POSITRON AND POSITRONIUM CHEMISTRY BY QUANTUM MONTE CARLO

Massimo Mella[a†], Simone Chiesa[†], Dario Bressanini[‡], and Gabriele Morosi[‡]
[†] *Dipartimento di Chimica Fisica ed Elettrochimica,*
Universitá degli Studi di Milano,
via C. Golgi 19, 20133 Milano (Italy)
[a] *Electronic address: massimo.mella@unimi.it*
[‡] *Dipartimento di Scienze Chimiche, Fisiche e Matematiche,*
Universitá dell'Insubria,
via Lucini 3, 22100 Como, Italy

Abstract Positronic compounds represent a unique family of systems whose chemical and physical properties are tightly related to the correlated motion of positrons and electrons. For this class of systems, standard *ab initio* quantum chemistry methods are often of little use in computing observables. Starting from this observation, we present quantum Monte Carlo (QMC) methods as an useful and accurate set of tools to study the leptonic structure of positronic atoms and molecules. Moreover, we show the information that can be routinely obtained from Monte Carlo simulations presenting specific examples and applications to atoms and molecules. Finally, an overview of the directions that we feel are worth pursuing is given.

1. INTRODUCTION

In the last years, the applications of positrons and positronium (Ps) atoms have widely spread out due to their ability to probe various features of the ordinary matter, specially in the fields related with condensed matter science, chemistry, and physics. This interest might be better represented by the large amount of papers and monographs published on these issues. For instance, basic and advanced uses of positrons and Ps in chemistry are well described by Mogensen [1], covering from basic physical information on positrons and positronium atoms up to complex applications. We cite as examples Ps reactions in solution, positron annihilation in molecular solids, and Ps trapping in glassy materials. Another field of applications is positron annihilation in semiconductors, a powerful tool to study point defects in the structure of these technologically important solids [2].

While those two books are just examples of the possible use of positrons and Ps atoms, a more complete bibliography can be found in the paper by Schrader [3].

Although the mass of experimental data and applications of positrons and positronium atoms is growing incredibly fast, much less effort has been devoted to the theoretical understanding of the complex interactions that take place between ordinary matter and positrons. More specifically, only few calculations on the bound states of positron containing systems has been published, and this fact is well emphasized in the chapter by Schrader in this book. The information provided by these calculations is fundamental to understand which level of theory, i.e. which specific method, could be used to describe these exotic systems in order to predict their properties and behaviors. While it is well known that these systems are correctly described by means of non-relativistic Quantum Mechanics (see for instance Ref. [1] and Ref. [3]), their features are poorly accounted for by standard *ab initio* Quantum Chemistry methods. We feel this is one of the main reasons of the lack of theoretical work on positronic compounds.

Following the direction set by Schrader [3], in this chapter we develop the thesis that for positron containing systems quantum Monte Carlo (QMC) methods are superior to any standard Quantum Chemistry method both in efficiency and accuracy. Moreover, for small systems QMC theoretical tools can obtain an accuracy comparable to explicitly correlated wave function methods, showing therefore the usefulness of these approaches [4].

The outline of this chapter is the following. In Section I, after presenting some of the observables that are worth to compute, we give some of the mathematical reasons why the *ab initio* methods fail to correctly predict them, and how explicitly correlated wave functions and QMC methods are able to correct these deficiencies. In Section II, a description of the QMC methods is presented in order to make them familiar to the reader and to discuss advantages and drawbacks. These are important issues in dealing with large and complex systems, where computational cost and efficiency are of great concerns. Section III reviews some of the numerical results already published. Finally, Section IV is devoted to illustrate our views about the developments that should be pursued in order to better understand the positron chemistry, making the QMC methods a complete tool to deal with positron complexes, and how they could be used to improve some of the approximate methods currently used in the theoretical positronic community.

1.1. EXPERIMENT-THEORY CONNECTION

Since the equations needed to correctly connect experiments and theory have been already presented in the literature (for instance, see Ref. [1], Ref. [3], and the Chapter by J. Mitroy *et al.*), we only summarize the main results in order to set the stage for the following sections.

From basic ideas, it is well known that all the stationary properties of an atomic or molecular positronic system can be computed using non-relativistic Quantum Mechanics, hence by solving the Schrödinger equation. Having an exact wave function Ψ, it is possible to compute all the interesting mean values using

$$\langle O \rangle = \frac{\int \Psi(\mathbf{R}) O \Psi(\mathbf{R}) d\mathbf{R}}{\int \Psi(\mathbf{R})^2 d\mathbf{R}} = \frac{\int \Psi(\mathbf{R})^2 O_{loc} d\mathbf{R}}{\int \Psi(\mathbf{R})^2 d\mathbf{R}} \quad (1)$$

where $O_{loc} = O\Psi(\mathbf{R})/\Psi(\mathbf{R})$ is the local form of the operator O. Here, $\Psi(\mathbf{R})$ must also be an eigenfunction of the two spin operators S^2 and S_z of the system.

Unfortunately, there is no standard way to solve the Schrödinger equation, and exact solutions are known only for simple model systems (it is worth to mention that the Ps atom is one of those!). This fact forces to seek for approximate solutions, i.e. to look for a trial wave function $\Psi_T(\mathbf{R})$ able to mimic the exact $\Psi(\mathbf{R})$. Of course, this introduces a systematic error in the mean values obtained using Eq. 1 when $\Psi_T(\mathbf{R})$ is substituted to $\Psi(\mathbf{R})$. This error will eventually be reduced upon increasing the "flexibility" of the trial wave function in reproducing the correct form of Ψ. Often, $\Psi_T(\mathbf{R})$ contains a set of parameters that must be chosen in order to approximate the quantum state we are interested in. This task is usually accomplished "optimizing" some cost function (for instance the mean energy $\langle H \rangle$, or its variance $\langle H^2 \rangle - \langle H \rangle^2$). This choice introduces the problem of computing the relevant integrals to obtain these two mean values, a non trivial problem that is usually circumvented introducing the orbital approximation [5].

Once a trial wave function has been optimized, Eq. 1 can be used to compute an approximation to $\langle O \rangle$ substituting Ψ with Ψ_T. This mean value, namely $\langle O \rangle_T$, differs from $\langle O \rangle$ by an amount that is first order in the difference $\Psi - \Psi_T$ if O does not commute with H. Among the interesting observables to compute for an e^+ complex, we cite the mean electron-electron $\langle r_{ij} \rangle$ and the electron-positron $\langle r_{ip} \rangle$ distances, the positron and electron densities, and the expectation value of the Dirac's delta over electron-positron distances $\langle \delta(r_{ip}) \rangle$.

The interest in computing $\langle \delta(r_{ip}) \rangle$ comes from its direct proportionality to the 2γ photon *spin-averaged* annihilation rate $\Gamma_{2\gamma}$ [6], i.e. the rate of the positron-electron annihilation *reaction* producing two γ photons.

Since a more formal and complete derivation of this important observable is given in the Chapter by Mitroy *et al.*, we restrict ourselves to this brief and schematic presentation.

1.2. STANDARD *AB INITIO* QUANTUM CHEMISTRY METHODS

During the last years, few groups have paid attention to the problem of the stability and annihilation rate of positronic atoms and molecules using standard *ab initio* methods like Self Consistent Field (SCF) [7-11], many body Perturbation Theory (MBPT) [12-14], and Configuration Interaction (CI) [15-20]. In spite of several successes in predicting the stability for various positronic atoms and molecules, these methods generally failed to compute accurately both binding energies and other expectation values for systems having more than two electrons. For instance, the positronic affinity (PA) of the polar molecules LiH, LiF, and BeO was mistakenly believed to depend only slightly on the correlation between the electrons and the positron [11]. This idea was proved to be incorrect for LiH by means of a CI calculation including only single and double excitations (CISD) [16], showing the PA for this system to be at least three times larger than the one computed using SCF methods. The misbelief was based on the fact that the positronic orbital in e^+LiH had a smaller overlap with the electronic orbitals in LiH than the excess electron orbital in LiH^- [11] does. When introduced in the second order MBPT to estimate the correlation energy between the excess lepton and the LiH electrons, the smaller overlap of the positronic orbital gives rise to a smaller contribution than the excess electron. Unfortunately, this estimate did not take into account the possibility of a large change in the electron density due to positron. More recent calculations using explicitly correlated wave functions [21, 22], settled the problem changing again the overall picture for this light system: the computed vertical PA, roughly 34 mhartree, turned out to be two times larger than the previous CI result (i.e. six times larger than the SCF PA), and the overall positron density was quite different with respect to the SCF one. Trusting this analytical result, one is forced to deduce that even MO correlated methods like CISD are not powerful enough to give accurate predictions of both energies and densities. Things get worser if one tries to compute $\langle\delta(r_{ip})\rangle$, these expectation values showing an incredibly slow convergence pattern [15, 19] towards the exact result. The mathematical reason for this unlucky behavior was already pointed out by Hylleeraas [23] in the early 30's, and it is due to the local analytical form of the exact wave function. In fact, it can be proved [24] that this must have a "cusp" when two charged particles collide, a feature that *ab initio* wave functions do not have.

Concluding, although standard Quantum Chemistry techniques are plagued by the aforementioned deficiencies, we feel it is fair to look at them as exploratory tools. They appear to be able to give some guidance on choosing candidate systems to be studied with more accurate and computationally expensive methods, and therefore we feel it is worth to better explore their capability on medium size atomic or molecular positronic complexes.

1.3. OTHER METHODS: A QUICK COMPARISON

To complete the presentation of the various computational methods that have been employed so far to study positronic systems, this section is devoted to introduce explicitly correlated wave functions and Density Functional Theory (DFT).

As far as the use of explicitly correlated wave function is concerned, highly accurate results have been obtained for small systems containing up to five active particles [25]. The advantages of this approach with respect to the Molecular Orbital *ab initio* methods is given by the possibility to introduce "explicitly" the inter-leptonic distances in the form of the wave function.

Historically, the first correlated basis functions were proposed by Hylleraas [23], and contained both even and odd powers of the inter-particle distances. For this basis set, widely used by Yan *et al.* [26] and Büsse *et al.* [27] for three and four electron atoms, the computational cost of the integrals needed to compute the energy is quite high, discouraging the application of the method to larger systems. We feel this is the main reason why no attempts have been made to carry out accurate calculations on positronic systems larger than PsH [28, 29]. Moreover, Strasburger [30] has recently shown that Hylleeraas functions are not the most appropriate basis functions to cope with positron complexes.

A better basis set is represented by explicitly correlated Gaussian (ECG) functions [31-33], where the explicit dependence on r_{ij} is given by the Gaussian form $\exp(\alpha r_{ij}^2)$. This analytical form is able to build the "pile up" of the electron density over the positron positions, and to correctly describe the formation of a virtual Ps complex inside the system [30]. This fact, together with the fast calculation of the integrals needed to compute the mean energy, has pushed the use of these functions to obtain "state of the art" results for small atomic and molecular systems [21,34-36]. For instance, using this approach Ryzhikh *et al.* [37] and

Strasburger and Chojnacki [38] were able to show that e^+Li is a stable system with respect to the break up in the two fragments Ps and Li^+. Among the studied systems with this approach we cite e^+Na, e^+Be, e^+Mg [34], e^+Cu [39], e^+Zn [40], LiPs, NaPs [34], KPs [41], and CuPs [19].

Another route that has been taken to tackle the problem of describing positron complexes is represented by the two-component density functional theory (DFT) [42]. Unfortunately, the exact functional is unknown, and so one is left with the problem of approximating its form [43, 44], a task that may be accomplished exploiting both ECG amd QMC accurate results. Nevertheless, this technique is routinely applied to positrons in solids, with a special emphasis on computing properties of the positronic state when a point defect is present [45]. Moreover, this approach has also been used to compute positron and positronium affinities of first and second row atoms [46, 47], showing for those cases scarce accuracy [48].

2. QUANTUM MONTE CARLO METHODS

Recently, QMC methods were proposed as an alternative approach to accurately describe properties of positronic compounds. During the last two decades these methods have shown to be quite efficient in computing accurate energies and expectation values for ordinary electronic systems. We feel this ability comes from two main reasons. First, the possibility to employ *any* analytical form for the trial wave function Ψ_T so that physically sounded forms can be chosen. Secondly, the fact that with these techniques it is possible to recover the "exact" solution of the Schrödinger equation in a statistical meaningful way.

These two features of the QMC methods allow one for an easy cure of many of the problems that *ab initio*, explicitly correlated functions, and DFT techniques present.

Since the basis of the techniques have been accurately presented in many books [49-51], and applications to ordinary electronic compounds have been recently reviewed [52-54], we refer the reader to the literature for a complete introduction to these numerical tools. Nevertheless, since applications to positron containing complexes have been pursued only during the last five years, we briefly present the methods with the aim to stress the features connected to this class of systems. This information is important in order to discuss advantages and drawbacks of the methods, and to propose improvements and corrections.

For a pedagogical purpose, we split the presentation in two parts, the first dealing with variational Monte Carlo (VMC) method and the second with the diffusion Monte Carlo (DMC) one.

2.1. VARIATIONAL MONTE CARLO: FLEXIBILITY

VMC technique merges Monte Carlo integration [55, 56]) with the energy Variational Principle [57]. It is basically a statistical method to compute quantum expectation values once an approximate wave function Ψ_T is given. More specifically, VMC allows one to obtain a statistical estimate of the quantity

$$\langle O\rangle_T = \int f(\mathbf{R})O_{loc}d\mathbf{R} \approx \frac{1}{N_s}\sum_{k=1}^{N_s} O_{loc}(\mathbf{R}_k) \tag{2}$$

where $f(\mathbf{R}) = \Psi_T(\mathbf{R})^2$ is a normalized probability distribution of the random variable $\mathbf{R}$, and $O_{loc}(\mathbf{R}_k)$ is the numerical value of the local operator O_{loc} at the point $\mathbf{R}_k$ in configuration space. In the right-hand side of Eq. 2 the N_s points $\mathbf{R}_k$ are distributed in such a way to "sample" the distribution f: if an infinite number of points were drawn and collected, their density would reproduce the form of the distribution f [58].

Since we are restricted to sample only a finite number N_s of points, Eq. 2 represents only an estimate of the exact value of the integral. It can be shown [55] that the statistical error in estimating $\langle O\rangle$ using Eq. 2 decreases following $(N_s)^{-1/2}$ for large N_s. This error is also proportional to the square root of the variance of $O_{loc}(\mathbf{R})$ over the distribution f, i.e.

$$Var(O) = \int f(\mathbf{R})O_{loc}^2 d\mathbf{R} - \left[\int f(\mathbf{R})O_{loc}d\mathbf{R}\right]^2 \tag{3}$$

if $Var(O)$ is bound. Differently, although the mean value in Eq. 2 might still exist, it is no longer possible to give an estimate of the error, and the result of the Monte Carlo integration might be difficult to interpret. It is interesting to note that the statistical error of the estimate does not depend explicitly on the dimensionality of the configurational space, but only on the properties of the local operator via $Var(O)$, and on the number of sampled points. When the dimensionality D_s of the problem grows, this property makes Monte Carlo integration advantageous with respect to ordinary lattice methods, that, to achieve a chosen error, require a number of points that grows exponentially with D_s. As a rough estimate, Monte Carlo integration beats lattice methods already when $D_s = 4 \sim 6$, especially for non smooth functions.

If $O_{loc} = E_{loc} = H\Psi_T/\Psi_T$, Eq. 2 and Eq. 3 allow to compute the mean energy and its variance, and so to *optimize* a trial wave function Ψ_T in order to obtain the "best" possible description for a given system. Specifically, both $\langle H \rangle$ and $Var(H)$ have their minimum value if and only if Ψ_T is the exact wave function. Therefore, minimizing $\langle H \rangle$ and $Var(H)$ is a way to improve the form of the trial wave function. If Ψ_T depends on a set of parameters $\mathbf{p}$, the optimization is carried out varying these parameters in order to find a minimum in $\langle H \rangle$ or $Var(H)$.

It is worth to stress that *any* form for Ψ_T may be chosen, as long as the integrals in Eq. 2 and Eq. 3 are bound. Therefore, it becomes possible to use trial wave functions that have the explicit dependence on the inter-particle distances. For instance, a linear term of the form $1+\alpha r_{ij}$ can be used to improve the description of the electronic correlated motion, while a term of the form $\exp(-\alpha r_{ip})$ may do the same job for electron-positron pairs [59]. Unfortunately, the direct application of the Variational Principle to the optimization task, i.e. computing $\langle H(\mathbf{p}) \rangle$ (or its variance) for various set of parameters and choosing the one that minimize it, represents a computationally demanding task. To overcome this difficulty many different approaches have been developed, the most used being a "fixed sample" optimization of the variance of local energy. The variance minimization was introduced by Frost [60] and Conroy [61], and subsequently developed by Umrigar *et al.* [62] into a practical method for wave function optimization based on the minimization of the estimate of $Var(H)$ over fixed set of configurations sampling Ψ_T^2. This is possible since the Variational Principle for $Var(H)$ is preserved even if it is estimated using only a small number of configurations [63]. Although it is a fast and compact method, the minimization of the variance of the local energy has some major drawbacks [64-66]. First of all, it is not always true that by minimizing the variance the energy decreases. This is an important point when energy differences have to be computed to obtain binding energies and leptonic affinities. Secondly, although it can be analytically proved that for an atomic or molecular system $Var(H)$ is always bound, this is not true for its variance, unless *all* the cusp conditions for the wave function are exactly satisfied. Although plagued by these defects, fixed sample optimization of $Var(H)$ has produced fairly accurate wave functions for systems up to 100 electrons [52].

A globally better approach would be the minimization of the energy for a given wave function form, a task routinely accomplished in *ab initio* methods. Unfortunately, fixed sample optimization of the energy is not a stable procedure when a finite number of configurations is used, since the energy Variational Principle holds only if the integrals are exactly computed. To overcome this problem when the wave function contains many parameters, few methods have been developed and tested in the last few years. Among these we cite the Newton-Raphson method proposed by Lin *et al.* [67] where both the gradient and the Hessian of $\langle H(\mathbf{p})\rangle$ over the parameters $\mathbf{p}$ are computed analytically during a VMC simulation, and the stochastic gradient approximation tested by Harju *et al.* [68] that appears to be able to handle correctly the intrinsic statistical noise of the energy calculation. Although these methods have shown to be practically useful for some model systems [66], a lot of work can still be done to improve their performances [69]. This is an extremely important goal, since optimizing the energy is now known to produce wave functions whose properties are on the average more accurate than the ones obtained from variance optimized wave functions [66, 70, 71].

In conclusion of this section it remains to be pointed out that, similarly to any method based on the Variational Principle, the total accuracy of the VMC is constrained by the quality of the trial wave function employed. To go beyond these limits, we now move to a different approach that appears to be able to correct deficiencies of Ψ_T with only a small increase of computational cost.

2.2. DIFFUSION MONTE CARLO: THE QUEST FOR ACCURACY

Introducing the diffusion Monte Carlo (DMC) method it is customary to start from the time dependent Schrödinger equation and make the Wick's rotation $\tau = it$ so that this differential equation reads

$$\frac{\partial\Psi(\mathbf{R},\tau)}{\partial\tau} = \sum_i \frac{\nabla_i^2}{2m_i}\Psi(\mathbf{R},\tau) - V(\mathbf{R})\Psi(\mathbf{R},\tau) \tag{4}$$

where $V(\mathbf{R})$ is the interaction potential.

Although we leave the analytical form of the interaction potential undefined as a way to stress the ability of Monte Carlo to cope with any local potential, we point out that the quality, accuracy and stability of the method strongly depend on the specific potential [72-74].

For the case of a function Ψ everywhere positive, the previous equation is formally equivalent to a classic diffusion process with sink and source terms depending on the position $\mathbf{R}$ in space [75, 76]. Actually, it was this formal equivalence that led to the first implementation of a DMC algorithm [75].

Equation 4 can be recast in integral form

$$\Psi(\mathbf{R}', \delta\tau + \tau) = \int d\mathbf{R} G(\mathbf{R} \rightarrow \mathbf{R}', \delta\tau)\Psi(\mathbf{R},\tau) \tag{5}$$

where $G(\mathbf{R} \to \mathbf{R}', \delta\tau) = \langle \mathbf{R}' \mid e^{-\delta\tau H} \mid \mathbf{R} \rangle$ is the imaginary time Green's function. Substituting Eq. 5 into Eq. 4, and remembering that if $\delta\tau = 0$ then $\Psi(\mathbf{R}', \delta\tau + \tau) = \Psi(\mathbf{R}', \tau)$, it is easy to show that the Green's function is a solution of the Schrödinger equation with the initial condition $G(\mathbf{R} \to \mathbf{R}', 0) = \delta(\mathbf{R}' - \mathbf{R})$ [77]. The general solution of both Eq. 4 and Eq. 5 is given by

$$\Psi(\mathbf{R}, \tau) = \sum_{i=0} c_i \psi_i(\mathbf{R}) e^{-\tau E_i} \tag{6}$$

where ψ_i and E_i are the eigenfunctions and eigenvalues of the Schrödinger equation, and $c_i = \langle \psi_i \mid \Psi(\mathbf{R}, 0) \rangle$. This equation shows that acting with the Green's function in imaginary time τ over a starting wave function $\Psi(\mathbf{R}, 0)$ projects out all the excited states, leaving only the ground state solution for $\tau \to \infty$. If the exact analytical form of the Green's function were known, this task could be accomplished by means of the Monte Carlo method [78]. Unfortunately, the exact Green's function is known only for very simple model Hamiltonians. For systems whose ground state wave function has no nodes, the DMC theory relies completely on the ability to find a short time approximation (STA) to the imaginary time Green's function [72, 74, 76, 79]. Once this approximation is known, equation 5 can be iterated to produce an asymptotic wave function $\Psi_{STA}(\mathbf{R}, \tau \to \infty)$ [51]. Using a STA of the exact Green's function introduces a systematic difference between $\Psi_{STA}(\mathbf{R}, \tau \to \infty)$ and the exact ψ_0 for any finite $\delta\tau$, an error that is usually called "time step bias" [80]. Nevertheless, using small time steps, this error can be reduced so that the difference between the computed values and the exact ones are smaller than any chosen threshold [81].

However, it is customary to improve the efficiency and the accuracy of the DMC algorithms by means of the Importance Sampling (IS) procedure [55]. Here, an approximate trial wave function Ψ_T is introduced to guide the displacement of the configurations [82], or to modify the reaction rate by which configurations are deleted or created [78]. The IS procedure is usually carried out simulating a modified form of Equation 4 that reads [82]

$$\begin{aligned} -\sum_i D_i \nabla_i^2 f(\mathbf{R}, t) + \sum_i D_i \nabla_i \cdot f(\mathbf{R}, t)\mathbf{F}_i(\mathbf{R}) + \\ [E_r - E_{loc}(\mathbf{R})] f(\mathbf{R}, t) = -\frac{\partial f(\mathbf{R}, t)}{\partial t}, \end{aligned} \tag{7}$$

where $f(\mathbf{R}, \tau) = \Psi(\mathbf{R}, \tau)\Psi_T(\mathbf{R})$, $D_i = (2m_i)^{-1}$ is the diffusion coefficient, and $\mathbf{F}_i(\mathbf{R}) = \nabla_i \ln[\Psi_T(\mathbf{R})^2]$. In this equation E_{loc} substitutes the interaction potential V, and the new term $\mathbf{F}_i(\mathbf{R})$ adds a "drift" to the random diffusive displacement of the configurations. This has the advantage to push the configurations (a.k.a walkers) towards the regions where Ψ_T is large.

Up to now, the theory of DMC has been based on the hypothesis that Ψ in Eq. 4 and f in Eq. 7 were positive everywhere. This is not true for fermionic systems, since the wave functions must be antisymmetric under particle permutations of odd parity. A way to fix this problem is to simulate both Eq. 4 and Eq. 7 in a restricted region of space where their solutions can be thought as positive [76]. To restrict the walker propagation to such a region, the nodal surfaces of an antisymmetric trial wave function Ψ_T are used as boundary [51]. This technique is usually called fixed node diffusion Monte Carlo (FN-DMC). Since Ψ_T does not have the exact nodal surfaces of the fermionic ground state ψ_0, this method gives just an upper bound to the exact result, whose accuracy depends only on the placement of the domain boundary.

2.3. THE INTERESTING OBSERVABLES: HOW TO COMPUTE THEM

Having chosen a STA of the Green's function, one can sample $\Psi(\mathbf{R},\tau)$ or $f(\mathbf{R},\tau)$ for large values of τ iterating Eq. 5. This means that a set of configurations will end up to be distributed as ψ_0 or as $\Psi_T\psi_0$. Once this steady state is reached, all the mean values can be computed using the formula [49-51]

$$\langle O\rangle_M = \frac{\int \psi_0(\mathbf{R})O\Psi_T(\mathbf{R})d\mathbf{R}}{\int \psi_0(\mathbf{R})\Psi_T(\mathbf{R})d\mathbf{R}} = \frac{\int f(\mathbf{R})O_{loc}(\mathbf{R})d\mathbf{R}}{\int f(\mathbf{R})d\mathbf{R}} \tag{8}$$

usually called "mixed estimator". In the case where $O = H$ it is easy to prove that $\langle H\rangle_M = E_0$, that is DMC is able, in principle, to compute exactly the ground state energy.

If the operator O does not commute with the Hamiltonian, the mixed estimator returns only an approximation to the exact $\langle O\rangle$ [49-51]. Nevertheless, this value is more accurate than $\langle O\rangle_T$, and it is often regarded as *almost* exact if $(\langle O\rangle_M - \langle O\rangle_T)/\langle O\rangle_M$ is small [4].

If O is a local operator, it is possible to correct for the difference $\langle O\rangle_M - \langle O\rangle$ using algorithms that sample ψ_0^2 [83-86]. This option is important for all the systems whose exact wave function is difficult to mimic or to optimize, allowing one to obtain quite accurate inter-particle distribution functions and mean values.

For systems that contain a positron it is always interesting to compute the mean value over $\delta(r_{ip})$. The calculation of this observable is recognized as a though problem for every Monte Carlo method [4, 87, 88]. This is due to the fact that they just *sample* the wave function, i.e. one does not have an analytical representation of ψ_0. To circumvent this problem, many different approaches have been proposed in the past. They range from approximating the Dirac's delta by means of a normalized Gaussian [4, 89] or a small sphere [90], to resorting to differential equalities from distribution theory [87, 88, 91]. Although all these methods have encountered a partial success in computing this important mean value, they are plagued by many deficiencies. Since most of them are pretty technical, we avoid to bore the reader with long discussions. Instead, we simply state that some of the major problems in carrying out those calculations are due to the difficulty that Monte Carlo faces in sampling inter-particle radial distributions in the small distance regions, and in estimating $\langle r_{ip}^{-2} \rangle$ whose variance diverges [92, 93]. More specifically, the sampled radial density in regions close to a chosen point in space (e.g. $r_{ip} = 0$) usually shows smaller values than the true ones, and this problem is made worse by the presence of a local cusp in the density [79].

3. APPLICATIONS TO ATOMS AND MOLECULES

3.1. POSITRONIC ATOMS: WHAT CAN WE LEARN FROM THEM?

Historically, the first application of QMC to positronic systems aimed at the study of the stability of the positronium complex with chlorine [94] using model potentials. More recently, calculations on Ps complexes with hydrogen and first-row atoms were carried out employing both DMC and VMC techniques. As to the smallest member of this family, namely PsH, many accurate DMC calculations of energy and annihilation rate have been published in the last five years. The values by Yoshida and Miyado (E=-0.789(1) hartree) [95], Harju *et al.* (E=-0.7885(5) hartree) [96], Bressanini *et al.* (E=-0.78917(1) hartree) [91], Jiang and Schrader (E=-0.78918(5) hartree) [90], and Mella *et al.* (E=-0.78916(3) hartree) [4] are in optimal statistical agreement with the most accurate analytical results (E=-0.78919 hartree [34, 97, 98]), showing both the accuracy of the method and its ability in handling this class of systems. Moreover, PsH has been used by Jiang and Schrader [90] as a model system to present a correction to the standard Second Order Estimate formula for an observable whose operator does not commute with the Hamiltonian [49, 50].

As far as the first-row atoms are concerned, all the published calculations employed the following analytical form for Ψ_T

$$\Psi_T = Det\,|\phi_\alpha|\,Det\,|\phi_\beta|\,e^{U(r_{ij})}\Omega\left(\mathbf{r}_p, r_{ip}\right) \tag{9}$$

$\phi_{\alpha,\beta}$ are orbitals and $e^{U(r_{ij})}$ is the electronic correlation factor used by Moskowitz and Schmidt in their works on atoms and ions [99, 100]. In Eq. 9

$$\Omega\left(\mathbf{r}_p, r_{ip}\right) = \sum_{l=1}^{N_{terms}} c_l \Phi_l\left(\mathbf{r}_p, r_{ip}\right) \tag{10}$$

where [89, 101, 102]

$$\Phi_l\left(\mathbf{r}_p, r_{ip}\right) = f_l(\mathbf{r}_p)\exp(k_{l,1}\sum_{i=1}^{N} r_{ip} - k_{l,2} r_p) \tag{11}$$

Here, the correlation between the electrons and the positron is described by means of Φ_l in Eq. 11, where the distances r_{ip} explicitly appear. $k_{l,1}$ and $k_{l,2}$ are optimizable parameters in every $\Phi_l\left(\mathbf{r}_p, r_{ip}\right)$ function.

Table 1 summarizes the numerical results, obtained by various groups, for the binding energy (BE) of Ps to the atom A, and the positron affinity (PA) for the atomic anion A^-. Be and N were excluded since they do not bind an electron in their ground state.

In Table 1, "SCF corrected" means that the BE was computed using the equation

$$\mathrm{BE} = \mathrm{EA}_{\mathrm{exp}} + \mathrm{PA}_{\mathrm{SCF}} - \frac{1}{4} \tag{12}$$

where the experimental value of the electron affinity (EA) was used instead of the computed SCF one. Since SCF misses all the correlation contribution to the energy, PA_{SCF} underestimates the exact PA. This suggests that the BE computed by Eq. 12 is a conservative estimate, i.e. it is just an upper bound to the exact BE.

As the results in Table 1 show, DMC [48] gives larger PA's and BE's than any other method, except for the ECG calculation on LiPs presented in the Chapter by Mitroy *et al.*, and the data computed by a DFT method including correlation between electron and positron [46]. The same method, without the inclusion of positron-electron correlation, gives results similar to standard SCF techniques, therefore showing the results to be strongly dependent on the accuracy of the correlation potential.

While the stability of PsF was an almost accepted fact [9, 105], DMC results showed that also other PsA systems (A = Li, C, and O) in their

System		BE	PA
LiPs ^1S			
	SCF [9]	-0.153	0.102
	SCF Corrected [9]	-0.106	
	DFT [103]	-0.148	0.102
	DFT [46]	0.098	0.325
	DMC [96]	-0.011(4)	0.222(4)
	DMC [95]	0.028(5)	0.256(5)
	VMC [48]	-0.2248(3)	0.0169(6)
	DMC [48]	0.0096(8)	0.2391(8)
	SVM-ECG [34]	0.012096	
	FCSVM [34]	0.012341	
PsB ^2P			
	SCF [9]	-0.126	0.134
	SCF Corrected [9]	-0.106	
	DFT [103]	-0.126	0.129
	DFT [46]	0.108	0.352
	VMC[48]	-0.098(2)	0.141(2)
	DMC [48]	-0.016(1)	0.221(1)
PsC ^3S			
	SCF [9]	-0.078	0.152
	SCF Corrected [9]	-0.051	
	DFT [103]	-0.066	0.148
	DFT [46]	0.159	0.398
	VMC [48]	-0.043(3)	0.160(3)
	DMC [48]	0.0176(6)	0.2183(6)
PsO ^1P			
	SCF [9]	-0.096	0.174
	SCF Corrected [9]	-0.062	
	DFT [103]	-0.072	0.168
	DFT [46]	0.249	0.398
	VMC [48]	-0.116(3)	0.084(3)
	DMC [48]	0.0159(6)	0.2154(6)
	DMC [104]	0.0289(64)	0.2283(63)
PsF ^2S			
	SCF [9]	-0.016	0.184
	SCF Corrected [9]	0.061	
	DFT [103]	0.009	0.177
	DFT [46]	0.352	0.435
	MBPT [13]	0.082	0.208
	MP–DMC [105]	0.072(6)	
	VMC [48]	0.078(3)	0.195(3)
	DMC [48]	0.1043(8)	0.2267(8)

Table 1. Positronium Binding Energy and Positron Affinity (hartree) for the positron complexes of Li, B, C, O, and F anions.

ground states are stable against the dissociation in the neutral atom and Ps. This behavior was found only in Ref. [46]. Moreover, the stability of PsO was already postulated in Ref. [8], but without giving any definitive numerical evidence. PsB in its ground state is found to be unstable when compared with its dissociation threshold.

Although all the DMC results for PsH were in excellent statistical agreement, discrepancies are present for the complexes LiPs, PsO and PsF. While the differences in DMC BE and PA for PsF can be easily explained by the fact that in Ref. [105] model potential were used to eliminate core electrons, the results for LiPs and PsO require a more careful examination. Taking PsO as an example, from Table 1 it is clear that the result by Jiang and Schrader [104] has a larger statistical uncertainty than the one by Bressanini *et al.* [48]. Doubling these two values to obtain a more conservative estimate of the statistical error, it is easy to see that the two energies are statistically consistent.

From Table 1 it is possible to notice that all the DMC PA's appear to be only slightly dependent on the atom, and close to the Ps ground state energy, namely -0.25 hartree. It is possible to understand this outcome postulating that the structure of the positronic complexes can be mainly described by a Ps bound to the atom A by means of polarization forces. This view is consistent with the heuristic model by Mitroy *et al.* [106], a model supported by the results obtained computing energies and electron-positron distributions on a single-electron model atom as a function of its ionization potential.

It is also worth to mention that VMC gives negative values for BE for all the systems except PsF. We believe this difficulty to be due to the inability of Ψ_T to correctly introduce the correlation between the electrons and the positron when only Ω (Eq. 10) is optimized minimizing $Var(E_{loc})$ [48]. This idea is supported by the small values of the computed $\langle\delta(r_{ip})\rangle_T$, quite similar to the SCF ones [9], and by the fact that the parameters $k_{l,1}$ were quite small after the optimization.

Since a similar wave function gave quite accurate results for PsH although the electronic part was kept equal to an optimized function for H^- [107], we feel this outcome is due to two different reasons. First of all, the correlation between positron and electrons is described by a simple exponential function whose parameter k_l does not depend on the distance from the nucleus. Secondly, not optimizing the determinatal part of Ψ_T forbids the electron density to relax and build the virtual Ps complex in the valence region.

These two explanations are supported by the VMC results obtained for e^+Li and LiPs when more flexible wave functions were fully opti-

	VMC [108]	DMC [108]	SCF [11]	CI [16]	CNDO [109]
LiH	0.0055(6)	0.0333(4)	0.0059	0.0170	0.0165
HF	0.0017(35)	0.0016(16)			-0.0308
H_2O	0.0038(31)	0.0016(13)			0.0033
BeO	0.0191(28)	0.0280(18)	0.0110		-0.0400
LiF	0.0047(17)	0.0174(13)	0.0066		-0.0297

Table 2. Vertical Positron Affinity (PA) (hartree)

mized [4]. Unfortunately, it does not appear possible to extend such an approach to larger systems due to the computational cost.

Summarizing this Section, we would like to stress the overall accuracy of the DMC method in computing energies for positronic atoms. However, some methodological improvements are needed in order to make VMC an effective method for first and (hopefully!) second row atoms.

3.2. POSITRONIC POLAR MOLECULES: LARGE CORRELATION EFFECTS AT PLAY

Having shown the accuracy of DMC on atomic complexes, this method was applied to the calculation of the ground state energy of the complexes e^+LiH, e^+LiF, e^+BeO, e^+HF, and e^+H_2O [108]. Already SCF calculations had found the first three positronic molecules bound [11], while for the last two there were only semi-empirical calculations [109]. Due to the small number of electrons, LiH is likely to become the benchmark system to test methods for computing bound positron-molecule complexes (see for instance Ref. [21, 22]). Moreover, nonadiabatic calculations using ECG have already proved the global stability of this seven-particle system with respect to any dissociation channel [110], showing a large increase of the average nuclear distance and of the annihilation rate with respect to the minimum energy geometry of the Born-Oppenheimer surface.

Table 2 shows the vertical VMC and DMC PA results obtained using a Ψ_T of the form given in Eq. 9, together with results from previous *ab initio* and semi-empirical calculations.

For these systems, the stability of the positronic complex versus the M^+ plus Ps dissociation threshold is assured by the large ionization potential of the neutral parent M (IP>0.25 hartree). Examining the numerical results of e^+LiH, e^+LiF, and e^+BeO, it strikes the large increase

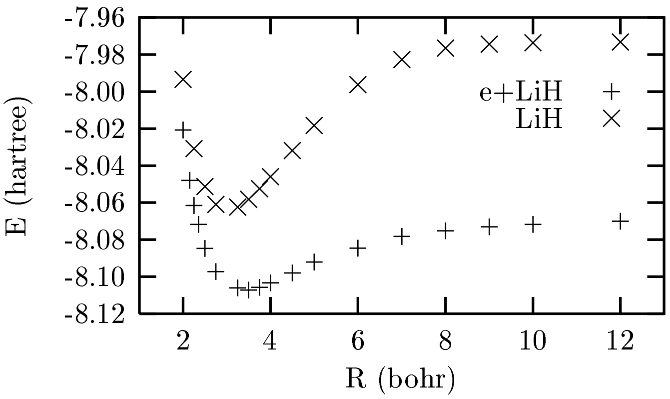

Figure 1. Potential Energy curves for e^+LiH and LiH

of the PA on going from SCF to a correlated method, a result that was anticipated in previous Sections.

Besides this large effect on E, the correlation between e^+ and e^- in these systems can play an important role in defining other molecular quantities like the equilibrium distance, the dissociation energy and the vibrational spectrum. For instance, a DMC calculation of the potential energy curve of e^+LiH [111] showed a large increase of the equilibrium distance (3.458 bohr) with respect to LiH (3.015 bohr), and a strong red shift of the infrared spectrum transitions. Moreover, the dissociation energy of e^+LiH in the two fragments PsH and Li^+ is 0.0381(1) hartree, more than twice smaller than the dissociation energy of LiH. Figure 1 shows the overall behavior of the LiH and e^+LiH potential energy curves.

e^+LiH, e^+LiF, and e^+BeO complexes could become even more interesting if one is seeking for a stable positronic molecular system that could be detected by different methods than recording the 2γ annihilation. Unfortunately, the PA of LiH is larger than the dissociation energy into Ps and Li^+ [111], so that a third body is needed to dissipate the excess energy and leave the complex in a stable state. However, recent DMC calculations [112] showed the PA of LiF and BeO to be smaller than their dissociation energy, making their positronic complexes suitable candidates for a direct experimental detection.

As far as e^+HF and e^+H_2O are concerned, the DMC energies of these complexes are statistically equal to the energies of the neutral parents. A previous R-matrix calculation on e^+HF gave numerical evidence for the existence of a bound state with a PA of 0.000175 hartree [113] when R_{HF} =2.5 bohr. This value, smaller than the statistical error of our

DMC result, could be hidden in the stochastic nature of the simulations. Besides running longer calculations to reduce the statistical errors, and so verify or disprove that prediction, we feel interesting to compute the PA for both HF and H_2O dimers [114]. This would allow one to obtain a deeper understanding of the positron energetics in the condensed phase of these two polar liquids.

3.3. POSITRONIUM-MOLECULE COMPLEXES: OLD QUANTUM CHEMISTRY REVISITED

Being composed by the positron-electron pair, Ps can be seen as an ultra-light isotope of the hydrogen atom. This idea opens up a new avenue of exploration on positronic systems simply substituting one or more H atoms by means of Ps atoms. This “not only formal” replacement gives rise to interesting theoretical problems. For these systems the standard Born-Oppenheimer approximation can not be used in dealing with the positron due to its small mass. This means that non-adiabatic effects are simply not a perturbation of the Born-Oppenheimer Hamiltonian, and a complete non-adiabatic method must be used [89].

Besides of being of theoretical interest, this class of compounds has been used in explaining the quenching effect in aqueous solutions of small inorganic molecules like H_2O_2 and NH_3 [115]. Moreover, complexes between organic radicals and Ps can play a important role in explaining the fragmentation pattern of large organic molecules, as discussed by Hullet *et al.* [116], Passner *et al.* [117], and Glish *et al.* [118].

So far, DMC simulations have been used to compute energies for the Ps complexes PsOH [119, 120], PsCH, and $PsNH_2$ [120]. Among the three, PsOH has been studied using different computational techniques, namely SCF [121] and MP2 [14], but the first calculation able to show its stability was the DMC simulations by Yoshida *et al* [119].

These three systems are isotopic analogues of H_2O, CH_2, and NH_3, a series of compounds that was a benchmark of the old Quantum Chemistry. Moreover, they seemed the best candidates to be stable against the loss of a Ps fragment. This is due primarily to the open shell electronic structure of OH, CH, and NH_2 that can accommodate an extra electron, giving raise to large electron affinities.

These are shown in Table 3 together with the DMC BE and PA results on these systems.

Besides the aforementioned complexes, also the ground state of the CH_3Ps [123] and Ps_2O [104] systems have been computed. While DMC calculations on Ps_2O showed this quite exotic system to be bound with

	PA_{DMC}	BE_{DMC}	EA_{DMC}	EA_{exp} [122]
PsOH $^{2,1}\Sigma^+$[120]	0.1941(10)	0.0102(12)	0.0661(9)	0.0673
PsOH $^{2,1}\Sigma^+$[119]	0.205(5)	0.027(5)	0.068(4)	0.0673
PsCH $^{2,3}\Sigma^-$[120]	0.2200(4)	0.0161(6)	0.0461(5)	0.0456
$PsNH_2$ $^{2,1}A_1$[120]	0.2277(7)	0.0056(9)	0.0279(9)	0.0272

Table 3. Diffusion Monte Carlo Positron Affinity (PA) and Positronium Binding Energy (BE) for the complexes. FN-DMC and experimental Electronic Affinity (EA) for the molecules OH, CH and NH_2. Energies in hartree.

respect to any possible fragmentation, the numerical results for CH_3Ps were inconclusive due to the large statistical error of the simulations.

4. WHAT IS LEFT FOR THE FUTURE?

Since QMC methods are still in their infancy, they are far from being a set of tools that could be applied as a "black box" to any physical and chemical problem. Nevertheless, by means of the examples provided so far we hope to have shown their power and accuracy in dealing with positronic complexes. With all this in mind, all the previous Sections were mainly intended as a way to stimulate more applications of QMC in the field of molecular physics and quantum chemistry, a goal that can not be obtained unless some of the existing limitations of the methods are overcome. To head towards this goal, we would like to share with the reader someone of the possible directions that we feel are worthy to be pursued in the next future in the field of positron and Ps complexes calculations. This list is not intended to be exhaustive, but only to represent our views of what should be done to substantially improve our understanding of positron chemistry.

4.1. THE DIRAC'S δ MEAN VALUES

In a previous Section we discussed briefly the practical problems in computing the $\langle\delta(r_{ip})\rangle$ value using both variational and diffusion Monte Carlo. Here, we want to point out a possible way to overcome one of these difficulties, namely the incorrect sampling of the positron-electron distribution around the coalescence point $r_{ip} = 0$. The idea comes from noticing that the only ingredient needed in order to compute $\langle\delta(r_{ip})\rangle$ is the spherically averaged positron electron distribution $\rho(r_{ip})$ [92]. If this density is normalized, i.e. $\int_0^\infty \rho(r) r^2 dr = 1$, then it can be easily shown that

$$\langle \delta(r_{ip}) \rangle = \rho(0) \tag{13}$$

Although this fact alone does not solve the basic problem of the sampling around $r_{ip} = 0$ from which $\rho(0)$ could be obtained, it shows that any trick able to give a good approximation of ρ in that region could be useful to estimate $\langle \delta(r_{ip}) \rangle$. It is worth to stress that also the long range behavior of ρ is important in defining $\langle \delta(r_{ip}) \rangle$. This is due to the normalization integral of the density, where the r^2 term weights more the tail of ρ than the coalescence regions in computing the normalization factor. This does not introduce any new problem in QMC [124], so one is left only with the task of devising a good strategy to estimate $\rho(0)$.

A possibility is given by fitting $\rho(r)$ over the whole range of positron-electron distances [124]. This can be done by approximating it with a linear combination of basis functions $\rho(r) \simeq \sum_k c_k \chi_k(r)$. The coefficients c_k are computed solving the simple linear system [124]

$$\mathbf{Sc} = \mathbf{b} \tag{14}$$

where $\mathbf{S}_{ij} = \int \chi_i \chi_j r^2 dr$, and $\mathbf{b}_i = \int \chi_i \rho_{MC} r^2 dr$. Using this approach, one can exploit the fact that Monte Carlo actually samples $r^2\rho(r)$ instead of $\rho(r)$. This makes less important the poor sampling around $r = 0$, and allows to obtain accurate values for the integrals and to extrapolate the density in regions where it is poorly defined.

Although this method is inherently approximate, it might be accurate enough to compare with experimental data [124], and to predict the $\Gamma_{2\gamma}$ annihilation rate for many interesting complexes. Moreover, analytic results on the behavior of the exact wave function can be introduced in this recipe without making it more complex [104], and perhaps improving its global accuracy.

4.2. EXPORTING METHODS TO LARGER ATOMS AND MOLECULES

Presenting the results on first-row positronic atoms and molecules, we have mentioned some deficiencies of the employed model wave function. These can be summarized by the inability to explicitly correlate electron-positron pairs. Therefore, one of the main tasks that remain to be performed is to improve the model Eq. 10 in order to correctly describe the physics and chemistry of these complexes at the VMC level, allowing to get better wave functions for systems larger than PsH, e^+Li, and PsLi. This will also help DMC to achieve better statistical accuracy with shorter runs [125].

As far as the PsA complexes are concerned (A being Li, B, C, O, or F), their leptonic structure is better described by a Ps atom "orbiting" around a neutral atom A than by a positron attached to A^-. This implies that a better wave function should be written as

$$\Psi_T(\mathbf{R}) = \mathcal{A}\Psi_A(\mathbf{r}_1, ..., \mathbf{r}_{N-1})\chi(\mathbf{r}_N, \mathbf{r}_p) \tag{15}$$

where $\mathcal{A}$ is the operator that antisymmetrizes electrons 1,..., $N-1$ with electron N, $\Psi_A(\mathbf{r}_1, ..., \mathbf{r}_{N-1})$ is a model wave function for atom A, and $\chi(\mathbf{r}_N, \mathbf{r}_p)$ is a function that describes both inter-particle and center of mass motion in the virtual Ps cluster. Here, only the correlation between one electron and the positron is introduced in order to simplify the theoretical development of the formalism. Although this choice might seem odd for this class of complexes where correlation energy plays a major role, they usually have BE of the order of few millihartrees with respect to the (usually) lowest dissociation threshold, namely Ps plus A [48]. In our view, this indicates that the binding of Ps to an atom is just due to polarization forces. Moreover, due to the repulsion with the nucleus, the positron is allowed to interact strongly only with the outer regions of the electronic cloud so that correlation with the remaining parts should not be so important. Similarly, PsM complexes, composed by a Ps and a neutral molecule M whose electronic affinity is small, could be described by means of Eq. 15.

Things get more complicated when dealing with positronic atoms and molecules e^+M. Here, the two lowest dissociation threshold, namely e^+ plus M and Ps plus M^+, might have similar energies and a two configuration wave function of the form

$$\Psi_T(\mathbf{R}) = \mathcal{A}\Psi_{M^+}(\mathbf{r}_1, ..., \mathbf{r}_{N-1})\chi(\mathbf{r}_N, \mathbf{r}_p) + \lambda\mathcal{A}\Psi_M(\mathbf{r}_1, ..., \mathbf{r}_N)\phi(\mathbf{r}_p) \tag{16}$$

is necessary to correctly describe the system. An heuristic guide to predict the weight λ for this two configuration function was discussed by Mitroy *et al.* [106], and it is based on the relative value of the ionization potential (IP) of M with respect to the Ps ground state energy $E_0^{Ps} = -0.25$ hartree. If $0.25 \gg IP$, the binding is primarily due to the polarization of Ps in the ion field. Conversely, the binding is due to interaction of the positron with the electron density of M, whose polarizability plays a important role in defining the PA of the atom or molecule [106]. For atoms and molecules whose IP is close to 0.25 hartree, both the configurations are relevant, and large PA or BE are expected.

The proposed trial wave functions represent only the basic ingredients we feel are needed to qualitatively describe many positronic systems. In the proposed form, many subtle aspects of positron-electron correlated motion are missing, and they may be introduced by means of DMC, or adding more correlation term to Ψ_T. Nevertheless, Eq. 15 and 16 allow one to introduce many of the mathematical properties of an exact wave function, a goal that *ab initio* methods are still far from obtaining. Moreover, a full electron approach like this one is needed when contact properties between core electrons and the positron are of interest [126].

4.3. COMPUTING SCATTERING OBSERVABLES

Before the advent of ECG functions and QMC methods that allow to deal with the bound states of positronic systems containing more than two electrons, most of the theoretical work on the interaction between positrons and ordinary matter was directed to compute scattering observables. Unfortunately, due to the mathematical complexity of the problem, accurate results are available only for really small targets like H and He [127, 128] where an explicitly correlated basis set can be used in order to satisfy all the requirements of the exact solutions. Although being really small, these two systems still represent quite complicated benchmarks for any method that is proposed to compute scattering observables. Theoretical results on larger systems are usually based on some approximate method to treat positron or positronium interaction with the target [129]. Most methods use model potentials whose accuracy is difficult to test against other more accurate theoretical results. For instance, it is worth to mention that even the scattering length for the scattering of Ps by He is not accurately known (see for a more insightful discussion the Chapter by Mitroy *et al*).

Besides phase shifts and cross sections, it is interesting to compute the annihilation parameter $Z_{eff}(k)$ [130] that represents the number of *active* electrons in the annihilation process with the incoming positron of linear momentum k. Although it was already known that molecules could have $Z_{eff}(k)$ larger than their total number of electrons N_{ele} [131], it has been shown recently that some organic molecules interacting with thermal positrons have Z_{eff} that are orders of magnitude larger than N_{ele} [132]. Although a theory [133] has been proposed, it seems necessary to carry out accurate calculations of the scattering process in order to compare with the experimental results. More specifically, the existence of meta-stable states where the positron is attached to a vibrationally excited molecule must be taken into account [133]. These states might allow the positron to remain close to the electrons of the molecules for a longer time, increasing the probability of an annihilation. For instance, Gianturco and Mukherjee [134] reported an increase of Z_{eff} at room temperature for O_2 and N_2 when coupling between the vibrational channels and the impinging positron was allowed during the calculations.

The necessity of dealing with vibrational excited states requires a computational method that is able to deal with the highly multidimensional nature of this problem, a feature that seems to rule out the possibility of using standard numerical integrations based on grid methods for molecules with more than two atoms.

Following the ideas proposed by Alhassid and Koonin [135], and by Carlson *et al.* [136], it is possible to use QMC in order to extract information about positron and positronium scattering on scatterers having an inner structure. Instead of resorting to an approximate treatment of the interaction between the target and the projectile, the QMC method introduces some approximation on the boundary conditions of the outgoing wave at large distances, recasting the problem in a bound state formalism. Specifically, the location of the first node of the outgoing wave $\sin(kr + d_s)/r$ is chosen and enforced by adding an infinite well potential for $r \geq R_{box}$, and this bound state problem is then solved by means of QMC. Here, R_{box} must be larger than the range of interaction between the target and the projectile.

Shumway and Ceperley [137] have recently developed this approach to treat exciton-exciton scattering, showing it to be quite promising.

Although this method has the same problems met by standard QMC in bound state calculations, it represents a novel way to get accurate values about interesting systems, and to test less accurate but more applicable techniques. Moreover, the use of e^+ and Ps as probes in many fields of condensed matter theory is somehow hindered by the scarce knowledge on scattering and transport properties of these two species, so it is worth to head for the development of this method.

4.4. POSITRON AND POSITRONIUM CALCULATIONS IN CONDENSED MATTER

As previously mentioned, the most common applications of positrons are in the fields of the condensed matter science [2, 45]. Although in our view both VMC and DMC can be useful tools in this field, often the issue of the computational cost forces to resort to other techniques or to simple physical models [138].

Among the methods routinely used in solid state physics and chemistry, DFT has a good accuracy/cost ratio for large systems [139], its value being limited only by the approximate knowledge of the exchange-correlation potentials. An accurate parameterization for these potentials does pay the effort required in order to improve them.

One possible way for tackling this task is represented by the exact inversion of the Kohn-Sham equations for systems whose densities are accurately or, even better, exactly known. The inversion could allow us to obtain the exact values for the potentials (for instance the positron-electron correlation potential), opening the possibility to get better parameterizations.

Actually, there are at least two ways to proceed. While one is based on obtaining directly the potentials [140, 44] from the Kohn-Sham formalism, the other exploits the adiabatic connection method [141]. Although better DFT potentials could certainly lead to more diffuse application of these methods to study positrons in crystals and in semiconductors, it could also help to enlarge the number of positron containing systems that can be treated at the level of chemical accuracy.

As to QMC, it can play a dominant role computing very accurate, if not exact, energies and densities for both electrons and positrons. Since a similar approach has already been used for few-electron systems [142], we hope to see such an application carried out on positronic systems in the near future.

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