LOWDIN: The Any Particle Molecular Orbital Code

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LOWDIN is a computational program that implements the Any Particle Molecular Orbital (APMO) method. The current version of the code encompasses Hartree–Fock, second-order Møller–Plesset, configuration interaction, density functional, and generalized propagator theories. LOWDIN input file offers a unique flexibility, allowing users to exploit all the programs' capabilities to study systems containing any type and number of quantum species. This review provides a basic introduction to LOWDIN's key computational details and capabilities. © 2013 Wiley Periodicals, Inc.

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Introduction

Over the years, quantum chemistry (QC) methods have become essential tools for understanding and predicting a wide variety of molecular phenomena.[1] The growing popularity and success of QC in molecular sciences is mainly due to continuous advances in QC theories and software and the gradual increase in speed and power of the computational hardware.[1–3] The impact of QC on molecular science research is such that nowadays it is common practice in experimental papers to include QC calculations to complement and support their findings and conclusions.[4] Despite the growing popularity of QC, there are still molecular phenomena that cannot be analyzed with current QC programs due to limitations on either the theoretical methodologies or the availability of their computational implementations.

In these cases, molecular scientists are forced to either (a) write their own codes or scripts to process and manipulate the data obtained by using available QC codes, (b) modify the existing computational codes to implement their new theories, or in the worst case scenario (c) write from scratch their own computational codes to implement their new theories.

The two groups currently involved in the LOWDIN project faced all the aforementioned problems. As a result, each group decided separately to create their own computational codes from scratch to use them as platforms for the efficient implementation of new theoretical methods. Andrés Reyes' group developed the Any Particle Molecular Orbital code known as APMO[5,6] and Roberto Flores-Moreno led the development of the electronic structure package named PARAKATA[7] (Butterfly in Purepecha, a native language of central-west Mexico).

At the time of the creation of APMO, GAMESS-NEO was the only freely available computational code capable of performing Nuclear Molecular Orbital (NMO) calculations of electrons and nuclei.[8] Despite all the computational possibilities offered by GAMESS-NEO, the code was only capable of handling two types of quantum species simultaneously (e.g., electrons and protons). APMO emerged as alternative to GAMESS-NEO, with the aim of extending electronic structure methods to any type and number of quantum particles such as nuclei, muons, positrons and pseudo-particles. The last existing version of APMO before it was merged into LOWDIN is capable of performing Hartree–Fock (HF) and MP2 calculations for systems containing any type and number of quantum species.[9–11]

On the other hand, PARAKATA implements Auxiliary Density Functional Theory (ADFT),[12,13] Auxiliary Density Perturbation Theory (ADPT)[14,15] and electron propagator theory (EPT) for electronic structure.[16–22] ADPT capabilities include calculation of electronic contribution to static and dynamic dipole polarizabilities,[14] hyper-polarizabilities,[23] electronic and nuclear Fukui function,[24,25] and other related fields such us the Shannon's entropy response to molecular ionization.[26] As it is inherent to, extensive use is made of auxiliary functions. Similarly to the deMon2k program,[27] auxiliary functions are generated automatically.[28,29] In contrast, PARAKATA uses Cartesian auxiliary functions.[30] In addition, auxiliary functions can also be used in Hartree–Fock and post-Hartree–Fock calculations, such as in electron propagator calculations. In the latter, it has been proven that only minor deviations are caused by using auxiliary functions and the gain in efficiency is considerable.[31]

With the aim of extending the electronic structure methods implemented in PARAKATA to study systems containing other

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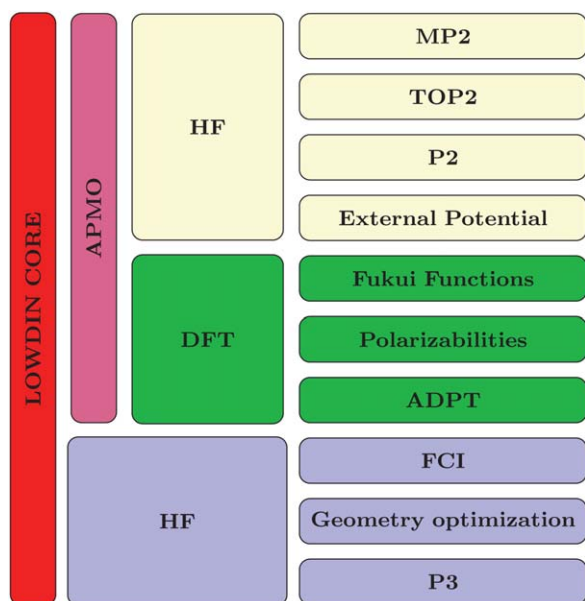E-mail: areyesv@unal.edu.co, roberto.floresm@red.cucei.udg.mx

Figure 1. Global structure of the program.

types of quantum species, it was decided to merge PARAKATA and APMO in 2010. This merging process is about to culminate. The resulting code has been named LOWDIN as a tribute to Per Olov Löwdin.

This review article is organized as follows: the section on technical details presents the computational aspects of LOW-DIN. The section on capabilities presents the features implemented in LOWDIN and summarizes some of the studies carried out with the code. The section on perspectives talks about the current research and points out theoretical and computational challenges of the APMO theory and the LOW-DIN code and strategies for the future.

Technical Details

LOWDIN has been designed to address two challenges:

- It must be capable of performing calculations for systems containing any type and number of quantum species.
- It must have a clear programming standard to simplify the implementation of new extensions.

In this context, LOWDIN has been fully coded in the FOR-TRAN 2003 standard, with some C/C++ bindings to external libraries. Although FORTRAN 2003 is not a full Object Oriented Programming (OOP) language, most OOP capabilities can be easily emulated, such as class definitions, some polymorphism, and inheritance.[32]

As observed in Figure 1, LOWDIN structure is based on a *CORE* program with small programs around it. These programs are completely encapsulated and independent from one another.

The CORE program

CORE is the main program of LOWDIN. It implements a set of tools to load the input file, generate the molecular system, and run all the requested tasks. This program also includes the *INTEGRALS* and *SCF* programs.

Figure 2 presents an example of an input file. The minimum required blocks to run a calculation are GEOMETRY, TASKS, and CONTROL.

The GEOMETRY block provides the information needed to build the molecular system. The first column declares the type

```
SYSTEM_DESCRIPTION='Muonic water molecule'

GEOMETRY
e-(O)    6-31G          0.0000  0.0000  0.1173    multiplicity=2 addParticles=-1
e-(H)    6-31G          0.0000  0.7572  -0.4692
e-(H)    6-31G          0.0000  -0.7572 -0.4692
u-       13s.ET.O.u.TF  0.0000  0.0000  0.1173
O_16     dirac          0.0000  0.0000  0.1173
H_1      DZSPDN         0.0000  0.7572  -0.4692
H_2      DZSPDN         0.0000  -0.7572 -0.4692
END GEOMETRY

TASKS
        method = "UHF"
        propagatorTheoryCorrection=2
END TASKS

CONTROL
        iterationScheme=3
        convergenceMethod=1
        readCoefficients=F
        hartreeProductGuess=T
END CONTROL
```

Figure 2. Basic input file.

of the quantum species. As shown in Figure 2, e-(H) and e-(O) define the electrons of a Hydrogen and an Oxygen atom, respectively; u- defines a negative muon, O_16, H_1, and H_2 define ^{16}O, ^{1}H, and ^{2}H nuclei, respectively.

The second column declares the basis sets. When the "**dirac**" basis is chosen, the particle is treated as a classical point charge. The third, fourth, and fifth columns declare the *x,y,z* coordinates of the particle basis set center.

The sixth column provides additional information via keywords **addParticles** and **multiplicity**. These keywords are used to change the default values. **addParticles** is used to modify the number of particles of a quantum species. As shown in the provided example, one electron is removed from the system. **multiplicity** defines the multiplicity for open shell calculations. In the example, an electronic multiplicity of 2 was chosen.

LOWDIN contains a large library of electronic basis sets. Some of the nuclear basis sets developed by Nakai[33,34] and Hammes-Schiffer[8] groups are also available. Home-made basis sets for nuclei, positrons, and muons have been generated by employing the even-tempered basis set scheme[35].

Any type of quantum particles or basis sets can be loaded even if they are not present in the main library. Users can upload new basis sets and quantum species through the addition or modification of some plain text files matching the information provided in the input file.

The TASKS block defines the type of calculation to be performed by LOWDIN. All capabilities are listed in section capabilities. Finally, CONTROL block contains all parameters needed to control the behavior of the program, such as thresholds, maximum number of SCF cycles, etc.

Once the input file is loaded in LOWDIN, the *CORE* program manages the execution of the requested tasks. The communication between the *CORE* program and the other subprograms is carried out through text files.

The INTEGRALS program

This program evaluates the one- and two-particle integrals. One-particle integrals such as overlap, kinetic, and nuclear attraction energy have been implemented for Gaussian basis functions of any angular momentum following Obara and Saika[36] and Head-Gordon and Pople[37] recursive schemes.

Two-particle interaction integrals of the type $(pq|r_{12}^{-1}|rs)$ are calculated either with proprietary routines or with LIBINT library.[38] Integrals of the type $\left(pq|e^{-\gamma r_{12}^2}|rs\right)$ are calculated with the LIBINT library. Integrals can be stored on either memory or disk. Integrals stored on disk are collected in stacks containing a maximum of 30.000 of them. Several stacks are calculated simultaneously to exploit the computational power of the machine. Different schemes have been implemented to exploit the permutational symmetry of the integrals.

The SCF program

The SCF program has been designed to minimize the energy of a molecular system composed of multiple quantum species. In a multispecies calculation, LOWDIN creates Fock-like opera-

tors for every quantum species. Multiple-species SCF cycles can be performed using any of these three iteration schemes:

1. Full convergence for each quantum species until global convergence is reached, as shown in Figure 3
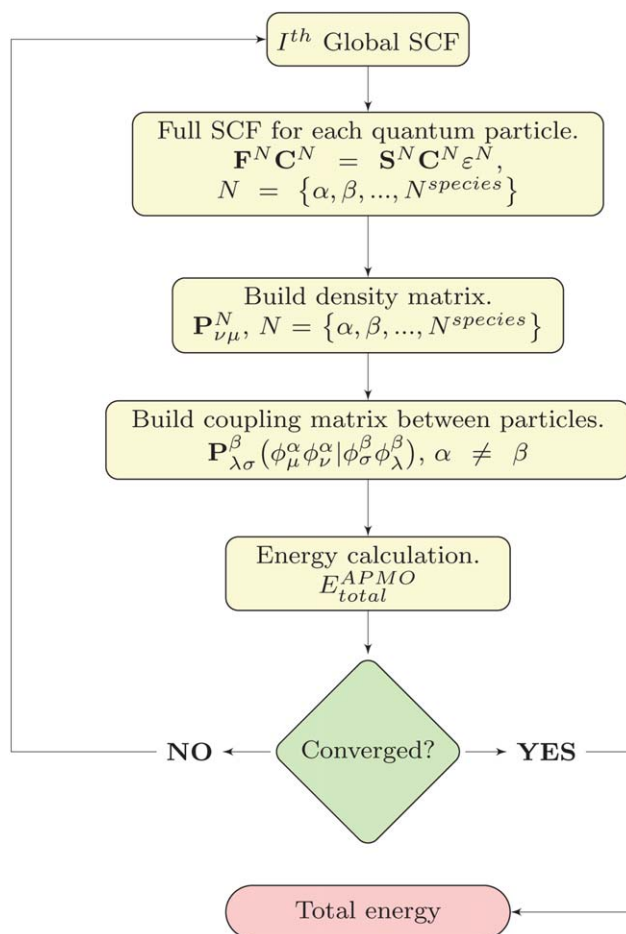

Figure 3. Simultaneous global SCF convergence algorithm.

2. Full convergence of electrons, if any, followed by one iteration for each nonelectronic species
3. One iteration for each quantum species until global convergence is achieved.

Convergence acceleration methods such as DIIS,[39] level shifting,[40] and optimal damping[41] have been implemented and are fully operational for any type of quantum species.

Capabilities

LOWDIN has been designed to be capable of handling different representations of the wavefunctions of fermionic and bosonic species. The current version of code supports Hartree-products, Slater determinants, and symmetric permutations of spin-orbitals. The SCF program can perform Hartree,[42] Hartree–Fock,[6] and DFT[43,44] calculations for any type of quantum species.
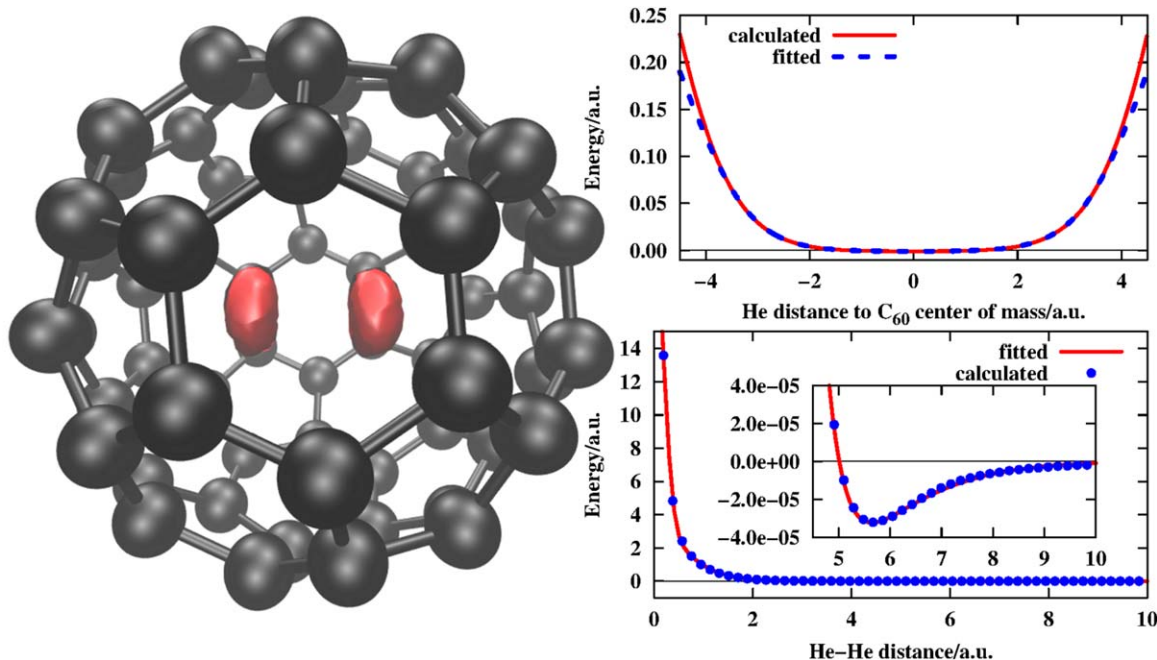
Figure 4. Left: Density contour (0.01 a.u.) of two Helium atoms confined in a fullerene. Right: He—He and He—C_{60} potentials employed in the calculation.

The DFT formalism implemented LOWDIN is an extension of the ADFT developed for electronic structure.[45] At present, the electronic Slater–Dirac exchange[46,47] and Vosko et al. correlation functionals.[48] Electronic BLYP, B3LYP, PBE, and PBE0 functionals are currently being implemented. Nakai's Colle-Salvetti-type nuclear-electron correlation functional[44,49] is also available. New interparticle correlation functionals for different combinations of quantum species are being developed.

LOWDIN contains a set of modules to perform post-Hartree–Fock calculations for systems comprised of any type and number of quantum species. Post-Hartree–Fock methods include second-order Møller–Plesset perturbation theory,[10,42] second-order propagator theory for the calculation of any particle binding energies,[50,51] and configuration interaction singles and doubles.[52] We are currently implementing coupled cluster and third-order propagator methods for any type of quantum species.

Full-CI (FCI) calculations for only one type of quantum species can be performed in LOWDIN. These calculations employ the FCI routine developed by Knowles et al. for electrons.[52,53] The FCI method can be used, for instance, to include electronic correlation using as reference the electronic wavefunction obtained from a APMO-HF calculation.[54] In a similar fashion, nuclear quantum effects (NQEs) on electronic polarizabilities and Fukui functions can be obtained by ADPT calculations, based on the electronic density of an APMO–ADFT calculation.[55] These methodologies will be extended to any type of quantum species in the near future.

APMO calculations for systems containing particles experiencing non-Coulombic interactions can be carried out in LOWDIN. To this aim, the interparticle interaction potentials are introduced as linear combinations of Gaussian functions. The resulting integrals are solved using the LIBINT library.[38] With this methodology the quantum nature of pseudo-particles, such as dressed nuclei and quantum, can be studied. For instance, Figure 4 shows the density of two helium atoms inside a fullerene, where the helium–helium and helium–fullerene interactions are described as a two-particles potential and a central potential, respectively. The study of the quantum behavior of confined species in fullerenes is in progress in our group. In addition, LOWDIN can perform APMO calculations on systems constrained to one or two dimensions. These capabilities will have direct application to study of quantum wires and wells.

Study of NQEs

Earlier applications of APMO and LOWDIN concentrated on the investigation of hydrogen isotope effects on covalent and non-covalent interactions. Similar studies have been carried out by other research groups employing NMO methodologies.[33,56–66]

In a first series of studies we examined, the H/D/T isotope substitution effects on the geometry and electronic structure of hydrogen molecule,[6] water,[6] hydrogen halide dimers,[5,67] and $[XO_3SOHOSO_3X]^-$ (X = H,K) complexes[68] at the APMO/HF level. These studies revealed that nuclear delocalization impacts the geometry and stability of hydrogen bonds, affecting macroscopic properties. Our APMO/HF results qualitatively agree with the experimental isotopic substitution trends.

With the APMO/MP2, we have studied NQEs on the geometries and energies of small protonated rare gas clusters (Rg_nX^+, Rg = He, Ne, Ar, X = H, D, T, and n = 13).[10,69]. We proposed an APMO/MP2 energy decomposition analysis scheme that revealed how NQEs impact the electrostatic, polarization,

charge transfer, and dispersion interactions contributing to the stabilization of the complexes.

A similar study was conducted for assessing the H/D secondary isotope effect on the binding energies of water–alkaline cation complexes, Alk^+ $(X_2O)_n$ (X = H, D; Alk = Li, Na, K; n = 1–4).[70] Our results revealed that deuteration reduces the magnitude of the electrostatic and polarization interactions between the cation and the water molecule via an inductive effect. This important result is the first in a series of studies aiming for understanding hydrogen isotope effects on hydration, an important topic for biomolecular sciences[71].

An APMO/MP2 study conducted for the $[CNHNC]^-$ complex[72] revealed the importance of including nuclear-electron correlation in APMO calculations. We discovered that while a NMO/HF calculation produced a minimal energy structure presenting an asymmetric hydrogen bond, the APMO/MP2 calculation produced a symmetric H-bond structure in agreement with available experimental data. This study confirmed the importance of including NQEs for an enhanced description of strong-low-barrier H-bonded systems.

We have proposed an extended propagator theory for electrons and other types of quantum particles.[50] In a first application of the method, we analyzed NQEs and isotope effects on electron ionization energies of molecular systems. An energy decomposition analysis of the total ionization energies revealed that the calculated electron ionization energies correspond to nearly vertical processes. Our results reveal that including NQEs improves the estimation of ionization energies for systems experiencing Jahn–Teller effects in the photo-electron spectra.

The APMO propagator theory has also been applied to study proton detachment processes.[51] We calculated the proton binding energies (PBEs) and proton affinities (PAs) for some inorganic and organic molecules, finding an excellent agreement between our predictions and the experimental values. We also combined our methodology with a systematic exploration of the energy surface of protonated water clusters, $(H_2O)_n H^+$ (n = 1−7), to estimate the proton hydration free energy. Our prediction of −270.2 kcal/mol is in excellent agreement with other results reported in the literature. This work suggests that the second-order proton propagator method has the potential to become a powerful tool for predicting proton acid/base properties (Fig. 5). Currently, we are working on the implementation of higher-order approaches and the combination of the proton propagator with an implicit solvation model aiming for the accurate prediction of pK_as.

Chemistry of exotic particles

Negative Muons Chemistry. In a series of recent papers, Fleming and coworkers[73–75] reported the measurement of reaction rates for the $^4He(\mu) + H_2 \rightarrow {}^4He(\mu)H + H$ collisional process. Perhaps, the most surprising finding of their research is that $He(\mu)$ chemically behaves as a heavy isotope of hydrogen. Inspired by this finding, the chemical properties of muonic atoms and molecules have also been investigated with LOWDIN. A muon is a particle with the same charge and spin of the electron but has a
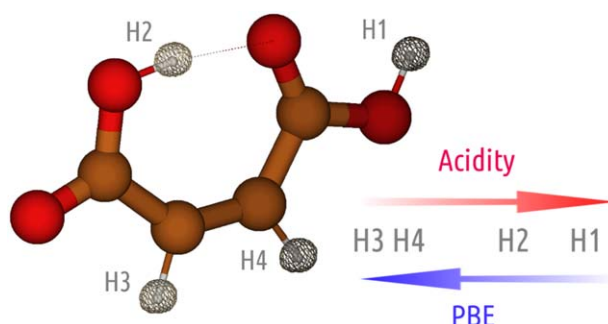

Figure 5. The proton propagator, implemented in LOWDIN program, is a promising tool for predicting proton acid/base properties. Here, an example of how the proton binding energies (PBE) describe differences in the acidity of the protons of maleic acid.

mass of 206.8 times larger. A comparison between the electronic and muonic radial distributions in atoms revealed that muons are much more localized than electrons. As a result, the muonic cloud screens almost one positive charge of the nucleus. Our results for electronic densities and ionization potentials revealed that by replacing an electron in an atom by a muon there is a transmutation of the electronic properties of that atom to those of the element with atomic number Z − 1.[35] In a more recent study of muonic systems, we found that the electronic properties of atoms containing two negative muons are very similar to those of all-electron atoms with atomic number Z − 2.[76] For diatomic molecules, these muonic effects are more diverse, ranging from the transmutation of atomic properties to drastic changes in equilibrium geometries and energies.[76] In Figure 6, we plot the muonic and electronic densities of a $He\mu H$ molecule. This figure clearly reveals that the muon is very close to the He nucleus, and that from the electrons perspective, the $He\mu^+$ moiety behaves as a H nucleus.
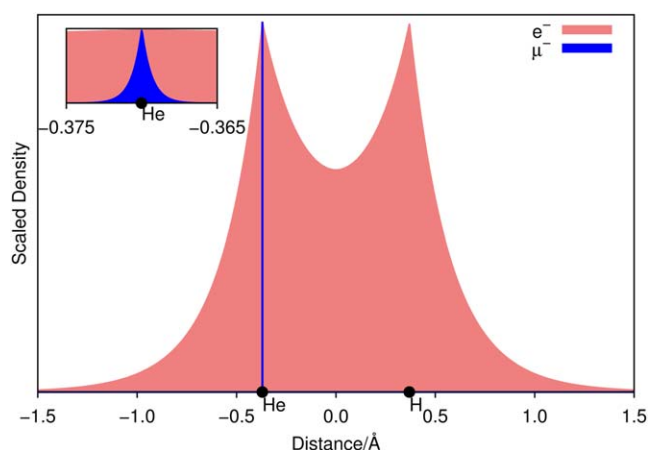

Figure 6. APMO/HF electronic and muonic densities of a $He\mu H$ molecule. Densities were scaled to share the same maximum. The muon density is zoomed at the upper left corner box.

In our latest study, we have compared the electronic ionization potentials of isoelectronic muonic and all-electron atoms

at the full-CI level.[52] We found that the differences in the ionization potentials are only of the order of meV. Furthermore, we found that the difference in nuclear masses and the incomplete screening of the muon account for the observed discrepancies. Therefore, from these calculations we conclude that muon–electron correlation as well as the muon relaxation energy is negligible upon the removal of an electron. In addition, we quantified the partial muonic screening effect for the $H_2 + {}^4He\mu$ reaction[52] by comparing our calculated energy barriers with those obtained considering infinite nuclear masses $H_2 + H$. We observed that the partial muonic screening reduces the energy barrier by 0.8 meV. Although this effect is very small for most chemical applications, it should be considered for precise calculations aiming for spectroscopic accuracy.

Positrons Chemistry. We have calculated the APMO/EP2 positron binding energies of the 20 standard amino acids considering three different molecular conformations: classical, H-bonded, and zwitterion (Charry et al., Chem. Phys. Lett. in preparation). Our results are in good qualitative agreement with those of Tachikawa and coworkers.[77] An analysis of these results reveals that positron binding energies and densities vary dramatically among the different conformers. Figure 7 depicts APMO/HF positronic (in red) and electronic (in blue) densities of a positronic glycine zwitterion. As observed in this figure, positron density is very delocalized throughout the molecule.
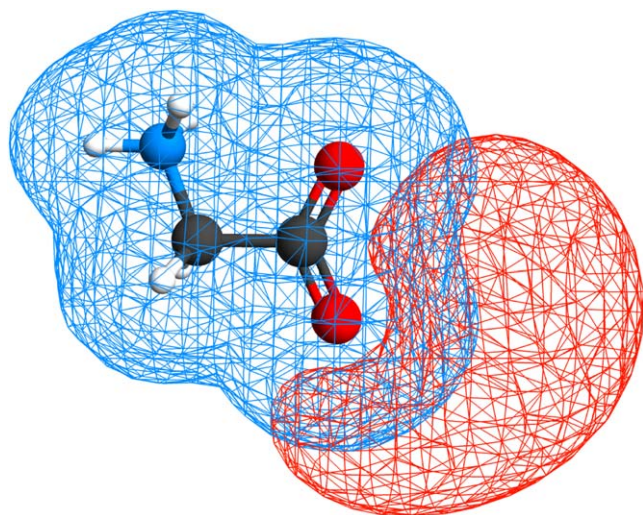

Figure 7. APMO/HF electronic (in blue) and positronic (in red) density plots for the positronic glycine zwitterion. A contour value of 0.001 was employed.

Perspective

LOWDIN code stands out as a versatile platform for the efficient computational implementation of new theories and for the quantum calculation of properties of regular and exotic molecular systems. At the programming level, electronic structure modules are generalized to an APMO framework using the OOP capabilities. From the theoretical and computational perspectives, these extensions entail new challenges.

One is the poor description of translations and rotations by Gaussian-type functions basis functions in the NMO method, which leads to the appearance of spurious terms in the multispecies Hamiltonian. We are currently working on removing these contaminations by implementing the schemes developed by Nakai.[34,78,79] Closely related is the possibility to implement basis set free molecular orbital calculations.

A second challenge is the interspecies correlation, in particular, when charges of the particles under consideration have different signs. In those cases, multiconfigurational[64] or explicitly correlated schemes[80] should be employed for accurate calculations. Both schemes are currently explored in our groups.

The convergence of the multispecies SCF presents another challenge. While electronic calculations take about 20 to 50 SCF cycles, multispecies calculations usually take from 100 to 1000, regardless of the iteration scheme chosen. New convergence schemes need to be explored for such cases.

Of special interest is the inclusion of temperature and solvent effects. We are working on the implementation of a temperature dependent SCF and propagator methods aiming for the direct calculation of temperature corrected acid/base and redox chemistry properties.

In its current stage, the LOWDIN program can handle SCF calculations of more than 100 atoms.[43] With the aim of studying larger systems, we are porting LOWDIN to graphics processing units (GPUs). We hope that combining the above strategy with the implementation of fragments and quantum mechanics/molecular mechanics (QM/MM) techniques, the calculation of systems of biological interest will be possible.

Finally, LOWDIN binaries can be requested for academic use.

Keywords: nuclear quantum effects · isotope effects · APMO method · exotic molecules · propagator method

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