Annihilation rate in positronic systems by quantum Monte Carlo. \( \text{e}^+\text{LiH} \) as test case.

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Abstract

An accurate method to compute the annihilation rate in positronic systems by means of quantum Monte Carlo simulations is tested and compared with previously proposed methods using simple model systems. This method can be applied within all the quantum Monte Carlo techniques, just requiring to accumulate the positron-electron distribution function. The annihilation rate of \( \text{e}^+\text{LiH} \) as a function of the internuclear distance is studied using a model potential approach to eliminate the core electrons of Li, and explicitly correlated wave functions to deal with all the remaining particles. These results allow us to compute vibrationally averaged annihilation rates, and to understand the effect of the \( \text{Li}^+ \) electric field on positron and electron distributions.

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I. INTRODUCTION

In positron and positronium (Ps) chemistry and physics, the annihilation rate $\Gamma_{2\gamma}$ plays an important role since it correlates with many aspects of the local environment where the positron annihilates. For instance, “pick-off” annihilation in solutions and in solid materials, “on the fly” annihilation in atomic and molecular gases, and bound state annihilation of positronic compounds are just few of the experiments where $\Gamma_{2\gamma}$ can be measured and successively interpreted.

Although these experiments are relevant both technologically and scientifically [1, 2], only few theoretical studies have been devoted to accurately compute annihilation rates for realistic systems like atoms and molecules in order to compare with experimental data or to predict trends [3, 4, 5, 6, 7, 8, 9, 10, 11]. Moreover, these have been restricted to deal at most with four active electrons, so that only a bunch of systems have been studied so far. We believe this scarceness of results to be primarily due to the intrinsic difficulty in obtaining accurate wave functions for larger systems, and to the computational effort requested with respect to ordinary matter compounds when standard ab initio methods are employed [12].

For these reasons, quantum Monte Carlo (QMC) methods [13] represent an alluring alternative to these methods, to Density Functional Theory, and to explicitly correlated wave functions in computing energies and properties of realistic positronic systems. QMC techniques are well described in the literature, so we avoid to burden this paper with the details of the methods and constrain ourselves to discuss only the technical issues relevant for the specific problem.

Not requiring the analytical calculation of integrals, QMC allows one to use any physically sensible wave function. This possibility increases the chances to obtain an accurate description of any class of systems once all the relevant physical information is included in the chosen analytical form of the wave function. Having defined a trail wave function $\Psi_T$ for a system, QMC techniques allow one to compute the differential and non-differential properties of the system by sampling $\Psi_T^2$, $\Psi_T\Psi_0$, or $\Psi_0^2$. Here, $\Psi_0$ is the exact ground state function of the system. This task is usually accomplished by creating a distribution of points (also known as configurations or walkers) in configurational space whose density is proportional to the aforementioned $\Psi_T^2$, $\Psi_T\Psi_0$, or $\Psi_0^2$.

Keeping in mind the above remarks, it might appear that the QMC methods should accurately predict any interesting observable for positronic systems. This is indeed correct except for extremely local operators like Dirac’s delta $\delta$, and hence for $\Gamma_{2\gamma}$ that is proportional to its expectation value, for which an accurate sampling of small configurational space volumes is needed. These operators are well known to represent a challenge for QMC due to the discrete nature of the configuration ensemble and the finite length of the simulations.

As far as the mean value of the Dirac’s delta $\delta$ operator is concerned, one faces an additional difficulty when trying to estimate its mean value. Even admitting a perfect sampling in the regions where two particles are close to each other, the primitive method of counting the number of times the interparticle distance $r$ is smaller than a given radius $r_w$ (i.e. counting the ones that fall into a spherical well of radius $r_w$) [5] has an associated statistical error that diverges for $r_w \to 0$ [11]. This fact means that the estimation of the statistical error of the extrapolated value is based on shaky grounds.

Although not a solution, a slightly better approach was devised by substituting the simple sphere with a Gaussian function centered at the coalescence point $\sum_i \delta(r_{i+})$. The variance of this estimator also goes to infinity upon decreasing of the Gaussian width, but it diverges less faster than the one of the spherical well, therefore allowing a statistically more accurate estimation of $\langle \delta(r_{-+}) \rangle = \sum_i \langle \delta(r_{i+}) \rangle$.

Due to the interest in computing $\langle \delta(r) \rangle$ for many systems, attention has been paid to solve these problems, and remedies have been suggested in the framework of all the QMC techniques.

As far as variational Monte Carlo (VMC) is concerned, different methods have been proposed that may solve this difficulty allowing one to compute the needed quantities. One of these methods starts from the distribution differential identity

$$\nabla^2 \frac{1}{r} = -4\pi \delta(r) \quad (1)$$
that allows one to write, after specializing for the electron-positron pair

$$
\langle \delta(r_{1+}) \rangle_T = \int \delta(r_{1+}) \Psi_T^2(R) dR =
$$

(2)

$$
-\frac{1}{2\pi} \int \Psi_T^2(R) \left\{ \frac{\nabla_T^2 \Psi_T(R)}{\psi_T(R)} + [\nabla_r \ln \psi_T(R)]^2 \right\} \frac{1}{r_{1+}} dR
$$

where $R = (r_1, r_2, ..., r_+)$ is a point in configuration space, and the trial wave function $\Psi_T$ is normalized. Although this integral has a well defined value that can be computed sampling $\Psi_T^2$, it is well known that its variance diverges over the same distribution [14]. This fact implies that no error bound (i.e. standard deviation) can be associated to its value, a dangerous situation one would like to avoid.

Langfelder et al. [14] proposed a possible way to circumvent this problem based on a modified importance sampling transformation where $\Psi_T^2 \sum_i 1/r_{i+}^2$ is sampled instead of $\Psi_T^2$.

Always starting from Eq. 2, one could also exploit the approach proposed by Assaraf and Caffarel [13] to compute the expectation value needed to obtain nuclear forces by means of the Hellman-Feynmann theorem. They showed that a judicious choice of a renormalized operator, whose mean value is equal to the original one, can reduce the infinite variance to a finite value [16].

A completely different approach was pursued by Alexander and Coldwell [17]. They proposed to compute all the mean values sampling an analytically normalizable distribution function $g(R)$, so that the normalization $N_T$ of $\Psi_T$ is easily estimated by means of

$$
\frac{1}{N_T} = M^{-1} \sum_{i=1}^{M} \psi_T^2(R_i)/g(R_i)
$$

(3)

where the $M$ points sample the normalized $g$. If a second normalizable distribution $g_c(R)$, constrained on the subspace $r_+ = r_1$, is employed to guide the simulation and to compute $N_T$ in Eq. 3 then $\langle \delta(r_{-+}) \rangle$ can be easily estimated by the $(N_T/N_{cT})^2$ ratio.

Although these three methods represent a step towards the solution of this complicate problem in the VMC framework and are currently used for ordinary electronic compounds with success, the situation still remains far from being satisfactory for positronic systems. For these systems beyond the problem of the method used to compute $\langle \delta \rangle$, there is another difficulty: as far as we know, nobody has been able to optimize an accurate $\Psi_T$ for a positronic system with more than four electrons. More specifically, for large systems explicit correlation between the electrons and the positron has been found difficult to introduce [11]. This means that the "pile up" of the electron density over the positron is not correctly described, therefore giving rise to too small annihilation rates [18]. Possible sources of this unwanted outcome are the lack of knowledge about the complicate analytical form that such an accurate wave function should have, and some drawbacks of the optimization method used [13].

In order to go beyond these difficulties, the diffusion Monte Carlo (DMC) method is usually employed to sample $\Psi_T \psi_0$ [20, 21, 22]. This technique is able to project out the contribution of the excited states from the starting $\Psi_T$, allowing the exact calculation of the ground state energy. Unfortunately, the $\delta(r_{-+})$ operator does not commute with the Hamiltonian of the system, so that the simulation results are only an approximation to the exact mean value when computed by means of the mixed estimator

$$
\langle \delta(r_{-+}) \rangle_M = \int \delta(r_{-+}) \Psi_T \psi_0 dR
$$

(4)

Although, this value represents a more accurate estimate of the exact $\langle \delta(r_{-+}) \rangle$ than $\langle \delta(r_{-+}) \rangle_T$, it has been found that the quality of the results strongly depends on how accurately $\Psi_T$ mimics the correct interparticle distributions.
Whereas both the spherical well and Gaussian method can be employed to estimate \( \langle \delta(r_{-+}) \rangle_M \) in Eq. 3, Jiang and Schrader \[2\] pointed out that the use of the differential identity Eq. 4 in a DMC simulation requires some uncontrolled approximation, since \( \Psi_T \Psi_0 \) is not known analytically but only sampled.

Nevertheless, it has been shown \[10\] that an accurate estimate of \( \langle \delta(r_{-+}) \rangle \) can be obtained simply substituting \( \Psi_T^2 \) in Eq. 3 with \( \Psi_T \Psi_0 \), if \( \Psi_T \) correctly describes the positron-electron distribution.

A possible solution to the difficulty that DMC meets in estimating the exact expectation values is represented by sampling \( \Psi_0^2 \) instead of \( \Psi_T \Psi_0 \), and computing \( \langle \delta(r_{-+}) \rangle \) without resorting to \( \Psi_T \) in any way. This idea rules out the possibility to use Eq. 4, since one just samples the exact \( \Psi_0^2 \) distribution and no analytical information is available about its form.

In order to overcome this problem, Langfelder et al. \[14\] proposed to correct \( \langle \delta(r) \rangle_T \) by accumulating the walker weights in a small sphere around the coalescence point. Although this may look as a promising way, we noticed in our work on positron complexes \[23\] that long decaying times are needed in order to project out all the excited state contributions and to correctly build the "pile up" of the electron density over the positron if \( \Psi_T \) poorly describes this feature. This fact produces large fluctuations in the weight values, therefore increasing the statistical noise of the results.

A better approach may be represented by the use of the tagging algorithm proposed by Barnett et al. \[24\] in connection with the branching step usually employed in DMC. Here, the ratio \( \Psi_0 / \Psi_T \), needed to sample \( \Psi_0^2 \), is computed by means of the number of daughters of each configuration.

Moreover, Baroni and Moroni \[25\] have recently proposed an alternative algorithm that appears to be well suited for this task. This is based on a "Path Integral" view of the DMC algorithm, where the branching step has been substituted by an accept/reject step in order to exactly sample \( \Psi_0^2 \).

Unfortunately, these approaches do not solve the problem of the scarce sampling in the volume around \( r = 0 \), a problem that is present even for small simulation time steps. As stated previously, this comes from the finite length and discrete nature of the QMC simulations. As an attempt to overcome this difficulty, Langfelder et al. \[14\] implemented in their algorithm the correct sampling of the electron-nucleus cusp region as proposed by Umrigar et al. \[26\]: this, however, does not appear straightforward to adopt to correct the sampling of both the electron-electron and electron-positron cusps.

Keeping in mind all the aforementioned problems in estimating \( \langle \delta \rangle \), we believe the Monte Carlo practitioners are left only with the hope of devising an approximate, but hopefully solid and accurate, method to compute this observable.

The main aim of this paper is to discuss and test the accuracy of computing \( \langle \delta \rangle \) using some simple methods based only on the sampling of the positron-electron distribution function without any usage of the differential identity Eq. 4. These methods will be compared with the Gaussian approximation discussing relative merits and applicability. Moreover, we apply them to the realistic \( e^+ \) LiH model case in order to study the annihilation rate as a function of the internuclear distance \( R \). The \( \Gamma_{2\gamma} \) versus \( R \) results will allow to compute the vibrationally averaged annihilation rate for this system and to discuss molecular environment effects on the annihilation rate itself and on contact distribution functions.

The outlines of this work follow. In Section II we present the basis of the methods. Section III describes their applications to model systems for which the exact \( \langle \delta \rangle \)’s are known. As application of this technique, we deal in Section IV with the model \( e^+ \) LiH. Our conclusions and proposals of future work are then presented in Section V.

II. METHODS

Since we want to develop a method that can be applied to any QMC technique, henceforth we will use \( f(R) \) to indicate cumulatively \( \Psi_T^2(R) \), \( \Psi_T(R) \Psi_0(R) \), or \( \Psi_0^2(R) \). Here, \( R = (r_1, r_2, ..., r_+ \) is a point in configuration space, \( r_i \) and \( r_+ \) being respectively the \( i \)-th electron and positron positions.

We are interested in computing the expectation value \( \langle \delta(r_{-+}) \rangle \) over the distribution \( f(R) \), i.e.
This simulation was carried out sampling a grand total of 3
by means of a standard VMC simulation using the Langevin algorithm and the accept/reject step
distribution of 

where \( \rho(r_-, r_+) = N_{\text{ele}} \int f(R) \, dR \) and 
\( r_- = r_+ - r_- \), after integration over \( R_- \) and spherically averaging over \( r_- \) one gets

where \( \Omega(r_-) \) is the spherically averaged positron-electron distribution. Although these manipulations are quite straightforward, they highlight that in order to compute \( \langle \delta(r_-) \rangle \) one must have accurate values for both \( \Omega(0) \) and the denominator \( \int \Omega(r_-) r_-^2 \, dr_- \). Therefore, both the coalescence region and the tail of the distribution must be correctly described.

In order to thoroughly present the complexity of the faced problem, Figure 1 shows a typical behavior of \( \Omega(r_-) \) as sampled from the model wave function for one electron and one positron

by means of a standard VMC simulation using the Langevin algorithm and the accept/reject step [5]. This simulation was carried out sampling a grand total of \( 3.75 \times 10^9 \) configurations and using a time step of 0.01 hartree\(^{-1}\), a fairly small time step for this simple wave function. The sampled distribution of \( r_- = r \) was collected on a grid with a bin width of \( \delta r = 0.025 \) bohr, and then the number of times \( r_- \) was found inside a given bin was divided by the volume of the spherical crown \( [r - \delta r, r] \), \( V(r, \delta r) = \frac{4}{3} \pi [3r^2 \delta r - 3r^3 - \delta r^3 + \delta r] \). The so obtained values were attributed to the mean radius of the spherical crown, \( \tilde{r} = \frac{\pi \delta r [4r^3 - 6r^2 \delta r + 4r^2 \delta r^2 - \delta r^3]}{V(r, \delta r)} \). This is equivalent to approximating \( \Omega(r) \) as a straight line inside each spherical crown, a fairly good approximation in such a small bin.

We want to stress that the shape of the distribution was found independent of the time step over a broad range of values. This ensures that no systematic bias is present due to the finite time step. From Figure 1 one can easily notice the abrupt decrease of the distribution in the region close to \( r = 0 \). This represents the aforementioned inability of Monte Carlo simulations to correctly sample the distribution close to a coalescence point in spite of the large number of sampled configurations. It also seems to indicate that, due to this inability, any well-based method (e.g. both the spherical well and Gaussian methods) should return an inaccurate answer for \( r_\infty \) smaller that a certain threshold. Conversely, all the regions with \( r > 0.5 \) bohr seem to be adequately described by the sampled distribution, and therefore we propose to analytically continue their shape extrapolating to \( r = 0 \) by means of a suitable functional form. This idea allows one to exploit the knowledge about the exact form of \( \Omega \) to improve the local description in the small radius regions. For instance, if one samples \( f = \Psi_0^2 \), the exact value of the cusp condition can be used as a way to constrain the model to behave correctly. This trick can also be used in both the VMC and DMC simulations, since it is often easy to obtain the cusp condition of the sampled \( f \) knowing the analytical form of \( \Psi_0 \). This method could be implemented in two different ways. First, one could choose an analytical function \( \omega(r) \) to fit \( \Omega \) for all the electron-positron distances. This function should be flexible enough to properly describe both short range and long range behavior of \( \Omega \). More specifically, close to \( r = 0 \) \( \Omega(r) \) behaves like \( \exp(-\alpha r) \), where \( \alpha \) is strictly related to the cusp condition. Differently, in the large \( r \) regions \( \Omega(r) \) follows \( \exp(-\beta r) \), where \( \beta \) is dependent on the positron affinity (PA) of the system. A possible choice for \( \omega(r) \) is the Padé-Jastrow form

\[
\langle \delta(r_-) \rangle = \frac{\int f(R) \delta(r_-) dR}{\int f(R) dR}
\]

Recalling that \( f(R) \) is symmetric under any exchange between electrons, Eq. [3] can rewritten as

\[
\langle \delta(r_-) \rangle = \frac{\int \rho(r_-, r_+) \delta(r_-) dR_+}{\int \rho(r_-, r_+) dR_+}
\]

where \( \rho(r_-, r_+) = N_{\text{ele}} \int f(R) \, dR \). Introducing the new coordinates \( R_- = r_- + r_+ \) and 
\( r_- = r_+ - r_- \), after integration over \( R_- \) and spherically averaging over \( r_- \) one gets

\[
\langle \delta(r_-) \rangle = \frac{\int \Omega(r_-) \delta(r_-) dR_-}{\int \Omega(r_-) dR_-} = \frac{\int \Omega(r_-) \delta(r_-) r_-^2 dR_-}{\int \Omega(r_-) r_-^2 dR_-}
\]

\[
= \frac{\Omega(0)}{\int \Omega(r_-) r_-^2 dR_-}
\]

\[
(\delta(r_-)) = \begin{cases} r_- - 0.25r_+ - 0.25r_- & \text{if } r_- \leq 0.5 \text{ bohr} \\ 0 & \text{otherwise} \end{cases}
\]

for all the electron-positron distances. This function should be flexible enough to properly describe both short range and long range behavior of \( \Omega \). More specifically, close to \( r = 0 \) \( \Omega(r) \) behaves like \( \exp(-\alpha r) \), where \( \alpha \) is strictly related to the cusp condition. Differently, in the large \( r \) regions \( \Omega(r) \) follows \( \exp(-\beta r) \), where \( \beta \) is dependent on the positron affinity (PA) of the system. A possible choice for \( \omega(r) \) is the Padé-Jastrow form
\[ \omega(r) = N_\omega \exp\left[ -\frac{\alpha r + \beta r^2}{1 + \gamma r} \right] \] (9)

where \( \alpha \) can be chosen in order to have \( \omega(r) \) satisfying the correct local behavior close to \( r = 0 \). The fitted form can successively be used to estimate both \( \Omega(0) \) and the denominator in Eq. 7.

Second, if the form of \( \Omega(r) \) is more complicated (e.g. it has multiple maxima), it is possible to resort to a local fit by \( \omega(r) \) in the region close to the cusp in order to get the \( \Omega(0) \) value. Then, the normalization integral could be split in two part, one computed using \( \omega(r) \) and the other directly using the sampled distribution. Specifically for the distribution in Figure 1, one could fit the sampled \( \Omega \) values in the range \([0.5,1.0]\) bohr constraining \( \omega(r) \) to have both the exact cusp behavior and to have the same value of the sampled \( \Omega \) for \( r=1.0 \) bohr. Then, the normalization integral can be estimated integrating numerically \( \omega(r) \) for \( 0 \leq r \leq 1.0 \), and employing the trapezoidal formula for the remaining sampled values. We would like to mention that this necessity is already present for small systems like \( e^+Be \).

Although the two proposed methods are approximate, they might prove themselves to be quite accurate in practice, allowing the Monte Carlo practitioner to easily estimate the collision probability between two particles. In turn, this will allow to compute the annihilation rate in positronic systems, therefore opening the chance to directly compare with the experimental results.

In order to show that this is exactly the case, in the next section we present the results obtained computing \( \langle \delta(r_-+) \rangle \) for some model systems whose exact values are easily obtained using different methods.

Methods similar to ours, although quite different in many details, have been applied by Ortiz [28] and by Mairi Fraser [29] to the case of a positron embedded in the jellium. Their methods were somehow tailored to the specific system under study, so that no direct comparison with our proposals can be made. Nevertheless, the results they extracted from the simulations can be useful to seek for possible correlations between the magnitude of the "pile up" effect and the local electron density.

### III. TEST OF THE METHODS USING MODEL SYSTEMS

To test the accuracy of the proposed methods, we computed the \( \langle \delta(r_-+) \rangle \) expectation value for simple model systems composed only by one electron and one positron. More specifically, some model wave functions \( \Psi_i \) were chosen in order to represent the variety of electron, positron and electron-positron distributions that could be found in a positron atomic system. Then, the \( \Psi_i^2 \)'s were sampled by means of VMC simulations similar to the one discussed above, in order to collect the electron-positron distribution \( \Omega \).

We selected three model systems as representative of a fairly large class of positron complexes. The first one is given by the wave function \( \Psi_1 \) (see Eq. 8). The second has the analytical wave function

\[ \Psi_2(r_-,r_+) = \exp\left[ -r_- + \frac{0.15r_+ - 0.5r_+^2}{1 + r_+} - 0.5r_-+ \right] \] (10)

where the simple exponential in \( r_+ \) of \( \Psi_1 \) is substituted by a Padé-Jastrow and the exact cusp condition between electron and positron has been introduced.

To mimic the presence of core and valence shells, we chose as a third function

\[ \Psi_3(r_-,r_+) = \{ \exp\left[ \frac{-r_- + 2r_-^2}{1 + r_-} \right] + 0.001 \exp\left[ \frac{15r_- - 3r_-^2}{1 + r_-} \right] \} \exp\left[ \frac{0.15r_+ - 0.5r_+^2}{1 + r_+} - 0.5r_-+ \right] \] (11)

To compute the exact value \( \langle \delta(r_-+) \rangle \) for these models we used its definition
\[
\langle \delta(r_{-+}) \rangle = \frac{\int \Psi_2^2(r_-, r_+){\delta(r_{-+})}dr_+dr_-}{\int \Psi_2^2(r_-, r_+)dr_+dr_-} = \frac{\int \Psi_3^2(r_-, r_-)dr_-}{\int \Psi_3^2(r_-, r_+)dr_+dr_-}
\] (12)

The simple radial integral at the numerator was computed by numerical integration on a grid, while the denominator was estimated by means of Eq. 3 using \( g(r_-, r_+) = A^4B^3\exp[-2Ar_+ - 2Br_-]/\pi^2 \).

The two distributions sampled as a function of \( r \) from \( \Psi_2 \) and \( \Psi_3 \) turned out to possess a behavior quite similar to \( \Psi_1 \). Therefore, we avoid to show all of them and refer to Figure 1 as a template for such distributions. Due to their smoothness, we fitted them using Eq. 3 over the range 0.3-10 bohr constraining the Padé-Jastrow form to have the exact cusp condition, i.e. -0.5, -1.0, and -1.0, for the three \( \Psi_i \), respectively. To test the correctness of the chosen fitting range, we modified slightly the lower limit without finding statistically meaningful differences. Then, the fitted \( \omega \) was used to estimate both \( \Omega(0) \) and the denominator in Eq. 3 by means of numerical integration. The computed results, shown as \( \langle \delta(r_{-+}) \rangle_{\text{Padé'}} \), are presented in Table 1 together with the "exact" values computed using Eq. 12.

During the simulations we also computed the mean values \( \langle G(r_{-+}, \gamma) \rangle \), where \( G(r_{-+}, \gamma) = N_\gamma \exp[-r_{-+}^2/\gamma] \) is a normalized Gaussian function, for \( \gamma = 0.01, 0.0033, 0.002, \) and 0.001. This technique was proposed by Kenny et al. [31] and successively applied in Ref. [3] and Ref. [11]. The \( \langle G(r_{-+}, \gamma) \rangle \) values were extrapolated to \( \gamma = 0 \) by fitting them with the simple function \( a\sqrt{\gamma} + b \), the extrapolation law deduced in Ref. [1] using model systems. The fitting was quite accurate for all the three cases, and the results for \( b = \langle G(r_{-+}, 0) \rangle \) are also shown in Table 1.

Comparing \( \langle \delta(r_{-+}) \rangle_{\text{Padé'}} \) with the exact results it strikes the really good agreement between these two sets of values, the relative error being 1% at most for all the models. It must be pointed out that this level of relative accuracy is sufficient to thoroughly compare with the experimental data. It is also worth to stress that the application to other model systems gave a similar or better relative accuracy, therefore showing the wide applicability of the method.

As already pointed out previously [3], also the extrapolated \( \langle G(r_{-+}, 0) \rangle \) values are in good agreement with the exact results. Nevertheless, one should expect to obtain really inaccurate approximations to the exact results using \( \langle G(r_{-+}, \gamma) \rangle \) with \( \gamma \) smaller than some threshold value. This simple idea is based on the incorrect sampling of the density close to \( r = 0 \) shown in Fig. 1, so the good agreement found in this and previous works calls for an explanation. This is easily obtained superimposing \( G(r_{-+}, \gamma)r_{-+}^2 \) to the sampled \( \Omega(r_{-+}) \), i.e. comparing the behavior of the two factors that form the function whose integrals must be estimated. It turns out that \( G(r_{-+}, \gamma)r_{-+}^2 \) for \( \gamma \geq 0.001 \) has its largest values where \( \Omega(r_{-+}) \) still behaves correctly, therefore allowing a correct estimate of the integrals. Tests carried out using smaller values of \( \gamma \) gave much worse results than the ones reported, so we believe it is safer to limit the values of this parameter to the range 0.001-0.01 in order to obtain a meaningful extrapolation. Although this may look some way problematic due to the aforementioned difficulties, from the results in Table 1 \( \langle G(r_{-+}, 0) \rangle \) appears to be a good first estimate of the exact \( \langle \delta(r_{-+}) \rangle \). In conclusion, we suggest Monte Carlo practitioners to carry out always both estimations, i.e. extrapolating \( \langle G(r_{-+}, \gamma) \rangle \) and fitting the sampled \( \Omega \), as a way to safely estimate \( \langle \delta(r_{-+}) \rangle \).

As far as diffusion Monte Carlo and the exact sampling of \( \Psi_0^2 \) are concerned, the application of these methods is straightforward, and no more complications are expected than in the VMC case.

IV. THE e⁺LiH SYSTEM

Having verified the accuracy of the proposed method in computing Dirac’s delta mean values, we applied it to the calculation of the annihilation rate \( \Gamma_{2+} \) of e⁺LiH for various internuclear distances \( R \).

Although this system has already been carefully studied employing both QMC methods [11, 12] and Explicitly Correlated Gaussian (ECG) functions [8, 9, 32], a description of \( \Gamma_{2+} \), as a function of the molecular geometry is still lacking. Up to now, there are only \( \langle \delta(r_{-+}) \rangle = \langle \delta(r_{1+}) \rangle + \langle \delta(r_{2+}) \rangle + \langle \delta(r_{3+}) \rangle + \langle \delta(r_{4+}) \rangle \) results at \( R=3.015 \) bohr (0.0240(8) from DMC simulations [11] and 0.024992
form ECG calculations [6], at the estimated equilibrium distance \( R = 3.348 \) bohr (0.027252) [7], and the non-adiabatic results of Mitroy and Ryzhikh, 0.034016 and 0.032588 [12]. These last values were obtained using ECG in connection, respectively, with the Stochastic Variational Minimization (SVM) and the Frozen-Core SVM (FCSVM) methods, and are roughly 15-20% larger than the ECG [6, 7] and DMC [11] clamped-nuclei ones. This unexpected result lead Strasburger [6] to consider the possibility of the flattening of the potential energy curve of e\(^+\)LiH with respect to the LiH one, a feature that may allow the positronic molecule to visit the large internuclear distance region where the Dirac’s delta mean value is expected to be larger. However, Mitroy and Ryzhikh [32] pointed out that simple ECG’s may not represent the best basis functions to describe vibrational nuclear motion, and that their vibrational averaged nuclear distances are probably too large.

In a previous work [31], we computed the complete curve using the DMC technique, showing that the flattening is indeed present, and that a strong red shift of the vibrational spectrum with respect to LiH must be expected. Unfortunately, due to the high computational cost of our highly correlated trial wave functions, at that time we did not compute the behavior of \( \langle \delta \rangle \) as a function of \( R \). In this work we still adopt the BO approximation, so we predict the annihilation rate for each vibrational state of the system and compare our values with the non-adiabatic results of Mitroy and Ryzhikh [32].

In order to study the effect of the molecular geometry on the annihilation rate without using the computationally expensive wave function used in Ref. [4], we decided to employ a model potential approach to eliminate the “core” electrons of the Li\(^+\) fragment. We believe such an approach to be physically well grounded, as explained by the following supporting reasons. First, the ECG calculations carried out by Strasburger [6, 7] on the e\(^+\)LiH system show that the annihilation takes place primarily with the two electrons that may be attributed to the H\(^-\) fragment. Secondly, the frozen core approximation developed by Mitroy and Ryzhikh [4] has been found to describe accurately the annihilation process in e\(^+\)Li, e\(^+\)Be, LiPs, and e\(^+\)He \(^4\)S when compared with the corresponding all-electron calculations.

In order to reduce the number of active electrons, we used for e\(^+\)LiH the model Hamiltonian

\[
\mathcal{H}_{mod} = -\frac{1}{2} \left[ \nabla_{1}^2 + \nabla_{2}^2 + \nabla_{+}^2 \right] + V_{mod}(r_1) + V_{mod}(r_2) - \frac{1}{r_{H1}} - \frac{1}{r_{H2}} + \frac{1}{r_{12}} - \frac{1}{r_{1+}} - \frac{1}{r_{2+}} + V_{mod}^+(r_+) \tag{13}
\]

Here, the \( r_{ij} \) are interparticle distances, 1 and 2 being the electrons, + the positron, and \( H \) the hydrogen nucleus. Moreover, the Bardsley’s model potential [33]

\[
V_{mod}(r_i) = \frac{-1 + 10 \exp[-6.202r_{Li}]}{r_{Li}} \tag{14}
\]

where \( r_{Li} \) is the distance between the \( i \)-th electron and the Li nucleus, has been used to represent the 1s\(^2\) Li\(^+\) core electrons. To model the interaction of the positron with the frozen Li\(^+\) fragment we simply added to the repulsive Coulomb potential of the nucleus the potential of the two frozen core electrons as described by an STO-1s orbital with Z=3, obtaining

\[
V_{mod}^+(r_+) = \frac{3}{r_{Li+}} + 6 \exp[-6r_{Li+}] - 2 \frac{1 - \exp[-6r_{Li+}]}{r_{Li+}} \tag{15}
\]

where \( r_{Li+} \) is the Li-positron distance.

To test the accuracy of this model potential, we computed the energy for the ground state of the three systems Li, Li\(^-\), and LiPs. The energy values are respectively -0.1953(2) hartree, -0.2191(3) hartree, and -0.4485(3) hartree. They give an electron affinity of 0.0238(4) hartree, a positron affinity (PA) of 0.2294(4) hartree, and a Ps binding energy (BE) of 0.0032(4) hartree. While the electron affinity turns out to be in fair agreement with the experimental value, namely 0.023 hartree [32], both PA and BE are roughly 0.009 hartree smaller than the best estimate [4]. These discrepancies might be due to the absence of polarization effects of the core electrons due to the two active electrons and the positron, and to a relatively inaccurate representation of the 1s\(^2\) electron density.
by means of a single STO-1s function. Nevertheless, since we are primarily interested in obtaining a semiquantitative description of the changes in $\Gamma^2$, for this system, we believe the approximations introduced in the model Hamiltonian to be small enough to allow for a correct prediction of the trend for this important observable.

In order to accurately describe the wave function of the three active particles at the VMC level, we employed a trial wave function form similar to the one used in Ref. [11], but slightly modified to include the polarization of the electron and positron density of the PsH fragment due to the Li$^+$ potential. Specifically, the analytical form in Eq. 7 of Ref. [11] has been multiplied by a Padé-Jastrow factor depending on the $z$ coordinate of each particle: the $z$ axis was chosen as the LiH bond axis, the H nucleus being located at the origin and the Li on the negative $z$ axis. The wave function parameters were fully optimized for every nuclear distance $R$ minimizing the variance of the local energy over a fixed sample of configurations [26, 30]. This procedure is already well described in the literature [13], so we skip the unnecessary details. The ensemble of walkers used in the optimization was generated by DMC simulations in order to bias the walkers distribution towards the exact density. Usually, four or five optimization steps were carried out for each $R$.

We started the optimization process of the wave function at $R=20$ bohr. At the end of the optimization procedure, $R$ was decreased and the wave function re-optimized for the new distance. This procedure gives the chance to monitor the changes of the wave function with $R$, but might increase the possibility to remain stuck in a local minimum in the parameter space during the optimization.

Having optimized at VMC level the approximate wave functions for various distances, these were employed in long DMC simulations to project out the remaining excited state contributions and to compute more accurate mixed expectation values. For all the simulations, a time step of 0.005 hartree$^{-1}$ was used, together with a population of 9000 walkers. These two simulation parameters were found adequate to make statistically negligible both the time step bias and the population bias in the DMC simulations.

The DMC results for the energy and for the $\langle \delta(r_{-+}) \rangle$ of this model system are shown in Table 2. There, the energy values represent the ground state energy of the model Hamiltonian Eq. (3), $\langle \delta(r_{-+}) \rangle_{\text{Padé}}$ are the total collision probabilities estimated using the electron-positron distribution, i.e. $\langle \delta(r_{1+}) \rangle + \langle \delta(r_{2+}) \rangle$, while $\langle G(r_{-+},0) \rangle$ are the extrapolated Gaussian values. Here, the electron-positron distributions were fitted with the function in Eq. 8, constraining its cusp to be $-0.5$-cusp($\Psi_T$).

The energy values obtained in Ref. [31], after having subtracted the repulsion $1/R$ between the H nucleus and the Li$^+$ core and the total energy of the Li$^+$ fragment (-7.279913 hartree [4]) to estimate the leptonic energy of the PsH moiety, are shown in Figure 2 together with the DMC results obtained in this work.

For $R \geq 4$, the results from the model system follow closely the more accurate all-electron FN-DMC values, showing that the model potential correctly describes the polarization of PsH due to the interaction with Li$^+$. For shorter distances the approximation of considering Li$^+$ frozen is no longer accurate, so that a discrepancy between the two sets of results is expected. It is also important to remember that the Bardsley’s potential was tailored only to describe the atom in its ground and valence excited states, not to describe correctly bonds in molecules.

Figure 3 shows the two computed $\langle \delta(r_{-+}) \rangle$ values as a function of the internuclear distance $R$, together with the ECG results of Strasburger [6, 7] and the DMC result of Ref. [11]. These last results can be used to evaluate the total accuracy of our computed collision probabilities.

From Fig. 3 it is clear that both the $\langle \delta(r_{-+}) \rangle_{\text{Padé}}$ and the $\langle G(r_{-+},0) \rangle$ are in good agreement, the second differing from the first one by two standard deviations at most. This allows us to think that we are accurately estimating the mixed distribution mean value obtained by the standard DMC technique. Improved results could be obtained only by sampling $\Psi^2$.

As far as the total accuracy is concerned, at $R=3.015$ bohr both all-electron ECG [6, 7] and DMC results [11] appear to be smaller than the model ones by roughly 7%. Instead, on going towards large $R$ the mean value seems to correctly converge to the very accurate ECG value, namely
and to the new DMC 0.0486 estimate carried out in this work using the electron-positron distribution. From this comparison, one could expect our estimation to slightly degrade on going towards small R, without becoming embarrassing inaccurate to create concerns about the usefulness of this model system.

The overall trend of the collision probability shows a net decrease on going towards short R, a feature already suggested by Mitroy and Ryzhikh [32]. This can be easily understood remembering that the Li+ model potential repels the positron, while attracting the two electrons. It is not easy to infer any possible analytical model to describe these joined effects, although for large R one could propose a limiting 1/R^2 form due to the polarization of the two distributions by the electric field of Li+. We show in the Appendix that this reasoning is indeed correct for any observable by means of first order Perturbation Theory. An “experimental” evidence that this is the case is given by the fairly good fitting of the ⟨δ⟩ results at R=10, 15, and 20 bohr with the simple form 0.0486 + b/R^2, where b = -0.20448.

Various other mean values were computed during the DMC simulations in order to obtain some physical insight on the electron and positron density behavior. Figure 4 reports the mean value of the z coordinate for the two particles giving information on the polarization of the two lepton densities. It is clear that the positron distribution is polarized by the model potential in the opposite direction to the electronic one. Moreover, it appears to be more easily polarized than the electronic one always showing larger ⟨z⟩ values. This fact can be easily explained by noticing that the positron distribution is more diffuse than the electron one, so that it is more strongly repelled by the electric field. Interestingly, at R=2 and 2.5 bohr the electron distribution reverse its polarization showing ⟨z⟩ > 0. We believe this effect to be due to the repulsive region of the Li+ core potential that pushes away the electrons for such small nuclear distances, therefore modeling the exchange effect created by an antisymmetric wave function.

Figure 5 shows the average values for the electron-electron and electron-positron distances. While the electron-positron mean distance ⟨r_{++}⟩ increases monotonically upon decreasing R, the electron-electron distance ⟨r_{--}⟩ shows a shallow maximum around R=8 bohr and a deep minimum around R=2.5 bohr. We believe the maximum to be due to the competition between the positron and the Li+ model potential to bind an electron. More specifically, although polarized towards positive z, the positron still attracts one of the two electrons to form the Ps sub-cluster, increasing the distance from the second electron that is free to be polarized in the direction of the Li+ core. On going towards smaller R, the positron is pushed far out the bond region, loosing its ability to polarize the electrons that are now both strongly attracted by the model potential. This interaction leads them to move in the small volume between H and Li+, therefore decreasing their mean distance. Then, for R smaller than 2.5 bohr, the electron-core repulsion pushes the electrons outwards the bond region, with the net effect to increase their mean distance. This effect has also been observed by plotting the intracule electron distributions obtained during the DMC simulations.

It is worth to mention that similar conclusions can be drawn analysing the VMC results obtained as a by-product of the optimization stages.

Having studied the overall behavior of ⟨δ⟩, ⟨z⟩, and ⟨r⟩, we now turn to compute the vibrationally averaged annihilation probabilities. To obtain these quantities, we interpolated our ⟨δ⟩ results by means of the analytical form \( \Delta(R) = 0.0486 - 2aR/(1 + bR + cR^2 + dR^3) \). The fitted parameters are \( a = 1.05945, b = 97.5779, c = -37.9705 \), and \( d = 12.2715 \). Then, the potential energy curve of e^+LiH obtained in Ref. [33] was fitted with the modified Morse potential

\[
V_M(R) = -8.0699 + A\{1 - \exp[-B(R - C)]\}^2 - A - D\{1 - \exp[-(R/F)]^6\}/(2R^4) \tag{16}
\]

obtaining \( A = 0.03444 \) hartree, \( B = 0.72030 \) bohr⁻¹, \( C = 3.3060 \) bohr, \( D = 21.1796 \) bohr⁻³, and \( F = 5.88217 \) bohr. The last term in Eq. [16] has been introduced in order to correctly represent the charge-induced dipole interaction between Li⁺ and PsH. The nuclear Schrödinger equation for this potential was then solved using the grid method proposed by Tobin and Hinze [37], and the numerical wave functions \( \phi_{\nu}(R) \) were then used to compute vibrationally averaged mean values for zero total angular momentum. More specifically, we computed
\[ \langle O \rangle = \frac{\int dR \phi_{O}^{2}(R) O(R)}{\int dR \phi_{O}^{2}(R)} \]  \hspace{1cm} (17)

where \( O(R) \) is \( \Delta(R) \) or any other function of \( R \).

In Table 3 we show the results for \( \langle \delta \rangle_0 \) and \( \langle R \rangle_0 \), computed over the first 16 bound vibrational states. The \( \langle \delta \rangle_0 \) values increase in an almost linear fashion on going towards large \( \nu \), as expected by the steady increase of \( \langle R \rangle_0 \) due to the vibrational excitation. Comparing \( \langle \delta \rangle_0 = 0.0295 \) with the value of \( \Delta(R) \) at the equilibrium distance of our fitted potential, namely 0.0291 at 3.353 bohr, it appears that the ground level vibrational motion only slightly increases the probability of collision between the electrons and the positron with respect to the one at the equilibrium distance. This finding is in line with the small difference between the equilibrium distance and the average nuclear distance \( R_0 = 3.42 \) bohr. We relate these outcomes to the almost linear behavior of \( \langle \Delta(R) \rangle \), and to the shape of \( R^2 \phi_{O}^{2}(R) \) in the region around the potential minimum, where it resembles a Gaussian.

Although our vibrationally averaged result for \( \nu = 0 \) \( \langle \delta \rangle_0 = 0.0295 \) appears to be roughly 8% larger than the ECG result (0.027252) at the equilibrium distance 3.348 bohr, suggesting a fairly large effect of the nuclear motion, we believe this outcome is primarily due to the 7% larger collision probabilities computed using our model system. These two evidences seem to rule out the Strasburger’s suggestion of a large increase of the collision probability due to the quantum nuclear motion for the \( \nu = 0 \) state. They indicate that approximating the averaged collision probability for the vibrational ground state simply by using its value at the equilibrium distance could be a fairly accurate procedure. Moreover, these conclusions agree with Mitroy and Ryzhikh’s warnings that both the SVM and FCSVM results, although proving the overall stability of \( e^+ \)LiH, are not well converged to the exact ones. For instance, their \( \langle R \rangle_0 \) values, respectively 4.182 bohr and 3.964 bohr, are larger than the minimum of the ECG and DMC potential curves by more than 0.5 bohr. This discrepancy cannot be accounted for by the zero point motion of the positron complex. These larger distances between the two fragments \( Li^+ \) and PsH in the non-adiabatic treatment imply a reduced distortion of the lepton densities of PsH with respect to the one at the Born-Oppenheimer equilibrium, and therefore a too large annihilation rate. However, it is interesting to notice that both FCSVM (0.032588) and SVM (0.034016) collision probabilities are really close to our Born-Oppenheimer one at \( R = 4.0 \) bohr. In our view, this agreement stresses, again, the importance of the local electric field in defining the collision probability and the overall accuracy of the SVM approach in describing the relative densities an a positronic complex.

As far as the behavior of \( \langle \delta(R) \rangle_0 \) is concerned, the steady increase on going towards large \( \nu \) indicates that the annihilation rate does depend on the quantum vibrational state of the molecule. Although the trend of these results could be specific of the \( e^+ \)LiH system and perhaps of other polar molecules as well, it strongly indicates that any theory formulated to describe “on the fly” annihilation of \( e^+ \) due to Feshbach resonances must include this effect in order to go beyond “order of magnitude comparison” and to predict accurately the annihilation rate. In our view, this opens a new avenue of exploration in positron physical chemistry where the understanding of the vibrational motion effect on positron annihilation by molecular systems is of prime importance.

V. CONCLUSIONS

In this work we have critically compared methods that may be useful to compute the annihilation rate in positronic systems in the framework of the QMC methods. Moreover, we have presented a simple, but nevertheless solid and accurate, method based only on the interparticle distribution sampling. After having tested it using model systems, we employed the method to compute \( \langle \delta(r_{-+}) \rangle \) for \( e^+ \)LiH for several internuclear distances. These results allowed us to discuss many interesting features of this positronic complex, and to predict that the annihilation probability increases upon increasing the vibrational quantum number \( \nu \). We notice that a similar behavior of \( \langle \delta(r_{-+}) \rangle \) may be expected also for \( e^+ \)LiF due to the polarization of the positronic density of the PsF fragment by the \( Li^+ \) core. The situation could be quite different for the \( e^+ \)BeO case where the positron density is
expected to be centered on Be at large nuclear distances (the two fragments e\(^+\)Be and O have lower total energy than Be\(^+\) and PsO \(^{[39]}\)), and to move on the O side of the molecule when the distance decreases. This effect is due to the electron transfer from Be to O that creates the large molecular dipole moment. From our experience on these systems we expect \(\langle \delta(r_{-+}) \rangle \) for e\(^+\)Be to be smaller than the one for the polar molecule, so the vibrationally excited states close to the dissociation threshold may have smaller annihilation rates than the ground vibrational state.

It is also interesting to speculate on the behavior of the annihilation rate versus the vibrational quantum number for other simple systems like e\(^+\)Li\(_2\) and e\(^+\)Be\(_2\). Here, the symmetry of the systems can play an important role in defining the annihilation rate. For instance, decreasing the nuclear distance one may expect to find the positron localized between the two atomic fragments due to its ability to polarize the two atomic electron densities: in this situation the annihilation rate could be quite different from the atomic one. Although it is easy to infer the existence of a bound state for these complexes at large nuclear distances employing the basic Valence Bond resonance idea

\[
e^+A_1 + A_2 \leftrightarrow A_1 + e^+A_2
\]  

(18)

it still remains to demonstrate the stability of these systems for nuclear distances close to the equilibrium geometry of the neutral parent molecules.

As a rule of thumb to predict the stability of a non-polar molecule, one can use the adiabatic ionization potential (AIP) as proposed by Mitroy et al. \(^{[40]}\). For the \(X^1\Sigma^+_g\) ground state of Li\(_2\) the experimental AIP is 0.189 hartree \(^{[41]}\), slightly lower than the atomic one, 0.19814 hartree \(^{[42]}\). Also for the \(X^1\Sigma^+_g\) ground state of Be\(_2\), one might expect a similar lowering of the AIP with respect to the atomic one, 0.343 hartree \(^{[42]}\), so that a value of around 0.335 hartree could be regarded as a safe upper bound to the true AIP. Both these values fall inside the upper and lower IP limits for positron binding obtained by Mitroy et al. \(^{[41]}\) for one and two valence electron atoms, therefore suggesting that the two complexes should be stable. We understand that this model is just a rough approximation for our molecular systems \(^{[43]}\). Nevertheless, a positron bound to an atom or a molecule is always characterized by a quite diffuse density. This allows one to neglect some of the real features of the electron density close to the nuclei as a first approximation, and focus only on the asymptotic properties of the positron cloud that are correlated to the IP and to the polarizability.

As far as Be\(_2\) is concerned, the AIP larger than the Ps binding energy (0.25 hartree) suggests a mechanism based on the electron cloud polarization as responsible of the binding. Moreover, the lowering of the AIP with respect to the atomic one, and the large polarizability of this molecule (roughly twice the atomic one) seem to indicate its ability to form a stronger bond with the positron than the Be atom alone \(^{[4]}\). Conversely, Li\(_2\) has an AIP smaller than the Ps binding energy, suggesting that the polarization of the Ps cluster may be held responsible for the positron binding. However, Li is close to the lower stability threshold of the positron-atom complexes, and we do not feel confident in proposing the stability of the molecular complex with respect to the Ps+Li\(_2^+\) dissociation pathway.

Right now, QMC methods are the best suited computational techniques to carry out such a study since 6 and 8 electron systems are too large to be studied with ECG’s unless the frozen core approximation is used. With the addition to the QMC “bag of tricks” of a robust method for computing annihilation rates such a study could become routine in molecular physical chemistry, allowing the exploration of many interesting features of these “exotic” compounds.

Moreover, many more other technically oriented applications could be devised. Positronium annihilation in polymers and membranes, positron annihilation in silicon nanocluster, nanodevices, fullerenes and carbon nanotubes are just few of them that could be quite easily interpreted with the help of such a method.

Our hope is that this work will help this kind of applications to blossom and to lead to a better understanding of the basic interaction schemes that positron has with ordinary matter.

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APPENDIX

In this Appendix we show that the correction to the expectation value of every observable \( O \) for PsH interacting with the Li\(^+\) core follows the limiting analytical form \( R^{-2} \) for large \( R \). This is indeed a general result for positronic atom systems immersed in a weak electric field. From Perturbation Theory one can write the first order corrected wave function for the ground state as

\[
\Psi^{(1)}_0 = \Psi^{(0)}_0 + \sum_{i \neq 0} \int \frac{\Psi^{(0)}_i V \Psi^{(0)}_0 d\mathbf{R}}{E^{(0)}_i - E^{(0)}_i} \Psi^{(0)}_i = \Psi^{(0)}_0 + \sum_{i \neq 0} c^{(0)}_i \Psi^{(0)}_i \tag{19}
\]

where \( \Psi^{(0)}_i \) are the eigenstates of the unperturbed Hamiltonian (i.e. the PsH), \( E^{(0)}_i \) its eigenvalues, and \( V \) the perturbation potential. The expectation value of the observable \( O \) can be computed using

\[
\langle O \rangle = \frac{c^i O c}{c^i I c} \tag{20}
\]

where \( O_{ji} = \int \Psi^{(0)}_j O \Psi^{(0)}_i d\mathbf{R} \), while \( c = \{1, c^{(0)}_1, c^{(0)}_2, \ldots\} \). If the perturbation potential is small with respect to the total energy, then \( c^{(0)}_i \ll 1 \) and \( c^i I c = 1 + \sum_{i \neq 0} (c^{(0)}_i)^2 \simeq 1 \). This fact allows to introduce a further approximation into Eq. 20,

\[
\langle O \rangle \simeq c^i O c = \langle O \rangle_{00} + 2 \sum_{i \neq 0} c^{(0)}_i \langle O \rangle_{0i} + \sum_{i,j \neq 0} c^{(0)}_i c^{(0)}_j \langle O \rangle_{ji} \simeq \langle O \rangle_{00} + 2 \sum_{i \neq 0} c^{(0)}_i \langle O \rangle_{0i} \tag{21}
\]

showing that the first order change in the expectation value \( \langle O \rangle \) is linearly dependent on the \( c^{(0)}_i \)'s.

For our specific case, namely PsH interacting with the Coulomb potential of Li\(^+\) at distance \( R \), for \( R \to \infty \) the perturbing interaction potential can be written as

\[
V = \sum_k \frac{q_k}{R_{q_k L_i}} \simeq \sum_k q_k \left( \frac{1}{R} - \frac{z_k}{R^2} \right) \tag{22}
\]

where the molecular geometry is as in the main text, while \( q_k \) are the leptonic charges. This approximation is equal to consider the electron and positron densities constant in a plane parallel to the \( xy \) plane. Introducing this approximation in the integrals in Eq. 19 one gets

\[
\int \Psi^{(0)}_i V \Psi^{(0)}_0 d\mathbf{R} \simeq \sum_k q_k \frac{1}{R} \int \Psi^{(0)}_i \Psi^{(0)}_0 d\mathbf{R} + \sum_k q_k \int \Psi^{(0)}_i \Psi^{(0)}_0 \frac{z_k}{R^2} \Psi^{(0)}_0 d\mathbf{R} = \tag{23}
\]

\[
\sum_k q_k \int \Psi^{(0)}_i \Psi^{(0)}_0 d\mathbf{R}
\]

This result shows that the \( c_i \) in Eq. 20 and 21 are proportional to \( 1/R^2 \), therefore proving that this is also the analytical form of the leading correction to the unperturbed ground state expectation values \( O_{00} \).
Figure Captions:

Figure 1: Behavior of $\Omega(r_{-+})$ sampled from $\Psi_1$.
Figure 2: Energy of the PsH moiety computed from Eq. 13 and from the $e^+\text{LiH}$ results of Ref. 31 as explained in the text.
Figure 3: Computed $\langle \delta \rangle$ results for $e^+\text{LiH}$ system at various internuclear distances.
Figure 4: Electron and positron mean value of the $z$ coordinate as a function of the internuclear distance.
Figure 5: Electron-electron and electron-positron mean distances as function of the internuclear distance.
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& \langle \delta(r_{+}) \rangle_{\text{exact}} & \langle \delta(r_{+}) \rangle_{\text{Pade}} & \gamma & \langle G(r_{-}, \gamma) \rangle \\
\hline
\Psi_1 & 0.0100 & 0.02140(8) & & \\
& 0.0033 & 0.0219(1) & & \\
& 0.0020 & 0.0222(2) & & \\
& 0.0010 & 0.0223(3) & & \\
& 0.022602(7) & 0.02229 & 0.0000 & 0.0228(3) \\
\Psi_2 & 0.0100 & 0.0979(2) & & \\
& 0.0033 & 0.1028(3) & & \\
& 0.0020 & 0.1043(4) & & \\
& 0.0010 & 0.1058(7) & & \\
& 0.10981(1) & 0.11052 & 0.0000 & 0.1095(7) \\
\Psi_3 & 0.0100 & 0.0842(2) & & \\
& 0.0033 & 0.0886(3) & & \\
& 0.0020 & 0.0901(4) & & \\
& 0.0010 & 0.0916(7) & & \\
& 0.09399(1) & 0.09382 & 0.0000 & 0.0950(7) \\
\hline
\end{tabular}

Table 1: $\langle \delta(r_{+}) \rangle$ expectation values for the three model systems $\Psi_1$, $\Psi_2$, and $\Psi_3$. The "exact" values are computed by Eq. 12. $\langle \delta(r_{+}) \rangle_{\text{Pade}}$ are computed fitting Eq. 9 to the sampled distribution as explained in the text. $\gamma$ is the width of the Gaussian used to compute $\langle G(r_{-}, \gamma) \rangle$. 
Table 2: Lepton energies, $\langle \delta(r_{-+}) \rangle_{Pade'}$, and $\langle G(r_{-+}, 0) \rangle$ mean values for the e$^+$LiH model system. All quantities in atomic units.

| R  | $\langle E \rangle$    | $\langle \delta(r_{-+}) \rangle_{Pade'}$ | $\langle G(r_{-+}, 0) \rangle$ |
|----|------------------------|-----------------------------------------|---------------------------------|
| 2.0| -1.16437(9)            | 0.01884                                 | 0.0182(2)                       |
| 2.5| -1.15936(7)            | 0.02178                                 | 0.0210(2)                       |
| 3.0| -1.13196(6)            | 0.02684                                 | 0.0256(2)                       |
| 3.5| -1.09798(5)            | 0.03000                                 | 0.0288(2)                       |
| 4.0| -1.06485(5)            | 0.03334                                 | 0.0324(2)                       |
| 6.0| -0.96985(4)            | 0.04166                                 | 0.0402(2)                       |
| 8.0| -0.91995(3)            | 0.04544                                 | 0.0436(3)                       |
| 10.0| -0.89160(3)           | 0.04666                                 | 0.0448(3)                       |
| 15.0| -0.85634(2)           | 0.04754                                 | 0.0458(3)                       |
| 20.0| -0.83932(2)           | 0.04794                                 | 0.0468(3)                       |
| $\infty$ | -0.78918(1)        | 0.04860                                 | 0.0484(3)                       |
| $\nu$ | $\langle \delta \rangle_\nu$ | $\langle R \rangle_\nu$ |
|-----|-----------------|-----------------|
| 0   | 0.0295          | 3.423           |
| 1   | 0.0305          | 3.571           |
| 2   | 0.0315          | 3.732           |
| 3   | 0.0325          | 3.906           |
| 4   | 0.0334          | 4.094           |
| 5   | 0.0344          | 4.294           |
| 6   | 0.0352          | 4.503           |
| 7   | 0.0361          | 4.718           |
| 8   | 0.0369          | 4.938           |
| 9   | 0.0376          | 5.166           |
| 10  | 0.0383          | 5.408           |
| 11  | 0.0390          | 5.675           |
| 12  | 0.0397          | 5.985           |
| 13  | 0.0405          | 6.356           |
| 14  | 0.0414          | 6.803           |
| 15  | 0.0421          | 7.243           |

Table 3: Vibrationally averaged $\langle \delta(r_{-+}) \rangle_\nu$ and $\langle R \rangle_\nu$ values for the $e^+\text{LiH}$ model system. All quantities in atomic units.