e^+]$.

4.1 Validation of the method

To test the accuracy of the method we have decided to use a set of fifty molecules taken out from ref.[55] that present different functional groups and compare our results with the same calculation performed in the computational package Gaussian 09[56]. In table 4.1 we report the CCSD correlation energy obtained with both packages, as well as the energy difference.

In figure 4.1 we plot a linear regression of the data obtained, and what it can be seen is that both values are in agreement, showing a R^2 coefficient close to 1. The average energy difference is below $0.4 \text{ kcal mol}^{-1}$ ($\approx 6 \times 10^{-4}$ Hartree). This difference is probably due to the implementation approach used, especially to the amplitudes calculation.

Regarding the performance of the method, it is important to note that the calculation time for the systems using LOWDIN is nearly seven times bigger compared to the same calculation executed with GAUSSIAN. This shows that, despite the fact that the method was successfully implemented, it is not yet an efficient code.

TABLE 4.1. CCSD correlation energy calculated for fifty systems using LOWDIN and GAUSSIAN. The 6-31G basis set was used to treat the electrons. All values are in kcal mol⁻¹

System	LOWDIN	GAUSSIAN	ΔE
H ₂	-15.6392	-15.5573	0.0819
He	-9.4102	-9.4136	0.0034
H ₂ O	-85.2572	-85.1652	0.0920
HF	-82.2402	-82.1198	0.1204
CH ₄	-74.6146	-74.6438	0.0293
NH ₃	-81.7068	-81.6909	0.0160
SiH ₂	-41.8162	-41.7849	0.0313
PH ₃	-54.9503	-54.9206	0.0296
H ₂ S	-47.8494	-47.7802	0.0692
C ₂ H ₂	-126.4649	-126.4685	0.0036
C ₂ H ₄	-131.5877	-131.6063	0.0185
C ₂ H ₆	-139.0168	-139.0663	0.0495
HCN	-137.8671	-137.7589	0.1083
H ₂ C=O	-145.6344	-145.2906	0.3438
CH ₃ OH	-149.3472	-149.2070	0.1403
H ₂ N-NH ₂	-153.8194	-153.7583	0.0612
H ₂ O ₂	-168.5559	-168.2007	0.3552
CO ₂	-216.1689	-216.0717	0.0972
NaCl	-34.2964	-34.1279	0.1684
BF ₃	-264.1661	-263.1349	1.0312
O ₃	-284.1777	-281.4373	2.7404
C ₃ H ₄	-190.1434	-190.1687	0.0253
C ₃ H ₆	-194.1213	-194.1703	0.0489
C ₄ H ₆	-252.5802	-252.5435	0.0367
C ₄ H ₈	-260.3331	-260.3963	0.0632
C ₄ H ₁₀	-269.6528	-269.7034	0.0506
C ₆ H ₆	-355.8181	-355.7718	0.0463
H ₂ CF ₂	-217.3438	-216.7774	0.5664
HCF ₃	-289.6405	-288.7301	0.9103
H ₃ CNH ₂	-145.8890	-145.8712	0.0178
CH ₃ CN	-199.1836	-199.0729	0.1107
CH ₃ NO ₂	-311.8020	-310.5663	1.2357
CH ₃ ONO	-308.6086	-306.8512	1.7574
HCOOH	-219.5501	-219.5765	0.0264
HCOOCH ₃	-284.4900	-283.5382	0.9518
CH ₃ CONH ₂	-277.2050	-276.5843	0.6207
NCCN	-265.8957	-265.6434	0.2524
(CH ₃) ₂ NH	-211.0480	-211.0008	0.0472
H ₂ CCO	-200.0039	-199.2825	0.7214
CH ₂ OCH ₂	-208.1760	-207.9040	0.2719
CH ₃ CHO	-208.7056	-208.3363	0.3693
OCHCHO	-280.2623	-279.5297	0.7325
CH ₃ CH ₂ OH	-214.3407	-213.8941	0.4466
CH ₃ OCH ₃	-214.1431	-213.9104	0.2327
CH ₂ SCH ₂	-169.4626	-169.3663	0.0963
H ₂ CCHF	-203.6373	-206.8212	3.1839
H ₂ CCHCl	-159.7956	-159.6619	0.1337
CH ₃ COCH ₃	-272.8556	-272.5710	0.2846
CH ₃ COOH	-283.3521	-282.5408	0.8113
(CH ₃) ₃ N	-277.2677	-277.2946	0.0269

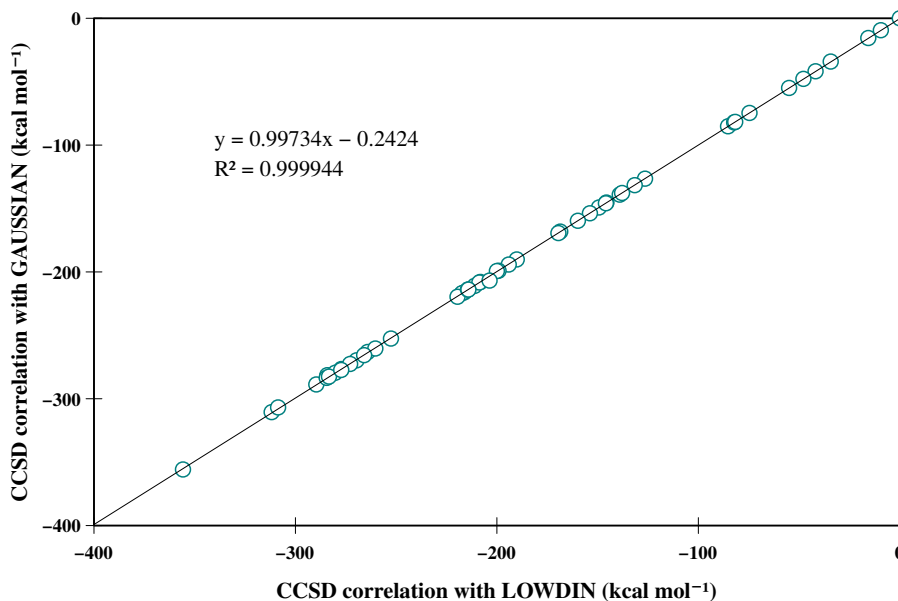


FIGURE 4.1. Linear regression of the data for the systems presented in Table 4.1

4.2 Calculation of electron-positron CCSD correlation energy in the $[\text{H}_2^{-2}; e^+]$ system

In the past few years, we have been very interested in the study of the role of the positron when it binds to atoms and molecules, as we stated in chapter 1, this phenomenon is known for changes in many properties of the system, and it has been widely studied, however, it is not known for stabilizing systems, considering that usually these are already stable before the addition of the positron. However, when we started studying systems comprising two closed shells anionic atoms, we noticed that the inclusion of a positron reverts the repulsive behavior of the potential energy surface (PES) of the anions creating an stable exotic complex.

4.2.1 Computational details for the positron

All calculations were carried out considering the electrons and the positron as quantum particles in gas phase. The electron-positron basis sets employed were aug-cc-pVTZ/7s7p7d. The latter was generated following an even-tempered scheme [57]

$$\zeta_{m,n} = \alpha_n \beta_n^m \quad (4.1)$$

where the m_{th} exponent of the set of Gaussian primitives of symmetry type n is generated with the parameters α_n and β_n^m . To construct different positronic basis sets for the hydrogen, we took the exponents of the diffuse s-, p-, and d- functions of the aug-cc-pVTZ basis set as values for α_n . For generating a basis set with $2n + 1$ s, p, and d basis sets, k was chosen to be $\{-l, -l + 1, \dots, 0, \dots, l - 1, l\}$. For β_n^m we employed a value of 3.1623.

Ideally, to obtain a better description of the system, several expansion centers should be placed around the molecular region. In practice, positronic basis sets are usually located

at a nucleus, choosing the coordinate of the most electronegative atom, as suggested in refs. [58, 59]. In this particular case, where the system only contains one type of atom, we chose three locations for the basis sets, placing one in each nucleus and one in the center of the internuclear region, given that the total APMO/HF energy is nearly insensitive when adding more basis sets trough the axis where the two hydrogen atoms are located, but it does increase significantly the computational cost.

4.2.2 Results

In figure 4.2 we have plotted the regular repulsive PES that the H_2^{2-} system presents, in addition to the PES when the positron is included. The decrease in the energy is evident, as well as the formation of a global minimum indicating the estabilization of the system. Although describing the exotic system at HF level already reverts this repulsive behaviour, it can also be seen that adding correlation (e^-/e^- and e^-/e^+) lowers the energy even more.

One way to evaluate the strenght of this positronic complex is to calculate the positron binding energy (PBE) which is usually taken as the energy difference between the system with and without the positron:

$$PBE = E_{[X;e^+]} - E_{[X]} \quad (4.2)$$

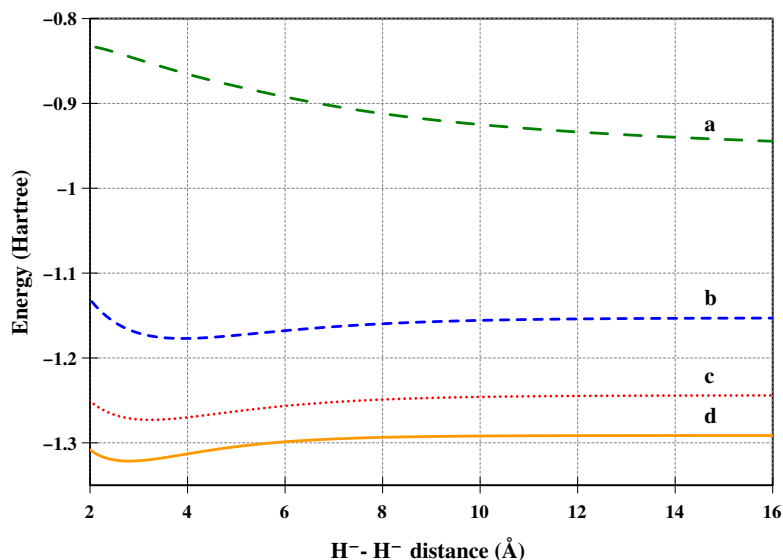
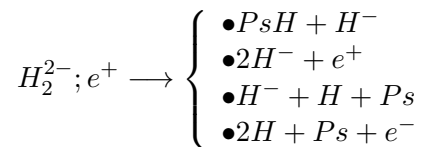


FIGURE 4.2. Potential energy surfaces for: a) H_2^{2-} (green curve), b) $[\text{H}_2^{2-}; e^+]$ at HF level (blue curve), c) $[\text{H}_2^{2-}; e^+]$ including MP2 e^-/e^- and e^-/e^+ correlation (red curve) and d) $[\text{H}_2^{2-}; e^+]$ including CCSD e^-/e^- and e^-/e^+ correlation (orange curve). All calculations were performed in LOWDIN. aug-cc-pVTZ and $7s7p7d$ basis set were used for electrons and positrons respectively

In this case, we need to evaluate the possible dissociation channels and compare the energy of the complex in the minimum to the lowest energy dissociation channel to obtain the PBE.

At large internuclear distances the possible dissociation channels are:



where Ps stands for positronium, which is the smallest exotic system containing one positron and one electron. Among these possibilities, the one with the lowest energy corresponds to the formation of the PsH and a hydrogen anion, meaning that separating the nuclei, the system will take the path to get to that channel.

In table 4.2 we present the values for the species involved in this dissociation channel (PsH and H^-) at the three different levels of theory, and the experimental values.

TABLE 4.2. Energy values (in Hartree) obtained for PsH and H^- using LOWDIN at different levels of theory compared to the experimental values. Basis sets aug-cc-pVTZ and $7s7p7d$ were used for electrons and positrons respectively.

	HF	MP2	CCSD	Exp.
PsH	-0.6664036	-0.7293176	-0.7656956	-0.789 ^a
H^-	-0.4876462	-0.5159683	-0.5264400	-0.5277
PsH + H^-	-1.1540499	-1.2452859	-1.2921356	-1.3167

^a SVM result, taken from Ref [60]

These results show that the inclusion of the CCSD correlation is not enough to correctly describe the PsH, nevertheless, is a big step forward from HF and MP2. It can also be seen that the energy at the dissociation limit changes with the method, meaning that we can calculate two PBE, one using the same level of theory, and other using the exact dissociation energy. This comparison is presented in table 4.3, as well as the equilibrium distance for each case.

TABLE 4.3. Equilibrium distances (in angstroms) and positron binding energies (in hartree) for the $[H_2^{2-}; e^+]$ complex

Method	r_{eq}	PBE ^a	PBE ^b
HF	3.92	15.2551	-86.8082
MP2	3.24	18.1175	-26.6949
CCSD	2.82	18.9248	3.5105

^a Binding energy at the same level of theory.

^b Binding energy with respect to the exact dissociation energy.

Table 4.3 shows that adding more correlation energy decreases the equilibrium distance between the two anions. It can also be seen that when compared with the dissociation limit calculated at the same level of theory, the positron binds to the system, but when it is compared with the exact limit, it only binds when the CCSD correlation is included.

Conclusions and perspectives

In this work, we have presented an extension for the coupled cluster method under the APMO framework. We derived the expressions for the CCSD model using the APMO/HF as the reference state and implemented these expressions in the LOWDIN computational package. In this section, we summarize our findings and state the work perspectives.

5.1 Conclusions

In chapter 2 we presented the theoretical background of the CC and the APMO theory, as well as the extended APMO/CCSD equations. We presented the corresponding amplitudes for the cluster operators in algebraic and diagrammatic form.

In chapter 3 we showed the reformulated equations for the amplitudes and intermediates that were implemented in the LOWDIN code. We illustrated the procedure of the program to calculate the total APMO/CCSD energy as well as the form of an input and output files for the calculation.

In chapter 4 we proposed a validation methodology for our new method by calculating the electronic CCSD correlation energy for a set of fifty molecules and comparing the results with an available software as GAUSSIAN, obtaining an acceptable agreement in the data with an average deviation of less than 0.4 kcal mol⁻¹, discrepancy that is most likely due to the way that the recursive calculation is carried out.

In this chapter we have also studied an exotic system comprising two hydrogen anions and one positron, finding that it forms a stable complex at an internuclear distance of 3.92 at the APMO/HF level, with a positron binding energy of 15.255 kcal mol⁻¹ compared to the dissociation channel calculated at the same level of theory. However, when we compare this to the dissociation channel obtained with the experimental values for PsH and H^- we find that the binding energy is negative (-86.808 kcal mol⁻¹), and this binding energy only becomes positive when we include the e^-/e^- and e^-e^+ CCSD correlation, giving a value of 3.511 kcal mol⁻¹.

These results allow us to conclude that this new exotic complex, where the positron serves as the binding specie for the anions can be qualitatively observed at the APMO/HF level, however, for a proper description of the strength of the so-called positronic bond, a high level method is needed, since the interparticle correlation appears to be significant

for this system. Even at the APMO/CCSD level, we are not recovering all the correlation needed to describe the system, this can be seen in the energy calculation for the PsH , where we recover more correlation energy than with the APMO/MBPT(2) method, but we are still around 15 kcal mol^{-1} above the exact value.

5.2 Perspectives

The CCSD is another step towards the full inclusion of interparticle correlation in APMO calculations. However, as we expressed above, it is not sufficient yet, as it may be further improved by extending the equations up to triples excitations, but since it would have a high computational cost, this would have to be implemented in a perturbative way. Another approach would be to extend the methodology to explicit correlation schemes. Nevertheless, up until now, the APMO/CCSD is the only available software to include the interparticle correlation at this level of theory, which makes it the method of choice for small-sized exotic systems.

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