QUANTUM MECHANICAL CALCULATIONS ON MOLECULES CONTAINING POSITRONS

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Abstract

Supercomputers and multi–node computer clusters have started to offer computer power sufficient to undertake projects in the area of molecular structure calculations that a few years ago were not at all feasible. This particularly applies to very accurate calculations concerning small molecular systems in isolation. In recent years we have carried out development and implementation of methods allowing very accurate quantum mechanical calculations of ground and excited stationary states of molecule–positron systems without assuming the Born–Oppenheimer (BO) approximation regarding the separability of the nuclear, electronic, and positronic motions. In this review we describe the current progress in the area of positron–molecule calculations, we review our approach and show our recent non–BO calculations of the ground state of the e^+LiH system, and we mention some of our future projects in this area.

The matter–antimatter interaction is an issue much debated in modern science. An understanding of the structure and chemistry of molecules and clusters containing positrons can reveal new ways in which matter–antimatter transformations can be accomplished and controlled. The application of computational tools to study positron molecules and to predict their structures and chemical behavior featured in this article may inspire new experimental research in the area. Of particular interest to us is the study of positron molecules in highly excited states without resorting to the clamped–nucleus model. The work may lead to discovery of long–lived positron bound states in polar molecules. This discovery may have important consequences in the development of molecular positron "storage" capabilities and also to our fundamental understanding of the positron chemistry.

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1. Introduction

The work of Löwdin on fundamental problems concerning the application of Quantum Mechanics to atoms and molecules has been an inspiration to our research group at Arizona, which, in recent years, has undertaken the development and implementation of very accurate methods–which depart from the Born–Oppenheimer approximation–for describing the coupled electron–nuclear motion in molecules. The use of one–center and multi–center explicitly correlated Gaussian functions as the basis of the wave function expansion has been the centerpiece of this development. We have recently demonstrated that the method reproduces very precisely the vibrational excitations and electrical properties of small diatomic systems [1]. The accurate predictive ability of the approach has been also recently employed to determine the structures and life times of molecular systems containing positrons [2].

Low–energy positrons have become more readily available in the laboratory leading to increased experimental activity concerning their interaction with matter. Thus understanding of this interaction becomes an increasingly important problem for both theoretical and experimental considerations. More accurate models of positron–molecule interactions could benefit research in such areas as interpretation of astrophysical gamma-ray spectra [3], positron–induced fragmentation of molecules [4], and characterization of thin films and material surfaces [5, 6]. In addition, positron–matter interactions pose a number of challenges to our fundamental understanding of atomic and molecular physics [7, 8]. Much recent research has been directed toward finding methods to treat electron–positron correlations and positronium formation as either an open or a closed channel problem in the theoretical calculations of elastic and inelastic cross sections, as well as annihilation rates [9–13].

In recent paper [14] Barnes et al. considered a question in the area of positron–molecule interaction which had remained unanswered for nearly four decades. In 1963, measurements by Paul and Saint–Pierre indicated unusually high annihilation rates for positrons incident on certain large molecules even though the positron energy was below the energy threshold for positronium formation [15]. While several explanations had been proposed to explain this phenomenon, clear experimental confirmation of the predictions generated by any model had been lacking [10, 11, 14, 16–20]. To explain the unusually high annihilation rates Barnes et al. [14] studied the annihilation rate for positrons incident on a sampling of molecules resolved as a function of positron energy. The measurements were made using a new technique allowing generation of

a positron beam tunable in energy from 50 meV to several eV with an energy spread of ≈25 meV full width at half maximum [12,21]. This beam had previously been used to study elastic and inelastic scattering of positrons [13,22–24]. The Barnes et al. study [14, 25] provided evidence that molecular vibrations are intimately connected with the observed large annihilation rates, and they pointed to the vibrational–excitation–mediated trapping into positron–molecule bound states, i.e., vibrational Feshbach resonances, as the specific mechanism of the enhancement. The study provided important guidance for theoretical attempts to explain the mechanism responsible for the large annihilation rates and lead to a better understanding of positron–molecule interactions.

Annihilation rates for positrons in molecular gases are typically expressed in terms of the dimensionless parameter, Z_{eff}, given by:

$$Z_{eff} = \Gamma/(\pi r_0^2 c n_m), \tag{1.1}$$

where Γ is the measured annihilation rate for positrons in the test gas, r_0 is the classical electron radius, c is the speed of light, and n_m is the molecular density. If the correlations between the positron and molecular electrons were neglected, Γ would be equal to the Dirac rate, $\pi r_0^2 c n_m Z$, with Z being the number of electrons in the molecule, and Z_{eff}=Z. However, near room–temperature (300 K) measurements for positrons at energies near 0.025 eV show that, there are cases where Z_{eff} is orders of magnitude larger than Z [15,20]. For example, for octane with 66 electrons (Z equal to 66), Z_{eff} was estimated to be 6×10^5. In general, it was found that the annihilation rates increase rapidly with molecular size. Large annihilation rate values of Z_{eff}=10^7 have been observed for alkanes with only twice as many electrons as in octane. Explanation of this almost resonance behavior has been a subject of several theoretical models which have attempted to explain this phenomenon in terms of a vibrational or electronic resonance or a positron–molecule bound state [16,20]. The common feature in these models has been the assumption that a long–lived quasi–bound state can increase the overlap of the positron and electron wave functions and enhance the probability of annihilation. In other models explanations have been proposed involving the excitation of virtual positronium and other mechanisms involving very strong positron–electron correlations [10, 11].

In an important development Gribakin proposed a model [19, 20] that explains some of the key features of the observed high annihilation rates in molecules. Gribakin's model distinguishes two mechanisms for the enhancement of Z_{eff}. The first mechanism called *direct annihilation* can contribute to Z_{eff} up to ≈1000 and the enhancement of the direct annihilation rate (first considered in Ref. [16]) occurs when a shallow bound state or low–energy virtual state of the system exists. In this case, an increase of the positron density

in the vicinity of the target occurs and it is proportional to $1/(\epsilon + |\epsilon_0|)$, where ϵ is the incident energy and ϵ_0 is the energy of the weakly bound or virtual state. The annihilation parameter Z_{eff} increases by the same factor. In the case of positrons with finite energy, the *direct annihilation* mechanism is limited by the presence of ϵ in the denominator. Thus for positrons at room–temperature, the direct annihilation can only enhance Z_{eff} by no more than $\approx$1000. [19]

According to Gribakin's model the second type of enhancement, *resonant annihilation* (i.e., Feshbach resonance enhancement), occurs when the sum of the energy of the incident positron and the energy of the ground state neutral target molecule matches the energy of an excited quasi–stable positron–molecule bound state. This quasi–stable bound state has to involve an electronic or vibrational excitation of the target molecule in order to absorb the energy given up by the positron localizing into a bound state. When such a positron capturing occurs, due to the resonance conditions present in the event, the overlap between the positron wave function and those of the target electrons is significantly increased resulting in a large value of Z_{eff}. If one assumes that the presence of the positron has little effect on the excited e.g., vibrational states of the target, [19] the condition on the incident positron energy for such a resonance to occur is: $\epsilon = E_{ex} - E_0 - \epsilon_b$, where ϵ is the incident positron energy, E_{ex} is the energy of the excited state of the target, E_0 is the energy of the ground state of the target, and ϵ_b is the binding energy of the positron to the target.

There have also been proposals [26–28] and further discussion [29–31] of models that do not involve vibrational resonances. These models were motivated, in part, by the observation that large values of Z_{eff} correlate with the energies of the electronic states of the molecules [32]. The models have involved such concepts as highly correlated electron–positron states, the excitation of virtual positronium, and generic behavior at inelastic thresholds. All these effects are expected to increase, at least to some degree, the overlap of the positron and electron wave functions leading to an increase of Z_{eff}.

For alkane molecules, Barnes et al. [14] data showed large vibrational resonance peaks that are down–shifted from the vibrational mode energies by an amount $\Delta\epsilon$, which increases with the molecular size. These observations are consistent with the predicted large enhancements of Z_{eff} due to vibrational Feshbach resonances in the model proposed by Gribakin. Since the model requires the existence of positron–molecule bound states, Barnes et al. interpreted the quantity $\Delta\epsilon$ as a measure of this binding energy. $\Delta\epsilon$ increases linearly with the number of carbons for alkane molecules from ethane (C_2H_6) to dodecane ($C_{12}H_{26}$). Interestingly, single fluorination of alkane molecules drastically reduces the annihilation rate at the C–H stretch mode even for fairly large alkanes despite a very little change in the binding energy. Also, a comparison of pentane and isopentane indicated that changes in molecular

shape had no effect on either the position, magnitude, or shape of Z_{eff} at the C-H stretch peak. Furthermore, to make the situation even more puzzling, for smaller molecules such as methane and carbon tetrafluoride no resonances have been observed, although methyl fluoride, difluoromethane, and trifluoromethane exhibited resonances. Experimental data collected for two–carbon hydrocarbons showed that in going from ethane (H_3C-CH_3) to ethylene ($H_2C{=}CH_2$), and then to acetylene ($HC{\equiv}CH$) reduces the magnitude of the C–H stretch peak, but enhances Z_{eff} at lower energies. These measurements have provided important guidance for theoretical calculations of Z_{eff} for smaller molecules. In general, it can be concluded that the measurements of $Z_{eff}(\epsilon)$ for the larger alkanes reasonably agree with the predictions obtained from Gribakin's model. Furthermore, these measurements provide unquestionable evidence for positron binding to alkanes. There are, however, many issues that are puzzling and remain to be addressed both experimentally and theoretically. One such issue concerns making a closer connection between values of Z_{eff} (300 K) measured for room–temperature positrons and measurements of $Z_{eff}(\epsilon)$ at higher energies. Furthermore, understanding of the possible role of intramolecular vibrational energy redistribution in the annihilation process, particularly in larger molecules, is another important question awaiting explanation. Also understanding the role of chemical structure in determining the magnitude and energy dependence of $Z_{eff}(\epsilon)$ is a question that needs to be addressed.

The physical picture of the electron–positron annihilation in small molecules is, at present, less well developed and understood. Experimental data indicate that the annihilation rate in many small molecules is also much larger than expected on the basis of simple collisions. However, it is not clear how the magnitude of $Z_{eff}(\epsilon)$ and its changes correlate with changes in chemical composition of the target molecule. In their work Barnes et al. [14] expressed a hope that quantitative $Z_{eff}(\epsilon)$ spectra measured using the cold positron beam will motivate new calculations for small molecules. They wrote that the calculated results, when compared with the experimental data, will help to elucidate the operative annihilation mechanism in small molecular systems. This understanding becomes increasingly important as antimatter becomes more readily available in the laboratory. The understanding of the phenomena related to the molecular electron–positron annihilation is also expected to become more important as the realizing of the range of new scientific and technological capabilities in this field increases. These new capabilities range from studies of fundamental symmetries of nature to the selective ionization of biomolecules and the characterization of materials.

The experimental capabilities, such as those demonstrated by Gilbert et al. [25], to study in detail the behavior of Z_{eff} at vibrational resonances has been allowing new and more precise tests of theories of annihilation in molecules.

The important prerequisite for such tests is theoretical determination of the molecule–positron binding energy with the use of computational methods. The ability of various atoms, ions, and neutral molecules to bind a positron or a positronium (Ps) atom is now well established by accurate theoretical calculations [33]. So far, the two most successful theoretical methods have been the variational calculations employing explicitly correlated Gaussians (ECGs), [34] and the quantum Monte Carlo (QMC) techniques [35]. Recently, *ab initio* configuration interaction (CI) calculations have also attracted interest as a promising method for describing positron and positronium interaction with one and two atoms (see Refs. [33, 34] for a more complete list of references). Conversely, for molecules its usefulness in computing bound states of positron complexes has still to be fully explored (e.g., see Ref. [36]). As often happens, each of the available methods has advantages and shortcomings, so that one should consider them as complementary tools in studying positronic complexes. For instance, while the method based on ECGs is undoubtedly the most accurate one, the computational effort requested grows faster than for QMC upon increasing the number of active particles in the system, therefore setting a practical upper bound to their maximum number. Up to now, no systems with more than five light active particles were computed. In principle, the limitation of ECG may be overcome by the CI approach, whose computational scaling with respect to the system size permits treatment of systems with more particles.

So far, the QMC methods, and especially the DMC method, have been applied to Ps–containing systems [37–41] where they have performed quite well, as well as to positron molecules formed by polar diatomic molecules with large dipole moments that bind a positron in dipole–bound states [42–44]. Second row atoms and their molecules, as well as systems composed of neutral polarizable fragments and a positron (LiPs, NaPs, e^+Be, and e^+Mg), have also been recently investigated with the all–electron fixed node DMC (FN–DMC) [45]. Positron affinity (PA) and positronium binding energy (BE) were computed for the LiPs, NaPs, and e^+Mg systems using either all–electron ECG or frozen–core ECG methods [46] by means of the stochastic variational method (SVM).

With the aim of obtaining information on the energetic and annihilation properties of positrons and positroniums interacting with molecules, the ongoing project of our group has been to study positron and positronium chemistry with the use of methods not assuming the Born–Oppenheimer approximation regarding the separability of the nuclear motion from the motions of the electrons and the positron and utilizing explicitly correlated one–center and multi–center gaussian functions for expanding the wave function. These functions have been shown to recover the majority of the fermionic and bosonic correlation energy, [1] and therefore they are expected to consistently deliver accurate

results for the energy components of the electron-electron and electron–positron interactions. In order to reach our goal, it is mandatory to gain expertise on a variety of "model" systems before dealing with more complicated ones. Here, the word "model" means a real system for which it is possible to obtain accurate results employing different methods in order to make meaningful comparisons, rather than "artificial" systems whose Hamiltonian has been invented or considerably simplified. Such a model system is, for example, e^+LiH, described later in this review.

The recently improved estimates of LiPs BE by Mitroy and Ryzhikh [46] appear to be of high quality: their accuracy is roughly 1% or better with respect to the exact value, so that there is no apparent fundamental reason to recompute its ground state. However this can not be said about excited states which have received very little attention. Due the small number of electrons, LiPs represents an excellent model for testing the accuracy of approximate methods devised to deal with larger systems containing Ps. For many of these systems, the electronic structure does not differ much from the structure of the parent atom or molecule since the Ps atom is usually weakly bound by means of dispersion forces (van der Waals A + B complex). For others, where the ionization potential (IP) of the parent system is higher than the electron affinity (EA) of the positron (equal to 0.25 hartree) the system is a complex of the parent molecule and a positron bound by electrostatic forces (ionic A^- + e^+ complex). Recently, [47] Mella et al. suggested that a study should be conducted of the ground states of some homonuclear diatomic molecules, namely e^+Li_2 and e^+Be_2, in order to explore the possibility of a behavior of the annihilation rate Γ versus R different from the e^+LiH case. More specifically, they suggested that there should be a range of nuclear distances where Γ is larger than the one of e^+Li or e^+Be due to the interaction of the positron with the electronic density of the two atoms. Also, Mella et al. in their work [47] implicitly assumed that the correct dissociation pattern for e^+A_2, A=Li, Na, were e^+A plus A, while they later showed [45] that the pattern was APs plus A^+. Using the BE's for LiPs [45] and the BE for e^+Li, of 0.002477 hartree from Ref. [34], it is easy to compute the energy difference ΔE between the two dissociation patterns as the energy released in the process: e^+Li + Li $\rightarrow$ Ps + Li + Li^+ $\rightarrow$ LiPs + Li^+ as ΔE(Li) = BE(LiPs) - BE(e^+A). ΔE(Li) obtained in this way equal to 0.00986 hartree [45] indicates the e^+Li_2 asymptotic breakup to be similar to the e^+LiH one, namely PsH plus Li^+. It is still unclear what is the asymptotic behavior of Γ versus R for e^+Li_2. where the polarization of LiPs, induced by Li^+, causes a reduction of Γ upon decreasing the nuclear distance. The situation is additionally complicated by possible appearance of the two different breakup patterns, e^+Li plus Li, and Li plus Li^+ plus Ps laying few mhartrees above the lowest one. Moreover, the finding of Mella et al. [45] that the LiPs plus Li breakup has an energy below the energy of Li_2 at the equilibrium

distance also indicates the possibility of forming LiPs upon collision between a swarm of positrons and lithium dimer gas. However, since other processes are also energetically allowed, e.g., the formation of Li_2 plus Ps, numerical calculations of the reactive cross sections are needed to determine the relative probabilities of the different outcomes.

Turning now to e^+Be_2: the overall picture for this system appears much less complicated than for e^+Li_2 thanks to its larger IP. This makes any ionic dissociation pattern much higher in energy than the e^+Be plus Be possibility. Although there is high probability that the e^+Be_2 system is bound, the mechanism responsible for the binding might be quite involved since the binding energy of the Be_2 dimer is very small (0.00360 hartree). Due to the fact that the atomic PA is of the same or larger order of magnitude of the dimer binding energy, one should not expect such a mechanism to be a simple sum of the different energetic contributions, but a more complicated dynamical interplay between different effects including the non–adiabatic coupling of the nuclear and positronic motions (i.e., electron–positron correlation). More accurate calculations are needed to study this problem. Thus, it is clear that even for small molecular systems containing positrons there are still many unanswered questions which may be explored with theoretical calculations.

In positron and positronium chemistry and physics, the two-photon 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 interpreted. Although these experiments are relevant with respect to both the fundamental and practical standpoints, [48,49] only few theoretical studies have been devoted to accurately compute annihilation rates for realistic atomic and molecular systems in order to compare with the available experimental data or with the predicted trends [46, 50–57]. Moreover, the studies have been mostly restricted to deal with systems with at most four active electrons.

Calculation of $\Gamma_{2\gamma}$ requires calculation of the expectation value of the Dirac's delta function, $\langle\delta(r_{-+})\rangle = \sum_i \langle\delta(r_{i+})\rangle$, where r_{i+} is the distance between the i electron and the positron and the summation run over all electrons in the system. Most of the studies of the annihilation rate of molecule–positron systems have been performed for e^+LiH employing QMC methods [43,57] and explicitly correlated Gaussian (ECG) functions, [52, 53, 58] However, a description of $\Gamma_{2\gamma}$ in highly excited of molecular vibrational states with a method departing from the Born–Oppenheimer approximation is still lacking. If the Born–Oppenheimer approximation is assumed, the $\Gamma_{2\gamma}$ is first calculated for different internuclear distances and then it is averaged over the ground and excited state vibrational wave functions. If the calculation is carried out without assuming

the Born–Oppenheimer (BO) approximation, $\Gamma_{2\gamma}$ is calculated directly as the expectation value for the total non–BO wave functions representing the ground or excited states of the whole system.

For e^+LiH there are several calculated results available for the quantity $\langle\delta(r_{-+})\rangle = \langle\delta(r_{1+})\rangle + \langle\delta(r_{2+})\rangle + \langle\delta(r_{3+})\rangle + \langle\delta(r_{4+})\rangle$. DMC simulations [57] calculated at R=3.015 bohr give a value of 0.02408 and ECG calculations [52] at the same geometry give 0.024992. At the estimated equilibrium distance of $R = 3.348$ bohr the ECG calculations give a value of 0.027252 [53]. The nonadiabatic results of Mitroy and Ryzhikh are 0.034016 and 0.032588 [58]. These last values were obtained using ECG and the stochastic variational minimization (SVM) and the frozen–core SVM (FCSVM) methods, and are roughly 15%–20% larger than the ECG [52, 53] and DMC11 clamped–nuclei values. This unexpected result led Strasburger [52] to consider the possibility of flattening of the potential energy curve of e^+LiH at larger R with respect to the LiH curve - a feature that would allow the positronic molecule to access a larger internuclear distance region where the average value of the Dirac delta function is expected to be larger. However, Mitroy and Ryzhikh [58] pointed out that their results may not be sufficiently converged due to their ECG basis inability to describe the vibrational motion of the molecule leading to their vibrational averaged nuclear distances being probably too large.

In recent work [59] Mella et al. used the DCM method and the BO approach based on vibrational averaging to calculate the annihilation rate in e^+LiH as a function of vibrational excitations. The calculations were done by averaging the Dirac delta function calculated as a function of the internuclear distance over the first 15 vibrational levels of e^+LiH. $\langle\delta(R)\rangle$ showed a steady increase on going towards larger v indicating that the annihilation rate does depend on the vibrational state of the molecule. Although the trend of these results could be specific to the e^+LiH system and, perhaps, to other similar polar molecules as well, it indicates that any theory formulated to describe "on the fly" annihilation of e^+ due to Feshbach resonances must include the vibrational effect in order to accurately predict the annihilation rate. It should be noted that the work of Mella et al. [59] was based on the Born–Oppenheimer approximation and, thus, it did not describe the coupling of the motion of the nuclei with the motions of the electrons and the positron. Including the coupling of these motions may be important in highly excited states and may affect the annihilation rate. Our study will explore this point.

2. Outlook

One of the aims of our studies of e^+LiH and e^+LiD is to search for long–lived bound positron states in these polar molecules. As mentioned, the calculations have been conducted with the use of the non–Born–Oppenheimer

quantum–mechanical approach we have developed in our laboratory for calculating nonadiabatic ground and excited states of molecular systems. In the approach we use explicitly correlated n–particle gaussian functions multipled by powers of inter–nuclear distances. As we have shown the use of these functions allow to achieve very high accuracy in calculations of vibrational states of diatomic molecular systems [60].

The posibility that positrons may occupy long–lived states in the e^+LiH and e^+LiD systems is related to the nature of their binding to the LiH and LiD molecules which is based on the positron–dipole moment interaction. In the positron bound states resulting from this interaction, the positron wave function is located mostly outside the frame of the LiH or LiD molecule and the overlap between this function and the electron wave function is relatively small. This small overlap may lead to reduction of the anihilation rate and facilitate the long-livedness of these states. Thus, the general focus of the project is to model dipole–bound positron states in polar molecules and to determine their life–time. Similar states exist for electrons as has been demonstrated by a number of workers including our group. For example, in the studies of anions of LiH, LiF and some other polar diatomics [61] performed with the use of the numerical Hartree–Fock (HF) and numerical MCSCF methods we calculated not only ground dipole–bound states of excess electrons in those systems, but also excited dipole–bound states located very close to the electron dissociation threshold. The term "numerical" means that the molecular orbitals in those calculations were represented as numerical functions on a 3–D grid and not as linear expansions in terms of some analytical basis functions. The use of numerical orbitals, which were essentially exact solutions of the HF or MCSCF Fock equations, allowed us to accurately describe the very diffuse character of the ground and excited dipole–bound states of excess electrons in the anions. We have demonstrated that, particularly in the excited states, these electrons are located far away from the parent molecules and overlap very little with the core electrons. More recently we have also studied electronic dipole–bound states in polyatomic molecules and clusters (see, for example, studies on dipole–bound anions of nucleic acid bases and their clusters [62]) and bound electronic states resulting from interaction of an excess electron with two or more molecular dipoles [63]. These type of states may also be relevant to the positron chemistry.

In analogy to excess electrons, positrons should also form diffuse dipole–bound states with polar molecules. The ionization potential of the polar molecule should be higher than the binding energy of the electron–positron pair (equal to -0.25 hartree) in order for the positron–molecule complex not to transform into a weakly bound (molecule)$^+$–Ps complex. Also, analogically to the excess electrons, there should exist excited dipole–bound states for excess positrons in positron–polar–molecule systems. As mentioned, in these states the overlap

between the electronic wave function and the wave function of the positron, though larger than in excited dipole–bound states of an dipole–bound excess electron, should be small leading to a relatively low positron–electron annihilation rate and to a long–lived positron–molecule complex.

In our approach we use the variational method and perform the calculations in the state specific manner optimizing the basis set of correlated gaussians individually for each root. The one–center gaussian basis functions we have used so far in calculating positron molecules are fully spherically symmetric and can describe only states with the total angular momentum equal to zero. Thus, the calculated states, both ground and excited, correspond to vibrational and electron–positron excitations of the ground rotational state of the system. We should, perhaps, more correctly call them vibrational–electronic–positronic states since the calculations have been carried out without assuming the Born–Oppenheimer approximation. The discrete spectrum of bound states of the e^+LiH system is complicated by the non–adiabatic coupling between the vibrational states and the dipole–bound positron states and by the fact that those latter states are embedded in the vibrational spectrum. The degree of coupling is expected to rise with the excitation level. This effect presents a challenge for the calculations because the non–adiabatic coupling effect is defficult to describe.

The importance of the search for long–lived positron bound states in polar molecules is related to the possibility of "storing" positrons in those states for relatively long times. However, before this aim can be accomplished one needs to demonstrate that non–adiabatic high–accuracy calculations can be performed on the e^+LiH system where these types of "storing" states can be determined.

3. The Method

In this work we employ explicitly correlated gaussian functions in variational calculations to determine energies and wave functions of non–adiabatic quantum states of systems consisting of nuclei, electrons and a positron. The procedure for non–adiabatic molecular calculations is derived from the non–adiabatic approach, which our group has pursued for the last few years, and based on several past applications of correlated gaussians in BO and non–BO calculations on atomic and molecular systems [1, 60, 64–70, 70–95]. There are also elements in the procedure that has been derived from the important works of Poshusta and Kinghorn concerning non–BO calculations [96–99]. The major challenge which our group is now pursuing is the extension of this method to describe molecules with two and more nuclei in ground and excited electronic and ro–vibrational states.

3.1 Hamiltonian

One can express the non–relativistic Hamiltonian for the system of N particles interacting with the isotropic potential (e.g., Coulombic two–particle attraction and/or repulsion), V, in terms of the coordinates of particles and their relative distances as:

$$H_{tot} = -\sum_{i}^{N} \frac{\nabla^2_{\mathbf{R}_i}}{2M_i} + V\left(\|\mathbf{R}_i - \mathbf{R}_j\| \; ; \; i < j, \quad i = 1...N\right). \tag{1.2}$$

The particles are numbered from 1 to N with M_i being the mass of particle i, $\mathbf{R}_i = [X_i \; Y_i \; Z_i]'$ a column vector of Cartesian coordinates for particle i in the external, laboratory fixed, frame, $\nabla^2_{\mathbf{R}_i}$ the Laplacian in the coordinates of $\mathbf{R}_i$, and $\|\mathbf{R}_i - \mathbf{R}_j\|$ the distance between particles i and j. The total Hamiltonian (1.2) is, of course, separable into an operator describing the translational motion of the center–of–mass and an operator describing the internal energy. This separation is realized by a transformation to the center–of–mass and internal (relative) coordinates. Let $\mathbf{R}$ be the vector of particle coordinates in the laboratory fixed reference frame:

$$\mathbf{R} = \begin{bmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \\ \vdots \\ \mathbf{R}_N \end{bmatrix} = \begin{bmatrix} X_1 \\ Y_1 \\ Z_1 \\ \vdots \\ Z_N \end{bmatrix}. \tag{1.3}$$

The center–of–mass and internal coordinates are given by the transformation $T : \mathbf{R} \mapsto [\mathbf{r}_0', \mathbf{r}']'$,

$$T = \begin{bmatrix} \frac{M_1}{m_0} & \frac{M_2}{m_0} & \frac{M_3}{m_0} & \cdots & \frac{M_N}{m_0} \\ -1 & 1 & 0 & \cdots & 0 \\ -1 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & 0 & 0 & \cdots & 1 \end{bmatrix} \otimes I_3, \tag{1.4}$$

where $m_0 = \sum_i^N M_i$. $\mathbf{r}_0$ is the vector of coordinates for the center–of–mass and $\mathbf{r}$ is a length $3n = 3\,(N-1)$ vector of internal coordinates with respect to a reference frame with origin at particle 1 (this particle is usually the heaviest particle in the system):

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{bmatrix} = \begin{bmatrix} \mathbf{R}_2 - \mathbf{R}_1 \\ \mathbf{R}_3 - \mathbf{R}_1 \\ \vdots \\ \mathbf{R}_N - \mathbf{R}_1 \end{bmatrix}. \tag{1.5}$$

Using this coordinate transformation, and the conjugate momentum transformation, the internal Hamiltonian can be written as [96,97]:

$$H = -\frac{1}{2}\left(\sum_{i}^{n}\frac{1}{\mu_i}\nabla_i^2 + \sum_{i\neq j}^{n}\frac{1}{M_1}\nabla_i\cdot\nabla_j\right) + V\left(r_{ij};\ \ i<j,\quad i=0...n\right), \tag{1.6}$$

where the μ_i are reduced masses, M_1 is the mass of particle 1 (the coordinate reference particle), and ∇_i is the gradient with respect to the x, y, z coordinates $\mathbf{r}_i$. The potential energy is still a function of the distances between particles but is now written using internal distance coordinates, $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\| = \|\mathbf{R}_{i+1} - \mathbf{R}_{j+1}\|$ with $r_{0j} \equiv r_j = \|\mathbf{r}_j\| = \|\mathbf{R}_{j+1} - \mathbf{R}_1\|$. Although the potential energy term, $V\left(r_{ij};\ \ i<j,\ \ i=0...n\right)$, is written in the form of a general function of inter–particle distances, for particles interacting with the Coulombic potential (*e.g.*, nuclei, electrons, and positrons) it is given by the conventional expression: $\sum_{i>j}\frac{Z_iZ_j}{r_{ij}}$, where Z_i's are charges of the particles.

3.2 Basis set

The centerpiece of the method is the use of N–particle explicitly correlated gaussian basis functions of the general form,

$$\phi_k = \left(\prod_{i<j}^{N} r_{ij}^{m_{kij}}\right)\exp\left[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}\right] \tag{1.7}$$

which can be represented in a more conventional form as:

$$\phi_k = \left(\prod_{i<j}^{N} r_{ij}^{m_{kij}}\right)\exp\Big[-\alpha_{1k}r_1^2 - \alpha_{2k}r_2^2 - \ldots$$
$$-\alpha_{nk}r_n^2 - \beta_{12,k}r_{12}^2 - \beta_{13,k}r_{13}^2 - \ldots - \beta_{nn-1,k}r_{nn-1}^2\Big]. \tag{1.8}$$

These functions, hereafter referred to simply as "ϕ_k", with the addition of rotational components and appropriate symmetry projections, are used as variational basis functions for wave functions describing internal non–adiabatic states of multi–particle systems consisting of nuclei and electrons (also including other particles such as positrons, muons, etc). In ϕ_k the term $\prod_{i<j} r_{ij}^{m_{kij}}$ is a product of "distance" coordinates, r_{ij}, raised to powers m_{kij} (positive, negative [100] or zero). In molecular calculations this term needs to only include the inter–nuclear distances.

The exponential component is an explicitly correlated gaussian (1.7) with $\mathbf{r}$ representing a length $3n$ column vector of internal (relative) coordinates ($\mathbf{r}'$ denotes the transpose of $\mathbf{r}$, *i.e.*, a row vector), A_k is an $N\times N$ symmetric matrix of exponent parameters (positive definite). Vector $\mathbf{r}$ will be defined later in this

section. The Kronecker product of A_k with the 3×3 identity matrix, I_3, insures rotational invariance. For diatomics the ϕ_k's the pre–exponential factor needs to contain only powers of the single inter–nuclear distance, r_1:

$$\phi_k = r_1^{m_k} \exp\left[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}\right] . \tag{1.9}$$

The basis set has been implemented and used in several projects concerning diatomic systems including the calculations of e^+LiH. However, a better convergence and more accurate results we expect to obtain with a basis containing powers of the two positron–nucleus distances (r_2 and r_{12}) included in the pre–exponential factor:

$$\phi_k = r_1^{m_{k1}} r_2^{m_{k2}} r_{12}^{m_{k12}} \exp\left[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}\right] . \tag{1.10}$$

since these types of functions can better describe the reduced probability of finding the positron at the nuclei. The functions (1.10) can also be used in non–BO calculations of systems with three nuclei. Functions (1.10) are currently being implemented.

Note that the ϕ_k's are angular momentum eigen–functions with zero eigen–value. Multiplying the basis functions by spherical harmonics, $Y_M^L \phi_k$, allows to describe higher angular momentum eigen–states when the factor Y_M^L is chosen as an angular momentum eigen–function for the desired state [101, 102]. This very important property allows to separate variational calculations for vibrational–electronic states corresponding to different values of the total angular momentum operator (different rotational states).

An alternative to basis functions (1.7) is to use N–particle explicitly correlated gaussian functions with shifted centers:

$$\phi_k = \exp\left[-(\mathbf{r}-\mathbf{s})'(A_k \otimes I_3)(\mathbf{r}-\mathbf{s})\right] . \tag{1.11}$$

This basis allows non–B–O calculation of wave functions for systems with more than two nuclei and of systems exposed to symmetry breaking external perturbations such as an electric field. Though these basis functions are not eigenfunctions of the square of the total angular momentum operator as are the functions without shifts, $\phi_k = (\prod_{i<j}^N r_{ij}^{m_{kij}}) \exp\left[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}\right]$, they can still be used to obtain very good non–adiabatic wave functions since they form a complete set and, in principle, can describe any non–BO bound state of the molecular system. However, since they are not eigenfunctions of the total angular momentum, it is difficult to use them to calculate excited states in a way that would allow separation of vibrational–electronic and rotational excitations. Such separation automatically occurs when one uses basis functions that are angular momentum eigenfunctions. In order to generate a wave function corresponding to the specific rotational excitation in the basis of shifted correlated Gaussians, one would need to project out from the wave function

the contributions from angular momenta different from the angular momentum of the calculated state. This may not be a practical way to proceed, especially if very high accuracy is required. Thus, we plan to use only the basis functions (1.11) to calculate the non–BO ground states of positron systems with more than two nuclei.

In some preliminary calculations with the shifted center fuctions we have considered the H_3^+/H_3 system and its isotopomers [103]. An interesting aspect of these types of calculations is the way we generate a good starting guess of the non–BO wave function. First, a conventional variational BO calculation for the system using a basis set of correlated Gaussians with shifted centers is performed. For this the method developed recently [70] that allows simultaneous optimization of the molecular geometry and the non–linear parameters (i.e. exponents and centers) of the basis functions is used. Next the converged BO wave function is multiplied by Gaussians dependent on the coordinates of the nuclei. These Gaussians are centered at the equilibrium positions of the nuclei that were obtained in the BO calculation (with the reference nucleus placed at the center of the coordinate system). The basis set (1.11) can also be used in a hybrid approach where some of the particles are described by the wave function and some are stationary and are represented by point charges. This type of approach described recently by us [1] can be used to study the chemistry of positron molecules with more than two nuclei, including some "heavy" nuclei.

3.3 Symmetry

Our expansion for the basis function, $\prod_{i<j} r_{ij}^{m_{kij}} \exp\left[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}\right]$, is written using the scalar "distance" variables $\{r_{ij}\}$ and the internal coordinate vector variable $\mathbf{r}$. The expansion of the wave function in terms of ϕ_k has to properly reflect the permutational symmetry of the considered state. Since the ϕ_k's are isotropic the problem of how to handle permutational symmetry is taken care of by appropriate symmetry projection operators. The operators ensure that the wave function obeys the Pauli principle and ensures the correct permutational symmetry. We recently described the details of the symmetry–adaptation of the non–BO wave function using the Young operator representation [73] (see also other references [96–98]). Consider a system of N particles whose permutational symmetry is given by the group, G, represented by a set, $\{P_{\alpha\in G}\}$, of $N \times N$ permutation matrices. A wave function represented as an expansion in ϕ_k is a function of the $n = N - 1$ component vectors of $\mathbf{r}$, the relative coordinates. The permutation P_α acting on the N particle coordinates induces a transformation on the center–of–mass and relative coordinates given by:

$$T\bar{P}_\alpha T^{-1} = I_3 \oplus \bar{\tau}_\alpha, \tag{1.12}$$

where T is the transformation matrix given in Eq.(1.4). The right hand side of this expression is the direct sum of the identity acting on the center–of–mass coordinates, $\mathbf{r}_0$, and τ_α, which is an $n \times n$ "permutation" matrix acting on the component vectors of the relative coordinate vector $\mathbf{r}$. The action of the permutation represented by P_α on ϕ_k is then,

$$P_\alpha \phi_k = \prod_{i<j} \left[\mathbf{r}'(\tau'_\alpha J_{ij} \tau_\alpha \otimes I_3)\mathbf{r}\right]^{\frac{m_{kij}}{2}} \exp\left[-\mathbf{r}'(\tau'_\alpha A_k \tau_\alpha \otimes I_3)\mathbf{r}\right]. \quad (1.13)$$

The action of a representation of the group G on ϕ_k is thus induced by the projector $\sum_{\alpha \in G} \tau_\alpha$.

3.4 Variational Calculations

An important development in our non–Born–Oppenheimer approach has been the derivation and implementation in our group of the analytical gradient of the variational energy functional with respect to the non–linear exponential parameters of the explicitly correlated Gaussian functions [67, 73, 78, 84, 92]. In our calculations the wave function for the ground state is obtained by directly minimizing the Rayleigh quotient:

$$E(a; c) = \min_{\{a,c\}} \frac{c'H(a)c}{c'S(a)c} \quad (1.14)$$

with respect to the linear expansion coefficients, c, of the wave function in terms of the symmetrized basis functions, and with respect to the non–linear exponential parameters, a, of the basis functions. In the ground state calculations, the diagonalization of the H matrix is usually not performed since it is believed that the energy can be more effectively lowered when the c and a variables are considered independent parameters. In minimizing the energies of the excited states, which has been done in separate calculations for each excited state, we used the diagonalization procedure that provides the eigenvalue only for the calculated root. In the minimization of the energy functional the analytical gradient of the energy with respect to the linear and non–linear parameters of the wave function is used. The energy gradient with respect to the non–linear variational parameters can be written as:

$$\nabla_a E = \frac{1}{c'Sc}\left(\frac{\partial vechH}{\partial a'} - E\frac{\partial vechS}{\partial a'}\right)'(vech[2cc' - diagcc']), \quad (1.15)$$

where a is a $m(n(n+1)/2)$ vector of all the non–linear parameters, m is the number of basis functions used, and the $vech$ operator vectorizes a symmetric matrix by stacking the columns of the lower triangular part of the matrix (excluding the upper triangular part) on top of each other. The vector a is made by stacking, function by function, the lower triangular elements of

L_k (where $A_k = L_k L_k'$). In the case of Gaussians with shifted centers, a also includes the elements of the s_k shift vector. The matrices of derivatives $\frac{\partial vechH}{\partial a'}$, $\frac{\partial vechS}{\partial a'}$ are sparse, since each row has at most $2(n(n+1)/2)$ non–zero elements ($2(n(n+1)/2+3n)$ for shifted Gaussians). The derivatives of the Hamiltonian matrix are determined by using the derivatives of the molecular integrals:

$$\frac{\partial vechH}{\partial a'} = \frac{\partial vechT}{\partial a} + \frac{\partial vechV}{\partial a'}. \tag{1.16}$$

The integrals and their derivatives were described in the previous papers [67, 73, 78, 84, 92]. The analytical gradients considerably accelerate the variational optimization of the wave function. In our recent calculations we have combined the stochastic variational method with the gradient–based optimization and we found this hybrid approach to be the most effective. The approach was used in the e^+LiH calculations described below.

3.5 Parallel implementation

Efficient parallel computational implementation of the N–particle non–BO code to perform large scale variational calculations on ground and excited states of positron molecules has been one of the major tasks in the development we have carried out. In the ground–state calculations for the e^+LiH described below we have used nearly 3000 basis functions and the work has been peformed on a 64–processor Athlon MP Linux Beowulf cluster. We estimate that it will take approximately 5,000–8,000 basis functions per state for the e^+LiH or e^+LiD system to achieve the level of accuracy we need in the calculations. Thus access to a computer cluster (e.g. a Beowulf cluster) with 500–1000 processors will be necessary. Parallization of our non–BO code to run on a system with that many processors is by far not a trivial matter. Although the calculation of the Hamiltonian matrix elements can be very effectively parallelized, there are some modules in the code that need to be restructured to fully utilize the parallel architecture of a computer cluster with a distributed operational memory. These tasks are being carried out in our group.

4. e^+LiH

This project concerning calculations of positron molecules has evolved from our previous works where we have used explicitly correlated gaussian functions in molecular non–BO and BO calculations of some small atomic and molecular systems [1, 64–73, 60, 74–87, 70, 88–95]. The results of the calculations shown here concern the ground state of the e^+LiH system and its fragmentation into HPs and Li^+ with our non–BO approach. Since, for both e^+LiH and HPs systems our non–BO variational energies are better (lower) than the energies obtained before, we decided to include them in this review.

The improvement was particularly significant for e^+LiH which was calculated before with the use of non–BO method and explicitly correlated gaussians by Mitroy and Ryzhikh [58]. Their total variational energy obtained with 580 gaussian functions of -8.089010 hartree is significantly higher than not only our best results obtained with 2800 gaussian functions of -8.104684 hartree, but also higher than our 580–term result of -8.1020734 hartree. The fragmentation energy is also much better converged than that reported by Mitroy and Ryzhikh [58] (see Table 1). Their result of 0.020815 hartree is much lower than our 0.03649 hartree result which is only about 1% off from the value of 0.03683 hartree obtained from extrapolation to an infinite number of the basis set. The much lower variational e^+LiH energy obtained in our calculations in comparison with that obtained by Mitroy and Ryzhikh can be attributed to our use of pre–exponential $r_1^{m_k}$ multipliers in the basis functions which were absent in their calculations. The multipliers are necessary to describe the vibrational component of the non–BO wave function.

Though in the calculations of excited states with more complicated node structure of the wave functions more basis functions will be needed, there is not fundamental reason not to expect the quality of the results to be lower than that for the ground state. This gives us confidence that high–quality results will be soon generated in our lab concerning the excited spectrum of the e^+LiH/e^+LiD system. This data, when available, can be used as a reference in future experiments concerning the e^+LiH/e^+LiD spectroscopy and chemistry.

Table 1.1. Total non–BO energy in hartrees of the HPs and e^+LiH systems as a function of the number of the explicitly correlated gaussian basis functions. Fragmentation energy corresponds to dissociation of e^+LiH into HPs and Li^+ (E_{Li^+} = -7.279325 hartree [58]). All energies in hartrees.

No. basis functions	HPs	e^+LiH	Fragmentation energy
800	-0.78887050403	-8.10307542904	0.03488
1200	-0.78887063984	-8.10390578874	0.03571
1600	-0.78887067901	-8.10425655075	0.03606
2000	-0.78887069403	-8.10447824966	0.03628
2400	-0.78887070145	-8.10459855237	0.03640
2800	-0.78887070576	-8.10468350271	0.03649
Literature results:			
Mitroy and Ryzhikh [58]	-0.788870	-8.089010	0.020815
Mella et al. [47] [b]		-8.105	

[a] Extrapolated results.
[b] Born–Oppenheimer QMC energy obtained for the ground vibrational state.

5. Summary and future work

To summarize, our work on the positron molecular systems has just started. The preliminary results have indicated that the methods we developed can deliver the needed accuracy in the calculations on such systems. However, there are a number of tasks that needs to be completed before studies can be extended to positron systems with relevance to the experimental studies. Some of the immediate tasks include the following:

1 Implementation of the basis functions

$$\phi_k = r_1^{m_{k1}} r_2^{m_{k2}} r_{12}^{m_{k12}} \exp\left[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}\right]$$

in non–BO calculations. This will require derivation of the Hamiltonian integrals and the integrals involved in the energy gradient. This development will not only allow more accurate non–BO calculations of ground and excited states of diatomic systems containing positrons (e^+LiH and e^+LiD), but, more importantly, it will for the first time enable non–BO studies of chemistry and spectroscopy of positron–triatom systems.

2 Parallel implementation of the non–BO approach on a computer cluster with several hundred nodes.

3 Implementation of basis sets allowing determination of spectra of e^+LiH, e^+LiD and other positron systems involving states with non–zero total angular momentum.

4 Development of methods for determination of possible dissociation pathways of positron molecules and the corresponding bonding energies.

5 Feasibility study of utilizing multi–center correlated gaussian functions in calculations of molecules with multiple nuclei.

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Dedication

We dedicate this work to the memory of Per-Olov Löwdin.

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